European Commission

JRC SCIENTIFIC AND POLICY REPORTS

Corrosion-Related Accidents in Petroleum Refineries

Lessons learned from accidents in EU and OECD countries

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2013

EUR 26331 EN

Joint Research Centre

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JRC25933

ISBN 78-92-79-34652-1
ISSN 1831-9424
doi: 10.2788/37964

Luxembourg: Publications Office of the European Union, 2013

Printed in Italy

Table of contents

EXECUTIVE SUMMARY 1

CHAPTER 1 INTRODUCTION AND BACKGROUND 8

1.1 Background 12

1.2 Aims of the Study 14

1.3 Corrosion as a major hazard concern for the petroleum refinery industry 15

1.4 Description of accident report sources used in the study 17

1.5 Type of events and consequences of accidents 22

CHAPTER 2 ANALYSIS OF THE POTENTIAL CONTRIBUTION OF PROCESS AND EQUIPMENT CONDITIONS 30

2.1 Process conditions contributing to corrosion in study cases 31

2.2 Analysis of cases in association with specific process conditions 34

2.3 Corrosion risk associated with chemical refining processes 39

2.4 Involvement of refinery equipment in corrosion-related accidents 44

2.5 Frequency that various equipment vulnerabilities were cited in the accidents studied 50

CHAPTER 3 ANALYSIS OF THE POTENTIAL CONTRIBUTION OF RISK MANAGEMENT FAILURES 57

3.1 Inadequate awareness of or attention to known corrosion hazards 58

3.2 Failure to conduct an adequate hazard identification or risk assessment for life cycle planning and events 61

3.3 Inadequate risk analysis at design and construction stage 64

3.4 Inadequate risk analysis prior to a change 68

3.5 Inadequate risk analysis for planning inspections 71

3.6 Inadequate identification of hazards and risks for other purposes 74

CHAPTER 4 CONCLUSIONS 77

APPENDIX 1: LIST OF ACCIDENTS STUDIED 80

APPENDIX 2: REFERENCES 88

TABLE OF FIGURES

Figure 1. Total case distribution by country 17

Figure 2. Accidents by year of occurrence 18

Figure 3. Percentage of cases in which some lessons learned information could be extracted 21

Figure 4. Accidents classified by type of event 22

Figure 5. Substances released in refinery accidents involving corrosion by number of accidents 23

Figure 6. Distribution of event type for each type of failure 24

Figure 7. Severity of accident consequences pre- and post-2000 25

Figure 8. Distribution of event type for each type of failure 26

Figure 9. Level of consequence vs. type of consequence 27

Figure 10. Process conditions cited as contributing to corrosive conditions accidents studied 31

Figure 11. Process-related substances cited as contributing to corrosion failures 36

Figure 12. Process substances contributing to corrosion failure in association with the process unit of origin.. 37

Figure 13. Observations on process conditions related to accident occurrence 38

Figure 14. Simplified diagram of a refinery process 39

Figure 15. Unit of accident by origin of cases studied 42

Figure 16. Severity of consequences associated with unit of origin of accidents studied 43

Figure 17. Accident origin by equipment component 46

Figure 18. Descriptions from case studies of corrosion failures in storage tanks 49

Figure 19. Types of vulnerabilities sited for pipework and pipelines contributing to corrosion acceleration of equipment involved 51

Figure 20. Observations from cases on related equipment conditions 52

Figure 21. Observations from cases on inadequate anti-corrosion protection 55

Figure 22. Percentage of accidents where an inadequate awareness or attention concerning a known corrosion hazard was indicated 58

Figure 23. Indications of a management failure in cases studied 59

Figure 24. Observations from cases studied indicating potential inadequate awareness of or attention to known corrosion hazards 60

Figure 25. Example of consequence event tree 62

Figure 26. Illustration of barriers influencing a process incident 63

Figure 27. Basic Safety Barrier Diagram 63

Figure 28. Percentage of accidents where risk analysis prior to design and construction was cited as potentially inadequate 66

Figure 29. Observations from cases on inadequate risk assessment prior to design and construction 66

Figure 30. Percentage of accidents where risk analysis prior to a design or process change was cited as potentially inadequate 69

Figure 31. Observations from cases on inadequate risk assessment prior to a change 70

Figure 32. Percentage of accidents where risk analysis for planning inspections was cited as potentially inadequate 71

Figure 33. Observations from cases on inspection deficiencies 73

Figure 34. Observations from cases on inadequate hazard evaluation prior to repair work 74

Figure 35. Observations from cases on the absence of adequate detection and mitigation systems .. 75

TABLE OF TABLES

Table 1. Total Oil Supply 9

Table 2. Number of Operating Refineries in OECD and EU Member Countries 11

Table 3. Typical refinery elements contributing to elevated corrosion rates 16

Table 4. Primary sources of accident reports analysed in this study 19

Table 5. Consequence Ranking Criteria 25

Table 6. Cumulative totals of consequence figures for all accidents 29

Table 7. Examples of stress corrosion cracking damage mechanisms proposed by API 571 32

Table 8. Typical process substances associated with refinery corrosion 35

Table 9. Typical refinery processes 40

Table 10. Classification of type of damage vs. systems/components in process plants from the RIMAP project 45

Table 11. Factors contributing to corrosion and aging equipment failures identified in various studies 47

Table 12. Corrosion and aging failures associated with pipework 47

Table 13. Factors contributing to corrosion and aging failures associated with atmospheric storage tanks 49

Table 14. Pressure vessels subject to potentially rapid deterioration 50

Table 15. Example of guidance for designing to minimize corrosion and challenges in monitoring and maintaining corrosion vulnerable areas 65

Table 16. Examples of criteria used to determine inspection frequency for pressure and pipe equipment in various RBI methodologies 72

EXECUTIVE SUMMARY

Petroleum refining industry continues to be of central importance to the global economy. Refined petroleum products are not only a primary source of energy for homes and businesses but also are fundamental to a thriving transport industry. Refinery oil products and byproducts of the production process such as ammonia and sulphur, also form the basic ingredients for a vast range of products such as plastics and other materials for consumer and industrial products, cloth and industrial fabric, paints and dyes, pharmaceuticals, fertilizers, and numerous other manufactured goods. The presence of this sector in any country is considered to be a significant advantage not only to the country but also to the surrounding region.

Petroleum refining is also a high hazard industry with most sites processing thousands of tonnes of oil into various product lines each year many of which are flammable, toxic to human health or toxic to the environment. At the same time refineries are also large, complex sites with many processes, several of which operate at very high levels of pressure and temperature, and a vast pipeline to transport process fluids throughout the site and eventually to external modes of transport. This combination of factors make refinery sites very vulnerable to a variety of corrosion phenomena that can eventually cause a loss of containment of process fluids, sometimes leading to a serious accident affecting workers, the environment, the surrounding economy and even on occasion the larger economy.

The majority of EU and OECD countries are host to at least one petroleum refinery, if not several, and those countries without refineries all have petroleum storage depots who share some of the same storage and handling issues as refineries. OECD countries represent an estimated 49.2% [1] of global refining capacity, and all together EU countries (including non-OECD members) represent an approximate 18% of global refining capacity. [2] It has been noted by a number of experts over the years that mechanical integrity consistently remains a contributor to major accidents in these countries despite numerous gains in knowledge about vulnerabilities of refineries and how they can be managed. Notably, of the 137 major refinery accidents reported by EU countries to the EU's eMARS database since 1984, around 20% indicated corrosion failure as an important contributing factor. This proportion of refinery accidents in eMARS with this profile has remained constant well into the 21st century.

This report focuses on corrosion risks in refineries in EU and OECD countries, looking at lessons learned from past corrosion-related accidents at these sites. The analysis was conducted as part of the long-standing collaboration on lessons learned between the European Union and OECD countries in the OECD Working Group on Chemical Accidents. The aim of the study was to analyse the reports in terms of known corrosion risks associated with oil refineries and determine to what extent a failure to recognize or control various known factors, technical and/or managerial, may have contributed to the accident. The study is aimed managers and inspectors of various expertise who are charged with overseeing or monitoring aspects of risk management at refinery sites. For these professionals, it is hoped that the analysis may provide some insight into specific types of vulnerabilities and potential risks that on occasion may be overlooked and lead to a serious event.

This study of corrosion-related accidents in refineries is based on 99 reports of important refinery accidents in which corrosion of an equipment part was identified or suspected as being the key failure leading to the accident event. Only reports listed in open sources and produced by or with the collaboration of parties directly involved in the accident investigation were used. Therefore, with a few exceptions, online government databases of accident reports were the main source of accident reports. Moreover, since the study was conducted on refineries in a specific geographic area, reports that did not specify geographic location of the refinery could not be used.

The accidents cannot be used for computing statistical trends either by year or on a geographic basis. The vast majority of EU and OECD countries have not consistently collected data or reports on major chemical accidents over the period by this study or in some cases the data are not easily available. There is a significant overrepresentation of accidents occurring in Japan, France and the other European countries who were part of the European Union prior to 2004. However, a collective analysis of these accidents can help to identify areas of ongoing concern generally for refineries. They also can provide insight as to whether the profile of corrosion-related accidents occurring in refineries a few decades ago has evolved or has stayed relatively the same.

Consequences of corrosion-related accidents in refineries

Uncontrolled corrosion can cause release of hazardous substances and components or can reduce both the performance and reliability of equipment until their failure. As such, corrosion hazards can put at risk the safety and well-being of both plant employees and the general public as well as lead to severe damage of process units, and in some cases shutdown of refinery operations. A good portion of the accidents studied appeared to be fairly representative of the types of high risk scenarios associated with petroleum refineries. Many of these events were notified to the data sources used by the study on the basis of high impacts in terms of effects on human health or the environment or significant cost either to the operator or in terms of offsite property damage or disruption. As evidence, it is observed that nearly 50% of the reports studied both pre- and post- 2000 were high or very high consequences [see Figure 7]. Accidents with low consequences represent about a third of the accidents studied and also the ratio of low impact accidents to total accidents remained virtually unchanged for pre- and post-2000 accidents studied. Many of these latter accidents contributed important insights to the study on conditions that continue to play a role in elevation of corrosion risk on refinery sites.

Public service interruption and property damage were the dominant consequences overall. Taking into account production loss as well, 55% of the accidents studied were projected to have a very high economic impact. Significant environmental damage was reported for nearly a third of accidents and mainly associated with toxic releases to water. Although there have been no deaths and only 17 injuries recorded in corrosion-related accidents in refineries since 2000, potential for catastrophic human health effects from any type of chemical accident in a refinery cannot be discounted. There have been several fatal accidents (related to other causes than corrosion) occurring in refineries in the EU and OECD in the last 10 years (and even in the last two), many of them in plants several decades old. The potential for a corrosion failure to cause a human disaster does not appear to have greatly diminished.

Process conditions contributing to corrosion in study cases

Refineries are most vulnerable to corrosion due to internal process conditions. The study analysed the cases to identify what types of substances and process units were associated with the accidents. In 53 cases process conditions were identified as contributing to the corrosive conditions preceding the accident. The most commonly cited contributor was the substance (cited 46 times). Flow (either high, low, turbulent or unequal) was cited in 10 cases, and temperature (mostly high, but in a few cases, low) and pressure (mostly high) were cited as contributors in 11 and 7 cases respectively. In 8 cases other exacerbating process conditions were present, including operation outside design parameters and variation across process cycles.

Refinery processes generally consist of either refining or treatment processes. Refining processes, such as distillation and thermal cracking, breakdown and manipulate the molecules in the crude oil feedstock to convert it into marketable products. Treatment processes remove impurities and byproducts from the feedstock and refining output. As much as possible these “unwanted’ substances are either recycled into the refining or treatment process (e.g., hydrogen) or sold as products in their own right (e.g., sulphur).

Out of 99 cases, the highest percentage (23%) started in the distillation unit, followed closely by hydrotreatment units (20%). In the cases studied there were substantially fewer cases involving such units after 2000 compared to prior years. Conversely, the number of cases involving the pipeline transfer network is proportionally somewhat higher after 2000. The “Other” category includes units for sulphur recovery, solvent extraction, saturated gas, olefin manufacturing and oil gasification. The study does not show any pattern linking specific units with accident consequences of a particular level of severity.

Involvement of refinery equipment in corrosion-related accidents

The magnitude of a petroleum refinery unit and the complex of the processes is such that a wide variety of equipment types can be subject to corrosion depending on the process. In general, the pipeline infrastructure and the pipework associated within a particular unit and/or piece of equipment are quite vulnerable. Storage tank failures can also occur due to corrosion and generally have high risk profiles due to the volumes that they may contain. Corrosion can also occur in other equipment components such as trays, drums, and towers. Some equipment types are more vulnerable to corrosion, or to certain types of corrosion, than others usually due to their role in the process, the design of the pipework, or physical location on the site. Sometimes faulty repairs or process re-design can increase corrosion vulnerability. Hence, equipment design and maintenance practices are critical to controlling refinery corrosion. A few types of equipment, notably the heat exchanger (a necessary component of many process units) and the storage tank, are also highly correlated with elevated corrosion risk.

Of the cases studied, corrosion failure originated predominantly in pipe works, causing 71% of the accidents studied. Fifty percent of accidents involved the internal pipework of the equipment. As noted in the previous section, 17% of the original failures took place in the pipeline infrastructure of the plant for transfer between units and to and from transport modes, and 4% took place in tubes associated with heat exchange and cooling units. FIfteen percent of the accidents occurred in storage tanks.

Various factors make some equipment components more vulnerable to the acceleration of the corrosion rate than others. Configuration and design of equipment play a particular role in creating opportunity for corrosive deposits to accumulate. Function and location can also determine the level of exposure to corroding agents. Integrity of corrosion protection and repair are applications that can alter the character of the equipment with an impact on its vulnerability to corrosive factors. Moreover, in any refinery, there will usually be points at which the pipework fails to meet the necessary design standards for a number of reasons. These reasons include age, process change, design change, risk assessment errors, and poor repair and maintenance. These vulnerabilities are common causal factors for other types of mechanical integrity failures besides corrosion.

The study highlighted the following vulnerabilities that were cited in numerous reports, individually or in combination with other factors, as contributing to an accident event.

- Material composition of the component

- Configuration
- Function
- Location
- Adequacy of anti-corrosion protection
- Welded parts

The study revealed that in nine cases, the inadequacy of the material composition in design or repair of the pipe component was considered a contributor factor to the corrosion failure. Six cases indicated that infrequent use may have resulted in a reduction in the frequency of monitoring and maintenance of an equipment component. Overall failure of the anti-corrosion protection was cited in 16 of the accidents studied. Corrosion failure was attributed to potential welding error in nine of the cases studied. Only four cases mentioned the age of the equipment as a contributing factor, although in several reports there were also references to the advanced age of the equipment involved in the accident without indicating it as a causal element.

In particular, configuration of the pipework plays a strong role in the corrosion process. Some design features create weak points in the system that are particularly vulnerable potential stresses, including corrosion. The elbow joint is the most common geometric configuration involved in a corrosion-related failure in the study, noted in 18% of all cases as the original site of corrosion. Elbow joints have practical and engineering advantages but they also are vulnerable to certain types of stresses, particularly erosion/corrosion, low of uneven flow, vibration, and external pressure from natural forces such as wind and floods. A slightly higher proportion of the pre-2000 cases cited an elbow joint as the origin of the corrosion failure.

In total 8 different cases referred to valves or branched piping as the original location of the corrosion failure. Valves, nozzles and branched pipework all represent pipe intersections that are joined to the system by various mechanisms, including welding. While the construction and design of these components varies considerably, it can generally be said that the process of making an intersection creates a weak point in the pipe system.

Aside from process location, other location factors also may affect corrosion vulnerability. In this study two additional location issues were highlighted in 13 separate cases: exposure to the external environment and accessibility. In one case a section of equipment pipework was poorly accessible for routine inspection. Seven cases concerned pipes that were on the ground or underground, 4 of which were considered also fairly inaccessible for routine inspection. Pipeline standards generally recommend that buried and submerged metallic equipment should have adequate protective coating. Five cases concerned pipes submerged in water.

Potential contribution of risk management failures

Every refinery is expected to have an appropriate risk management strategy to minimize the risks with adequate layers of protection supported by an effective safety management system. From the reports, there was an indication that a failure in risk management was a contributing cause to the vast majority of accidents studied.

Due to the variation in reporting detail and style, it was not possible to analyse the risk management failures associated with these accidents in a systematic way. Nonetheless, the study was able to summarize potential risk management failures in terms of five general deficiencies:

- Inadequate awareness or attention to known corrosion hazards

- Inadequate risk analysis at design and construction stage
- Inadequate risk analysis prior to change, which is essentially a lack of or failure in the management of change process
- Failure to identify or address process risks in planning inspections
- Inadequate identification of hazards and risks for other purposes, such as safe performance of repairs and establishment of detection and mitigation systems

According to the study, an inadequate awareness or attention of management to known corrosion hazards could was implied as a contributing factor in 23 % of the cases studied. This incidence was flagged in cases where one or more of the following conditions appeared to exist according to the observations found in the accident report:

- General lack of management attention to corrosion issues
- Lack of awareness in the process unit of potentially unsafe conditions and potential accident triggers
- Inadequate corrosion monitoring and feedback mechanisms for known areas of elevated corrosion risk.

The remaining four categories of risk management failure identified in the study can be traced to a failure associated with hazard identification or risk assessment at an important stage in the life of the equipment. Most major accidents imply at least a partial failure in the identification and risk assessment of a major hazard resulting in an inadequate evaluation of the hazard and associated risk. For corrosion hazards, risk is normally expressed as the product of the probability of a corrosion-related failure and the consequences of such a failure. The outcome of the assessment has implications for downstream decisions associated with design, operation and maintenance of the process.

It could be deduced from numerous accident reports studied in this analysis that an inadequate risk assessment of the process at a critical operational phase was a contributing cause of the accident. Usually the risk assessment was inadequate for a number of reasons, including:

- The hazard was not identified and a risk assessment for that hazard was never performed at a critical point in the safety life cycle
- Critical information about the hazard and potential risk was available but omitted from the risk assessment.
- Critical information about the hazard and potential was not fully available for the risk assessment

This study found that these inadequacies into four different categories according to their occurrence in the safety management process, as follows:

- Inadequate risk analysis at design and construction stage
- Inadequate risk analysis prior to change, which is essentially a lack of or failure in the management of change process
- Failure to identify or address process risks in planning inspections

- Inadequate identification of hazards and risks for other purposes, such as safe performance of repairs and establishment of detection and mitigation systems

According to the study, the risk assessment prior to original design or a later equipment design change was not adequate over a third of all accidents. Some of the reports were not entirely clear as to whether a design error was the result of a decision in the original design of the process or was part of a change to process equipment at a later stage. As a practical matter, the study assumed that, if change was not mentioned, the error was part of the original design; however, this choice could not be fully verified.

Changes and modifications to processes and process equipment are a natural part of a refinery plant life cycle. A core element of any safety management system is a properly functioning management of change process. The 1974 Flixborough explosion is perhaps the most well-known catastrophe associated with a failure in the management of change process. Eight out of 60 accidents investigated by the U.S. Chemical Safety Board between 1998 and 2012 also were associated with failure to manage a process or equipment change. In this study 10% of accidents were cited as potentially resulting from a failure in the management of change process.

The estimated corrosion risk associated with a process or piece of equipment should be a leading factor in scheduling routine inspections of equipment integrity. A more detailed risk assessment may also be warranted to identify specific degradation threats, the remaining life of the equipment and to feedback information into the overall risk assessment and control system. The initial corrosion risk assessment should identify also points in the life cycle when the corrosion risk assessment should be upgraded. According to the reports studied, a third of the accidents might have been avoided with appropriate planning of inspections on the basis of known risk criteria.

Several reports also highlighted other situations where a risk analysis might have been used to avoid a potential accident. In six cases it was reported that adequate assessment of conditions was not conducted prior to repair work. In general this type of failure is primarily associated with neglecting to follow good practice for performing hot work.

In seven cases there were observations in the associated report(s) concerning detection and mitigation mechanisms that could have prevented a release from becoming a serious accident if they had been in place. An effective risk management approach relies on assigning appropriate technical measures to reduce and eliminate the risks. The severity of consequences associated with some cases, for example, an accident occurring during a loading operation in which 478 tonnes of fuel were spilled, suggested that, in addition to measures to prevent loss of containment prevention, second order protection, such as sensors, alarms, automatic shut-off controls and/or other possible measures, could have significantly reduced the impact of the event.

Conclusions

Corrosion control remains a particularly challenging phenomenon in the effort to reduce refinery accident risks, further elevated in many EU and OECD countries by the aging infrastructure and variation in crude oil supply and market conditions. The study identified 40 accidents occurring since 2000, many of them serious, indicating that major accidents at refineries involving corrosion failure continue be a particular cause of concern in the 21st century.

Generally, significant corrosion failures occur either because the hazard was not properly identified or the hazard was substantially ignored. It appeared from the studies that experts sometimes overlooked how the various elements of a process could combine to create the conditions for accelerated corrosion. There is also a question about how much experience specifically in mechanical integrity disciplines is available at some refineries to diagnose these properly. However, there appeared to be a number of cases studied in which the corrosion risk was quite obvious, and yet the management chose to ignore or underestimate it.

The study seems to indicate that one of the most important challenges in managing refinery corrosion is also the element of change. Already changes to process design and equipment pose a challenge and need a certain competency to identify if a new corrosion risk has been introduced. However, other changes that can affect corrosion rates may go unrecognized and thus not be evaluated for an elevated risk. Inconspicuous changes, such as loss of experienced personnel, lack of knowledge of the original process and equipment design, and aging equipment, can also create risk and in this regard, the refinery's greatest risk may be change over time.

Neglecting to identify or manage corrosion hazards also continues to be a problem on some refinery sites. Some accident reports are quite clear that the lesson learned was less about the technical challenge of managing corrosion but simply about having an effective risk management program. The work of inspection authorities is most certainly challenging in these situations.

In essence this study provides some evidence to confirm concerns among experts in both government and industry that the risk of corrosion failures causing major accidents remains a strong area of concern. In illustrating the kinds of decisions that may have led to certain accident, or the severity of their consequences, it is hoped that inspectors and refinery engineers who are looking to improve their awareness of corrosion risks will have gained some knowledge that will help them in their work. In addition, it is possible that the findings can also help key leaders in government and industry point out that corrosion remains a significant refinery hazard deserving serious and sustained management attention.

CHAPTER 1 INTRODUCTION AND BACKGROUND

Petroleum refineries are generally acknowledged to be high hazard sites due to the nature of petroleum products and the processing technologies that produce them in the current era. For the most part, however, the risks are well-known and refinery operators have applied considerable knowledge and resources over the past decades to control and minimize risk potential. Nonetheless, major accidents in refineries tend to regularly occur with impacts not only on human health and the environment, but also in many cases on social and economic well-being. A recurring cause of accidents in petroleum refineries is well-known to be corrosion. This report studies corrosion-related accidents in refineries within the European Union (EU) and the Organization for Economic Co-operation and Development (OECD), comparing accident occurring before and after 2000 and with the view to providing insights into recent causal trends and identifying lessons learned that could influence prevention strategies in future.

This report was developed on behalf of the EU Committee of Competent Authorities for the Seveso Directive (CCA Seveso)[1] and OECD's Working Group of Chemical Accidents (WGCA) which manages the OECD Programme on Chemical Accidents and consists of representatives of OECD member countries as well as experts from observer countries, international organizations, industry, labour, and environmental organizations. The European Commission is represented on the WGCA by DG-ENV and the Joint Research Centre's Major Accident Hazards Bureau (MAHB). In addition, OECD members contribute accident reports on a voluntary basis to the eMARS database of chemical accidents managed by MAHB. A list of OECD Member Countries, indicating those that are also EU Members, is provided in Table 2 on page 12.

The majority of EU and OECD countries are host to at least one petroleum refinery, if not several, and those countries without refineries all have petroleum storage depots who share some of the same storage and handling issues as refineries. OECD countries represent an estimated 49.2% **Error! Reference source not found.** of global refining capacity, and all together EU countries (including non-OECD members) represent an approximate 18% of global refining capacity. [2] Studies about causes associated with refinery production and storage remain highly relevant. Moreover, it can be assumed that most or all refineries in EU/OECD countries strive to follow common international standards of good practice for managing refinery risks.

[1] Directive 2012/18/EU of the European Parliament and of the Council of 4 July 2012 on the control of major-accident hazards involving dangerous substances. All EU Member States are obliged to implement the Seveso Directive in their national legislation.

TABLE 1. TOTAL OIL SUPPLY (THOUSAND BARRELS PER DAY) [1]

	2008	2009	2010	2011	2012
EU-27	2647.227	2542.01	2413.188	2162.712	1992.969
Austria	27.35455	28.19153	28.71441	30.39195	29.48281
Belgium	8.5207	12.60347	12.70007	10.53035	10.53035
Bulgaria	3.51701	3.3409	3.58363	3.38363	3.38363
Cyprus	0.2	0.2	0.1	0.1	0.00847
Czech Republic	10.90856	10.38968	10.28301	13.01232	10.00915
Denmark	290.3941	264.3081	249.4648	226.2842	207.3841
Estonia	7.6	9	10	11	11
Finland	8.53291	9.54122	15.30335	14.2309	13.5309
Former Czechoslovakia	--	--	--	--	--
France	73.07799	76.31161	76.5425	75.88213	72.30336
Germany	124.8994	133.0608	125.0016	141.0002	144.5077
Germany (Offshore)	20.81967	23.72877	20.88219	24.08767	25
Germany, East	--	--	--	--	--
Germany, West	--	--	--	--	--
Greece	6.00839	6.41675	8.47986	7.57805	7.49677
Hungary	36.9994	35.36659	34.45847	27.64039	27.9886
Ireland	-0.45946	-0.2957	1.07504	0.72561	0.72561
Italy	160.7857	145.5256	156.1428	152.7214	154.5105
Latvia	0.9	1.2	1.1	1	1
Lithuania	10.04207	9.45376	9.71077	9.11077	9.11077
Luxembourg	0	0	0	0	0
Malta	0.02	0.02	0	0	0
Netherlands	31.47712	37.83117	34.84203	40.98095	54.7248
Netherlands (Offshore)	34.07377	25.56438	20.30137	17.5863	16.99727
Poland	35.27595	34.24601	28.65921	28.33946	27.68447
Portugal	6.96014	5.41664	5.57404	5.17594	5.24991
Romania	116.9844	112.6989	107.1448	105.3409	101.6478
Slovakia	10.30085	7.53781	7.68135	9.85793	9.27711
Slovenia	0.165	0.145	0.405	0.305	0.305
Spain	25.3903	29.48995	28.75125	28.45621	29.29182
Sweden	8.4702	11.19146	10.41947	11.26664	11.26664
United Kingdom	85.14396	87.38141	87.13009	82.65457	86.17039
United Kingdom (Offshore)	1502.864	1422.145	1318.737	1084.068	922.3808
OECD	20968.22	21160.93	21505.25	21623.91	22571.73
Australia	587.717	592.4863	604.1056	530.5067	519.065
Austria	27.35455	28.19153	28.71441	30.39195	29.48281
Belgium	8.5207	12.60347	12.70007	10.53035	10.53035
Canada	3343.577	3318.829	3441.73	3597.333	3868.956
Chile	12.12632	12.97693	18.42176	18.36149	17.33709

	2008	2009	2010	2011	2012
Czech Republic	10.90856	10.38968	10.28301	13.01232	10.00915
Denmark	290.3941	264.3081	249.4648	226.2842	207.3841
Estonia	7.6	9	10	11	11
Finland	8.53291	9.54122	15.30335	14.2309	13.5309
Former Czechoslovakia	--	--	--	--	--
France	73.07799	76.31161	76.5425	75.88213	72.30336
Germany	124.8994	133.0608	125.0016	141.0002	144.5077
Germany (Offshore)	20.81967	23.72877	20.88219	24.08767	25
Germany, East	--	--	--	--	--
Germany, West	--	--	--	--	--
Greece	6.00839	6.41675	8.47986	7.57805	7.49677
Guam	0	0	0	0	0
Hawaiian Trade Zone	--	--	--	--	--
Hungary	36.9994	35.36659	34.45847	27.64039	27.9886
Iceland	0	0	0	0	0
Ireland	-0.45946	-0.2957	1.07504	0.72561	0.72561
Israel	4.023	5.98119	5.839	5.839	5.839
Italy	160.7857	145.5256	156.1428	152.7214	154.5105
Japan	125.2716	137.6242	142.4722	136.257	135.5125
Korea, South	33.6573	54.65003	58.47474	59.78946	61.04358
Luxembourg	0	0	0	0	0
Mexico	3184.164	3000.791	2978.599	2959.989	2936.009
Netherlands	31.47712	37.83117	34.84203	40.98095	54.7248
Netherlands (Offshore)	34.07377	25.56438	20.30137	17.5863	16.99727
New Zealand	65.27087	61.02682	60.77085	52.17398	48.19111
Norway	2463.917	2352.555	2134.621	2007.35	1902.084
Poland	35.27595	34.24601	28.65921	28.33946	27.68447
Portugal	6.96014	5.41664	5.57404	5.17594	5.24991
Puerto Rico	0.66277	0.53813	0	0.8536	0.6737
Slovakia	10.30085	7.53781	7.68135	9.85793	9.27711
Slovenia	0.165	0.145	0.405	0.305	0.305
Spain	25.3903	29.48995	28.75125	28.45621	29.29182
Sweden	8.4702	11.19146	10.41947	11.26664	11.26664
Switzerland	3.65681	3.87793	3.60576	3.61281	3.61281
Turkey	47.73348	54.59644	57.75023	57.63345	56.65329
U.S. Territories	NA	NA	NA	NA	NA
United Kingdom	85.14396	87.38141	87.13009	82.65457	86.17039
United Kingdom (Offshore)	1502.864	1422.145	1318.737	1084.068	922.3808
United States	8564.232	9133.129	9692.433	10135.55	11124.05
Virgin Islands, U.S.	16.64497	16.76659	14.88036	14.88036	14.88036

Table 2. Number of Operating Refineries in OECD and EU Member Countries [3] [4] [5]

OECD Members Only		OECD and EU Members	
Australia	7	Austria	1
Canada	18	Belgium	4
Israel	2	Czech Republic	3
Japan	30	Denmark	2
Korea	6	Estonia	0
Mexico	6	Finland	2
Switzerland	2	France	12
United States	144	Germany	13
Norway*	2	Greece	4
Turkey±	6	Ireland	1
		Italy	16
EU Members Only		Luxembourg	0
Bulgaria	1	Netherlands	7
Cyprus	0	Poland	2
Latvia	0	Portugal	2
Lithuania	1	Slovak Republic	1
Malta	0	Slovenia	0
Romania	6	Spain	9
		Sweden	5
		United Kingdom	11
Total EU & OECD		317	

* European Economic Area (EEA) Member

± EU Candidate Country

1.1 Background

Chemical, refinery and petrochemical industries are complex large establishments that by nature of their operations are subject to a number of high risk factors, among them the maintenance of the mechanical integrity of process and storage equipment. It has been noted by a number of experts over the years that mechanical integrity consistently remains a contributor to major accidents despite numerous gains in knowledge about vulnerabilities of refineries and how they can be managed. These concerns have been driven by recent accidents, observations from the field by numerous government safety inspectors, and a general awareness of changing conditions in refineries potentially affecting mechanical integrity such as plant aging, the chemical and physical properties of crude feedstocks in current supply, and other economic and market factors.

To illustrate, of the 137 major refinery accidents reported by EU countries to the EMARS database[2] since 1984, around 20% indicated corrosion failure as an important contributing factor. This proportion of refinery accidents in eMARS with this profile has remained constant well into the 21st century. Considering gains in knowledge in regard to both control technologies and risk management over the past 30 years, the unchanging influence of corrosion on refinery accident rates in the EU could be considered as evidence that these experts' concerns are not misplaced.

Uncontrolled corrosion can cause release of hazardous substances and components or can reduce both the performance and reliability of equipment until their failure. Corrosion hazards can put at risk the safety and well-being of plant of both plant employees and the general public as well as lead to severe damage of process units, and in some cases shutdown of refinery operations. The human impact, from death, injury, trauma, income or property loss resulting from an accident can be particularly devastating. Though less frequent, the environmental impacts when they occur tend to be severe in an industry where high volume production is the norm.

In particular, the economic impact of corrosion phenomena and its consequences on refineries is significant, taking into account maintenance and repair costs and production loss from planned and unplanned shutdowns. As such, indirect consequences associated with short and long term social and economic disturbances (e.g., infrastructure outages, job loss, fuel price increases) from a refinery accident may be particularly severe.

Of all potential impacts, the financial impact of corrosion is most consistently and alarmingly high. Corrosion in refineries also can significantly decrease the financial efficiency of the different refinery processes since failure of equipment due to corrosion can result in a shutdown of all or part of the facility. According to Ruschau et al., yearly costs related to corrosion in the oil industry have been estimated in the range of $3.7 billion per year in the U.S. This study also estimated that total property damage losses from major refinery accidents between 1972 and 2001 equated to around $ 5 billion (January 2002 dollars). A refinery operation may have in excess of 3,000 processing vessels of varying

[2] The Major Accident Reporting System (MARS and later renamed eMARS) was first established by the EU's Seveso Directive 82/501/EEC in 1982 and has remained in place with subsequent revisions to the Seveso Directive in effect today. Reporting an event into eMARS is compulsory for EU Member States when a Seveso establishment is involved and the event meets the criteria of a "major accident" as defined by Annex VI of the Seveso III Directive (2012/18/EU). For non-EU OECD and UNECE countries reporting accidents to the eMARS database is voluntary.

size, shape, form, and function. In addition, a typical refinery has about 3,200 km (2,000 mi) of pipeline, much of which is inaccessible. Some of these pipelines are horizontal; some are vertical; some are up to 61 m (200 ft) high; and some are buried under cement, soil, mud, and water. The diameters range from 10 cm (4 in) up to 76 cm (30 in). [6]

Some common general conditions associated with refineries in EU and OECD countries today are believed to be leading to an elevation in corrosion risks, notably aging, changes in the overall refinery infrastructure, and the quality of crude oil available in the marketplace. For example, in 2003 Marsh Property Risk Consulting indicated that losses in the refinery industry were continuing to increase most notably due to aging facilities in this category. [7] Aging was cited as one of the most important factors creating the potential for the disaster that occurred at the BP Texas City refinery in the U.S. in 2005. Recently, a spate of guidance and expert recommendations have been produced by major oil refining countries, notably the United Kingdom and France, on managing aging plants and refineries. The majority of refineries in OECD and EU countries are over 20 years old.

Demand and supply trends in the oil industry in these countries also have given rise to a concern regarding impacts of reduced profit margins on plant maintenance and new infrastructure investment. Refinery profitability is particularly vulnerable to market fluctuation because the operator has little influence over the pricing of both input (crude oil feedstock) and output which are driven by worldwide, and to some extent also regional, markets. In 2009 profit margins for EU refineries were reported as the lowest observed in fifteen years. [2]

The fall in profitability has caused several refineries to close, a circumstance that increases demand on remaining refineries, some of which may be operating near capacity limits. Notably, the EU, the US and Japan have experienced closures of major oil refineries since 2008 and more closures are predicted in future. [8] In these regions, the refining industry has maintained capacity demands largely by expanding existing facility capacity, often by increasing the capacity of individual processes, particularly the crude distillation process, and storage units and tanks to manage greater volumes. [1] Nonetheless, older process units remain in use often operating at an increased rate of production than in past years.

At the same time in the EU region in particular, market conditions have increased dependence on crude oil feedstocks that are heavier and more sulphurous, requiring more intense processing with the accompanying higher corrosion risk associated with higher proportions of napthenic acids. In Europe North-Sea crude production (from Norway, UK, Denmark) fell from 6.4 to 4.3 million barrels per day between 2000 and 2008. Over the same period, the supplies to Europe of heavier, sourer/more sulphurous, crudes from Russia and Africa have been growing. The result has been an increase in the proportion of heavy and sulphurous crudes purchased by EU refineries and resulting heavier processing demands. [2] [3][2]

As noted by Yeung, “crude selection is the most important decision refiners must make on a daily basis.” The composition of crude varies with the source and can significantly impact on the corrosion resistance of refinery equipment, and particularly in refineries that were designed with heavy crudes in mind. The operator has to evaluate market costs such as oil source reliability and term deals, delivery advantages, discount versus other crudes, and product demand mix against the potential impact on operational costs related to plant operational flexibility, potential processing problems and

[3] The corrosion risk is not necessarily lessened in production of biofuels and synthetic gases where various conditions can present potentially different but equally serious corrosion risks (e.g., the use of chloride-rich biomass for biofuel production). [9]

risks, mitigation options and costs, and environmental concerns. [9] Heavy crude can therefore bring changes in other indirect economic forces, such as profit margins, maintenance practices (e.g., outsourcing), the availability/reliance on in-house expertise for corrosion engineering and the increasing loss of historical knowledge regarding the design and operational history of older equipment. [10] [4]

All these factors have raised concerns about the risk of a serious accident due to the elevated presence of corrosion risk in refinery sites in EU and OECD countries. A serious refinery accident can have grave impacts on production alone which threatens the economic viability of the refinery itself. Moreover, numerous past accidents have demonstrated the potential for refinery accidents to cause injury and death to workers on the site, environmental damage to natural resources covering, on occasion, vast geographic regions, threaten the health and safety of the community, and significantly disrupt its quality of life for days or weeks at a time. This study of corrosion-related accidents in refineries explores lessons learned from past accidents is intended to provide insights that may assist operators and the enforcement community in evaluating vulnerability of refineries to corrosion-related risks in future.

1.2 Aims of the Study

Over the past few decades, a vast amount of scientific literature has been generated on the subject of corrosion in processing and storage activities associated with industrial activity, a significant portion of which is devoted to corrosion specifically in the energy sector. From these publications, it is evident that corrosion subdivides into a number of subcategories of corrosion phenomena with varied and complex profiles dependent on product and equipment composition and interactions as well as some factors independent of operational activity (e.g., location, atmospheric conditions). The corrosion potential in petroleum refineries is made infinitely more varied and complex due to the additional size, variation and complexity of activity in most refineries. For this reason there is a concern that corrosion control in EU and OECD refineries may be inconsistently effective across the industry and geographic locations in current times.

A small but significant portion of corrosion literature has been aimed at summarizing the research, lessons learned and trends to facilitate practical application of corrosion control measures in a wide variety of industrial sectors and economic circumstances. Notably, various industry associations associated with the energy sector have made substantial contributions to the theoretical framework and good practice recommendations available for corrosion control in refineries. Moreover, alarmed by recent accidents in older refineries, a number of EU and OECD national government authorities have invested effort over the last several years, conducting substantial scientific research, field studies and accident analyses, in order to assess the extent and severity of the aging phenomena in refineries and how to control its associated risks such as corrosion.

[4] The U.S. is another significant OECD refining country that has experience a downgrade in the quality of crude oil supply over the last two decades, with an associated impact on the integrity of its refining infrastructure. However, in future the U.S may eventually benefit from greater availability of lighter, lower sulphur feedstocks as a proportion of its totally supply with the exploitation of shale oil reservoirs.

This report cites particular publications produced by the American Petroleum Institute (API), the Institute of Chemical Engineers (IChemE), the Institute of Energy (IE), the United Kingdom Health and Safety Executive (UK HSE), the French National Institute of Environment and Industrial Risk (INERIS), the U.S. Department of Energy, the U.S. Department of Transportation, the U.S. Occupational Safety and Health Administration and NACE international. While there are no doubt other valid publications that this report ignores, these reports were considered to be sufficiently exhaustive and recent to represent the state of the art theory and practice in EU and OECD countries. Moreover, language, accessibility and prominence of these reports as references for refinery operators played a role in defining the scientific references for this study.

These works add considerable value as catalogues of corrosion and corrosion inducing phenomena and by providing an increasingly robust arsenal of effective control strategies as time goes on. However, the daunting task of prioritizing and processing this information to minimize risk necessarily remains with the refinery operator. Likewise, enforcement agencies must sift through this wealth information and with relatively little time or other resources, try to find an effective focus and approach that can give meaningful oversight and assistance to the operator’s own efforts.

With this in mind, the authors of this study aimed to provide insight on the collective knowledgebase from another perspective, that is, using accident data related to one particular, corrosion in refineries, to help operators and inspectors to refresh their knowledge and perhaps also focus their attention on particular aspects associated with this phenomenon. Using reports from a number of open sources over the last few decades, the authors aimed to identify repeated patterns in accident occurrences both in terms of specific causal factors and failures in control strategies.

The intention is not simply to re-emphasize the significance of some known challenges, for example, corrosion under insulation or the lack of sufficient protective coating, but also to identify potential failures and opportunities regarding strategic approaches to corrosion control that may be relevant for future planning of control strategies. Moreover, the analysis also compares findings between accidents pre- and post-2000 to identify whether certain causal and control failures may have become more or less relevant in recent times. It is hoped that this information is of particular assistance to inspectors by providing a concise summary of refinery corrosion hazards and examples of how they have been manifested in past accidents. The findings may be also useful to operators in renewing aspects of their risk management strategy or training personnel on how to recognize and evaluate potential corrosion risks.

1.3 Corrosion as a major hazard concern for the petroleum refinery industry

Corrosion does not stand for a single phenomenon but is a generalized term to cover a destructive attack on a metal as a result of either a chemical or electrochemical reaction between the metal and various elements present in the environment. For instance, iron is converted into various oxides or hydroxides when reacting with the oxygen present in air/water, when in contact with a more noble metal such as tin or when exposed to certain bacteria. The international standard defines corrosion more specifically as a “physicochemical interaction between a metal and its environment which results in changes of the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part.” [11] According to other authors, corrosion derives from “the natural tendency of materials to return to their most thermodynamically stable state." [12]   Table 3 below identifies four broad categories of refinery elements that can contribute to corrosion risk.

Corrosion of a metal occurs either by the action of specific substances or by the conjoint action of specific substances and mechanical stresses. Depending upon environmental conditions, corrosion can occur in various forms such as stress corrosion, pitting corrosion, embrittlement and cracking. The particular type of corrosion occurring in a specific component can often be difficult to classify. For example, several forms of corrosion (e.g., galvanic corrosion, pitting corrosion, hydrogen embrittlement, stress sulphide corrosion cracking) are characterized by the type of mechanical force to which the metal component is exposed. It is not within the scope of this work to address in depth either corrosion electrochemistry or the identification of different forms of corrosion. The basics of corrosion mechanisms are described as a basis for understanding the conditions that make corrosion risks highly relevant for refinery operations and more specifically to provide some insight into the underlying causes of the corrosion events leading to the accidents analysed in this report. Also, corrosion of certain metals (e.g. aluminium) enhances their corrosion resistance, but in this work corrosion is assumed to be solely an undesirable phenomenon.

TABLE 3. TYPICAL REFINERY ELEMENTS CONTRIBUTING TO ELEVATED CORROSION RATES

Refinery element	**Examples**
Corrosive substances in feedstock or added or produced in process	Hydrogen chloride, hydrofluoric acid, amines, sulphuric acid, polythionic acids and other sulphur compounds, oxygen compounds, nitrogen compounds, trace metals, salts carbon dioxide, and naphthenic acids
Refinery processes involving extremes of temperature or velocity	Distillation, desulphurization, catalytic reformers, fluid catalytic cracker, hydrocracker, alkylation
Local conditions	Age of equipment, volume and rate of production, atmospheric conditions (e.g., climate), planned and unplanned shutdowns
Risk management measures	Frequency of inspection, risk assessment and ranking practices, equipment inventory management, maintenance and repair procedures, auditing and implementation of feedback, use of safety performance indicators

1.4 Description of accident report sources used in the study

This study of corrosion-related accidents in refineries is based on 99 reports of important refinery accidents in which corrosion of an equipment part was identified or suspected as being the key failure leading to the accident event. Only reports listed in open sources and produced by or with the collaboration of parties directly involved in the accident investigation were used. Therefore, with a few exceptions, online government databases of accident reports were the main source of accident reports. Moreover, since the study was conducted on refineries in a specific geographic area, reports that did not specify geographic location of the refinery could not be used.

Table 4 provides a description of all the primary sources of accident reports used in this study. When available, official investigation reports, or summaries produced by government or industry, were used to supplement information in the primary sources. Mainstream media reports containing information on an accident were not considered sufficiently reliable technical sources for this study and therefore, were not used.

Some reports were listed in more than one database and sometimes additional reports on the same accident from other credible sources were used to supplement the first report (e.g., an in-depth investigation report, a workshop presentation of the accident). Since reporting accidents with significant consequences to eMARS is compulsory under EU law, any accident with significant consequences recorded in the French national database (ARIA) or the German national database (ZEMA) will also be reported to the eMARS database.

These particular sources also tend to collect accidents based on reporting criteria or otherwise based on screening criteria applied by the source. This factor was considered to provide some additional weight to the lessons learned offered by the collective experience represented by these accidents.

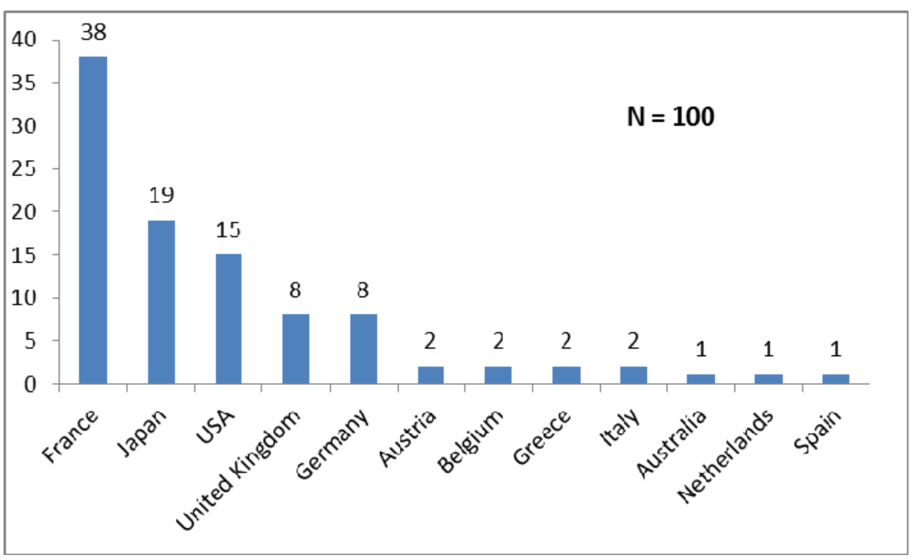

FIGURE 1. TOTAL CASE DISTRIBUTION BY COUNTRY

The study covers accidents reported in EU and OECD countries over a span of nearly fifty years, from 1965 through 2012. There is no particular statistical significance in terms of variations in the frequency or location of accidents studied per year or geographic. Notably, several sources used for this study, including eMARS, ARIA, MHIDAS and Lees' Loss Prevention in the Process Industries were all established in the mid-1980's. Fewer databases recorded such incidents prior to this date and in any case much of the data are not available in electronic form which was the principle source of information.

The accidents reported in each year are not in any way representative of a trend. The vast majority of EU and OECD countries have not consistently collected data or reports on major chemical accidents over the period by this study or in some cases the data are not easily available. In some cases it is possible also that reports may be available electronically but not in languages known to the study's authors. For all these reasons, the study was limited to the sources identified in Table 4 such that there is a significant overrepresentation of accidents occurring in Japan, France and the other European countries who were part of the European Union prior to enlargement in 2004 (the so-called EU-15)[5] and a significant underrepresentation of potential important chemical accidents occurring in all other EU and OECD countries. With the exception of the U.S. and Japan, finding a significant collection of accident reports from OECD countries outside the EU is challenging.

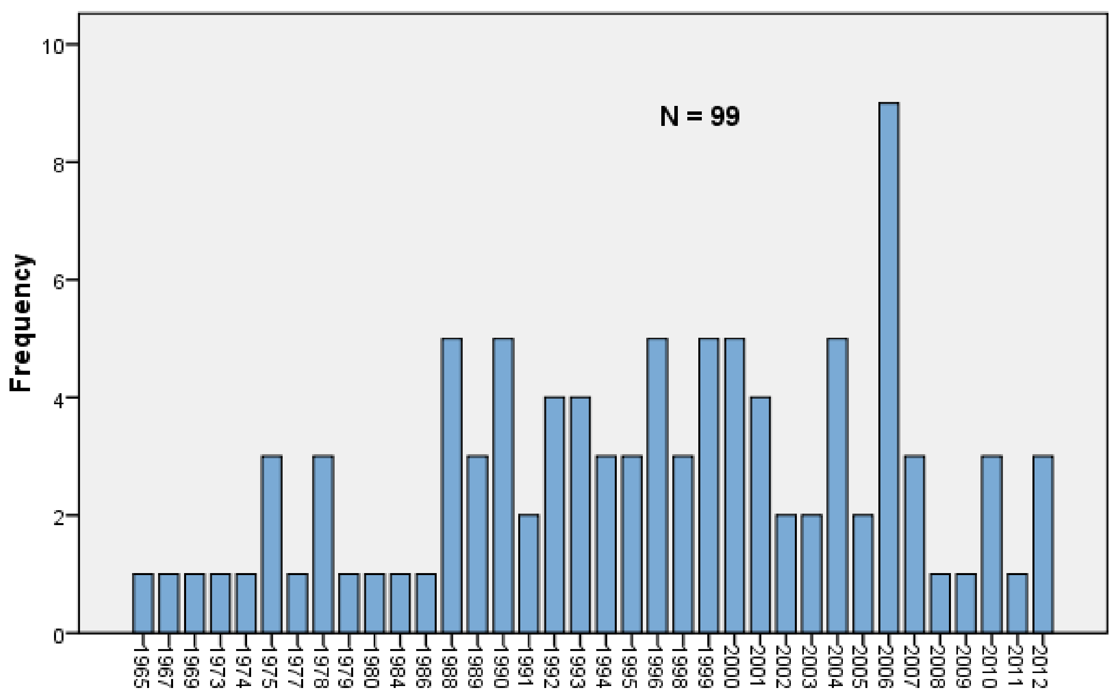

FIGURE 2. ACCIDENTS BY YEAR OF OCCURRENCE

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[5] Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, the Netherlands, Luxembourg, Portugal, Spain, Sweden, and the United Kingdom.

TABLE 4. PRIMARY SOURCES OF ACCIDENT REPORTS ANALYSED IN THIS STUDY[6]

Source	No.	Time span Geographical coverage	Comments
eMARS https://emars.jrc.ec.europa.eu Accidents reported to the European Commission in compliance with Seveso Directive Annex VI criteria.	29	> 1984; EU/OECD	Completeness and precision of descriptions varies considerably. Includes details on substances, consequences and cost.
ARIA (France) http://www.aria.developpement-durable.gouv.fr/ A database operated by the French Ministry of Ecology, Energy, Sustainable Development listing the accidental events which have, or could have damaged health or public safety, agriculture, nature or the environment. Chemical accidents are reported that meet established criteria.	47	> 1970 France, some Germany & UK/US	Concise, comprehensive technical summaries. Reports are verified by technical experts.
JST Failure Knowledge Database http://www.sozogaku.com/fkd/en/index.html Created by the Japan Science and Technology Agency. A main purpose in creating the Failure Knowledge Database was precisely to provide a means of communicating failure knowledge.	18	> 1970 Japan	Selected major accidents analysed by experts. Scenario diagrammes include.
Lees' Loss Prevention in the Process Industries, 3rd edition [13] First published in 1980, this comprehensive source for process safety management in the process safety industries.	4	> 1911	Well-known or accidents with important lessons learned or significant impacts on life and/or property

[6] This table only counts cases in which the reference was used as the original source for cases studied though in many cases it turned out that it was not the primary source of the information. When available, original investigation reports or other more detailed summaries were used when available to supplement information on these data sources. Moreover, many accidents were recorded in more than one source above with often different and complementary information about the same event.

Source	No.	Time span Geographical coverage	Comments
Marsh 100 Largest Losses, 20th edition, 1972-2001 [7] Every other year this insurance company publishes a review of the 100 largest property damage losses that have occurred in the hydrocarbon-chemical industries since 1972.	3	1972 – 2001 World	Low level of detail. Precise loss figures.
MHIDAS MHIDAS was established by the U.K. Health & Safety Executive in 1986, and provides key information on major accidents involving chemicals. It does not appear to be available anymore on the Internet for downloading.	3	1959 - 2005 World	Mainly a secondary source of information on accidents analysed in this study.
ZEMA (Germany) http://www.infosis.uba.de/index.php/de/site/12981/zema/index.html Database managed by the German Federal Environment Agency of hazardous incidents and incidents in process engineering facilities.	5	> 1980 Germany	Concise technical summaries of chemical accidents.
U.S. Chemical Safety Board (CSB) The CSB is an independent federal agency of the United States government charged with investigating industrial chemical accidents.www.csb.gov	4	> 1998 USA	Comprehensive analysis by experts.
Louisiana Department of Environmental Quality (LDEQ) Under U. S. law (EPCRA section 304), if an accidental chemical release exceeds the applicable minimal reportable quantity, the facility must notify state authorities and provide a detailed written follow-up as soon as practicable. http://www.labucketbrigade.org/article.php?id=498	3	2005-2008	An advocacy group posted a number of official company accident reports submitted to the LDEQ between 2005 – 2008 including refinery accidents involving corrosion.

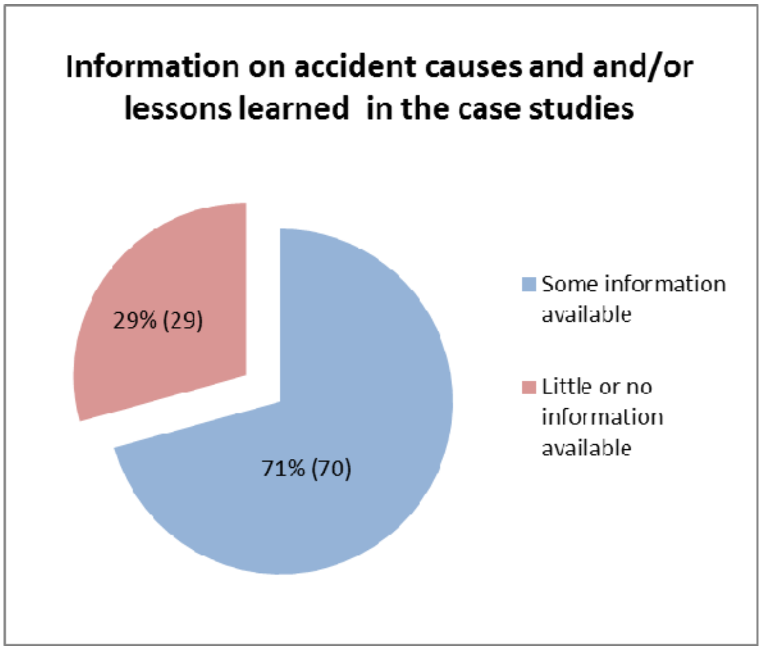

FIGURE 3. PERCENTAGE OF CASES IN WHICH SOME LESSONS LEARNED INFORMATION COULD BE EXTRACTED

Also it should be noted that reports varied considerably in their detail. For example, in many cases lessons learned per se from an accident were not given (see Figure 3 above) In most cases the type of accident (e.g., toxic release, fire, explosion), location (pipe or tank, process unit) and known consequences were provided. In general the least detail was provided in reports from the MHIDAS and Marsh accident registers while the Japanese Failure Knowledge Database and the U.S. Chemical Safety Board reports were extremely detailed. ARIA, ZEMA and eMARS were more uneven in this regard, but for the most part contained numerous detailed reports as well as some reports with sparse detail. In some cases also more details could be found for the same accident in a more extensive investigation report published separately online as an academic study or by the responsible competent authority itself.

In the interests of identifying differences and similarities over time, the study looks at findings from pre-2000 accidents to those of accidents occurring in 2000 or later. In particular, on a qualitative basis, it remains interesting as to whether various types of errors or failures are repeated (and to what degree) in accidents reported before 2000 and in 2000 and afterwards. The comparison may also reveal some new types of failures or errors being recorded after 2000. While in itself such findings could not be confirmed as a trend – for example, it can be argued that in many cases certain details are recorded more frequently in recent years due to better quality reporting – the comparison helps identify what types of errors and failures remain relevant to today's refineries. Moreover, if such findings are analysed in combination with experience and other findings related to safety management in refineries today, it may be possible to have more precise insight on the patterns that are most relevant from this analyses.

1.5 Type of events and consequences of accidents

Because of the volume of flammable and explosive substances typically present in refineries, scenarios tend to include fires and explosions with potentially high consequences if not adequately controlled. In particular, production of hydrocarbon products leads to a high presence of flammable compounds onsite. Not surprisingly, therefore, nearly 80% of the events studied involved a fire or explosion (see Figure 4 below). In addition, a significant amount of toxic substances may be present such that refineries are also exposed to the risk of potential toxic releases. Many crude oils contain a significant percentage of hydrogen sulphide that is eventually separated from the crude and usually processed to produce sulphur for the marketplace. Other processes require the presence of sulphuric acid or hydrofluoric acid (for alkylation) or ammonia (to remove nitrogen from the crude feedstock). In fact, over one third of the refinery accident events involving corrosion have also generated toxic releases. Toxic releases to the soil were slightly higher in relation to toxic releases to water and air, probably resulting from a number of accidents stemming from tank and underground pipe failures included in the database.

Releases were most often hydrogen and hydrocarbon compounds including process gases, naphtha, crude oil and various types of fuels. (See Figure 5 on the next page). The largest release was estimated to be around 100,000 tonnes of crude oil followed by 50,000 tonnes of fuel. Hydrogen sulphide was the toxic gas released more often than any other (16 cases). Fewer than 10% of accidents involved releases of other toxic gases such as hydrogen fluoride, carbon monoxide and sulphur dioxide. The highest (known) release of a substance toxic to human health was 15 tonnes of furfural, followed by 1 tonne of sulphur dioxide.

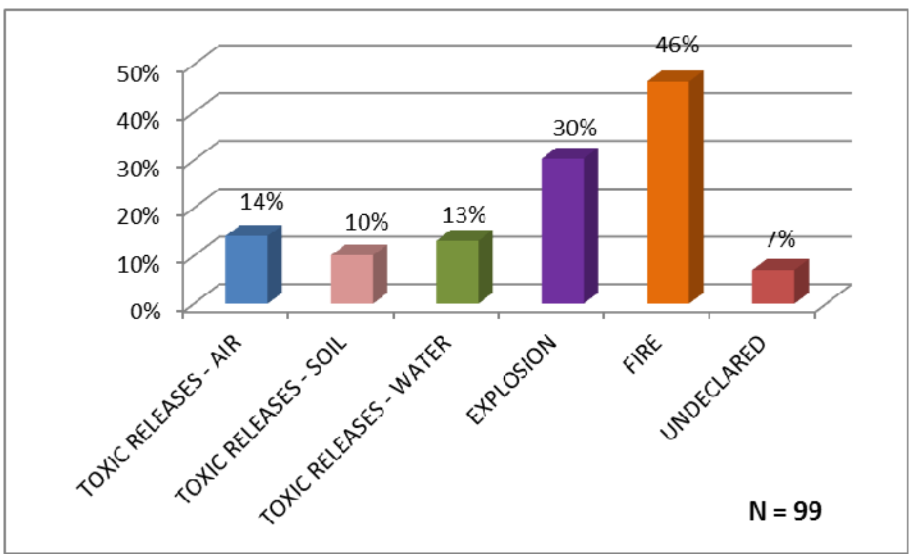

FIGURE 4. ACCIDENTS CLASSIFIED BY TYPE OF EVENT[7]

[7] There may be more than one type of event per accident.

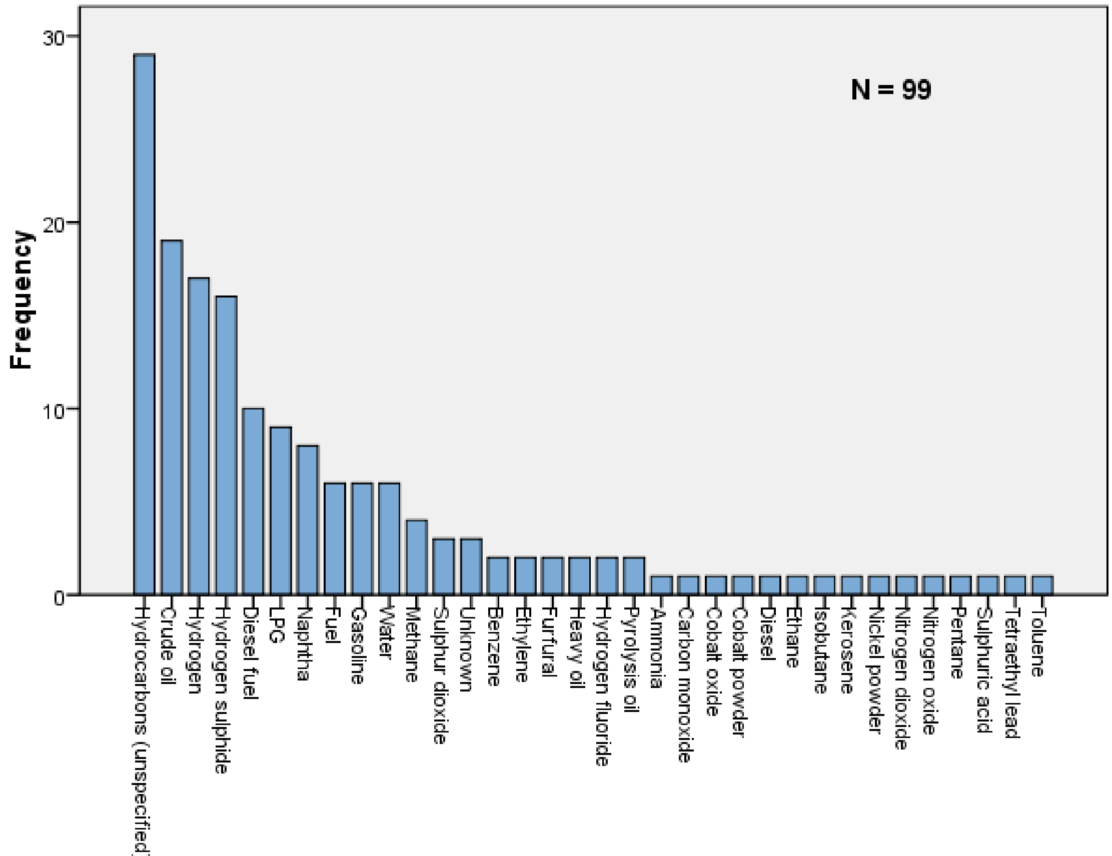

FIGURE 5. SUBSTANCES RELEASED IN REFINERY ACCIDENTS INVOLVING CORROSION BY NUMBER OF ACCIDENTS[8]

As shown in Figure 6 on the next page, most events were initiated by a leak, rupture or structural collapse. A leak consists of a release from a small opening that over time facilitate the formation of a pool of dangerous substances that may eventually catch fire or explode. A rupture generally results from a leak that releases a flammable substance internally which over time increases pressure and explodes inside a pipe or tank, causing a rupture. Structural collapse is defined as an accident in which, according to the report, corrosion was first manifested in the destruction or collapse of the unit (e.g., collapse of the distillation tower) rather than in a localized leak or rupture. In the accidents studied, leaks were less likely to lead to explosions (vapour clouds) than ruptures and ruptures were less likely to lead to toxic releases. However, both scenarios seemed to be equally capable of resulting in a fire. Two structural collapses were recorded. One occurred after the start of the fire in which the distillation tower, weakened by corrosion, collapsed. In the other the structure collapsed first and a fire followed.

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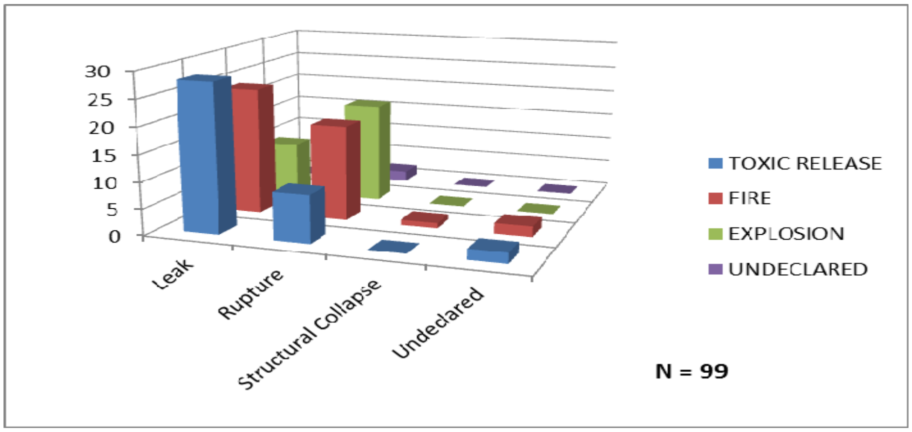
[8] An accident may have involved the release of more than one substance and therefore, the total number of accidents counted in the figure above exceeds the total number of accidents studied.



EFFECT	TOXIC RELEASE	FIRE	EXPLOSION	UNDECLARED
LEAK	28	24	10	0
RUPTURE	9	18	19	2
STRUCTURAL COLLAPSE	0	1	0	0
UNDECLARED	2	2	0	0
GRAND TOTAL	39	45	29	2

FIGURE 6. DISTRIBUTION OF EVENT TYPE FOR EACH TYPE OF FAILURE

To evaluate impacts, the authors developed a simplified methodology based on the European Gravity Scale. (See Table 5 on the next page). The simplified version combines some categories and criteria of the gravity scale for analytical purposes and also in recognition of the sometimes limited consequence data provided in some reports. In the case of environmental impacts, additional calculations were also made on the data provided to facilitate a consistent ranking of environmental impacts based on the scale.[9] Using this consequence ranking methodology, the accidents studied appear generally representative of the types of high risk scenarios that are typically associated with petroleum refineries. Most of these events were notified on the basis of high impacts in terms of effects on human health or the environment or significant cost either to the operator or in terms of offsite property damage or disruption. As evidence, it is observed that nearly 50% of the reports studied both pre- and post-2000 were high or very high consequences. [See Figure 7 on the next page). Accidents with low consequences represent more than a third of the accidents studied and also the ratio of low impact accidents to total accidents remained virtually unchanged for pre- and post-2000 accidents studied.

[9] In particular environmental impacts are not recorded in a consistent manner. The reports studied cited environmental impacts often provided one or a combination of the following as an indicator of impact: cost of restoration and clean-up, area of contamination, or volume or mass of the release. To facilitate comparison of environmental impacts between accidents, the study used information from the scientific literature to estimate environmental costs from mass or volume of the release when such costs were not available. The price of clean-up per cubic metre of contaminated soil was provided by Khan et al. [15] and a study by Etkin was the source of algorithms to estimate clean-up of contaminated water bodies in different world regions. [16]

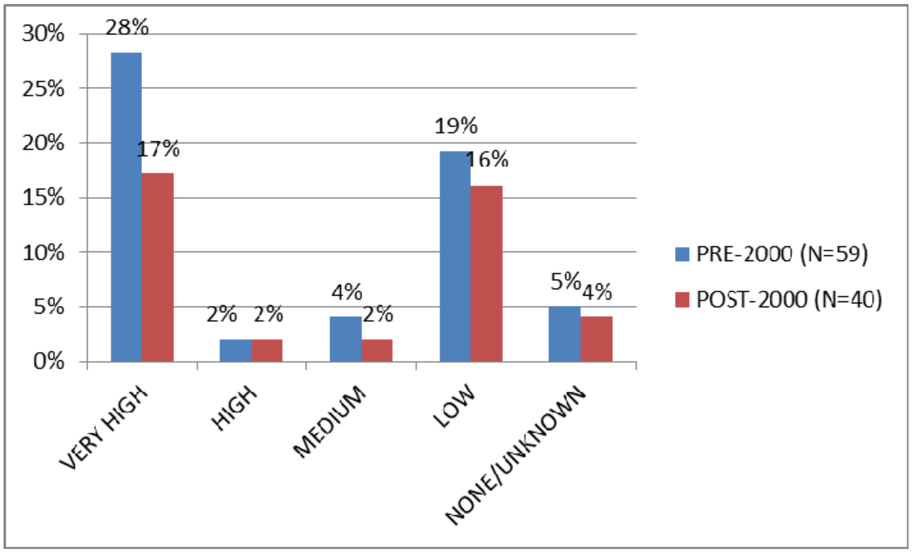
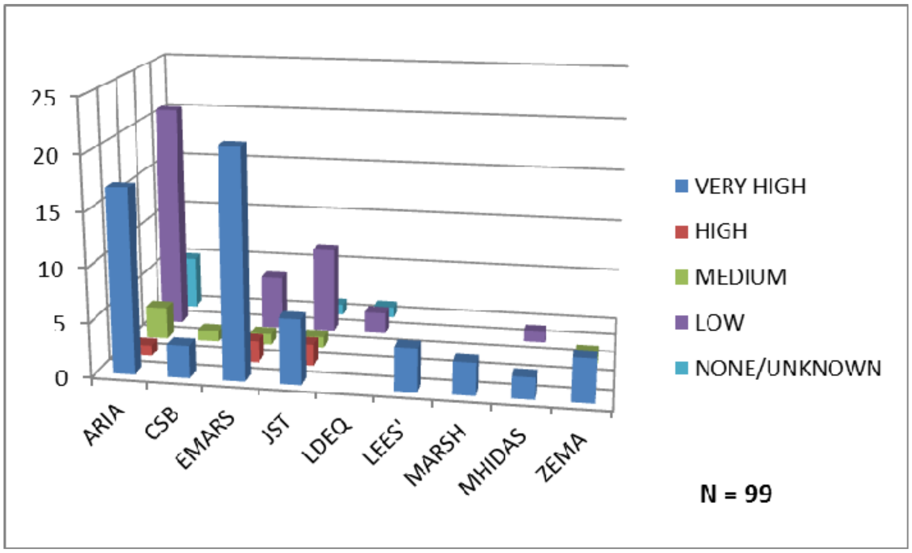


FIGURE 7. SEVERITY OF ACCIDENT CONSEQUENCES PRE- AND POST-2000

TABLE 5. CONSEQUENCE RANKING CRITERIA

For human consequences, production loss and public disruption, the scale approximates the European gravity scale (condensed into 5 categories). [14] For material and environmental damage, level of impact was assessed using a logarithmic scale from Low to High for costs starting with < €10,000.

	Deaths	Injuries	Material Damage	Environmental Damage	Public Service Disruption
Very High	>100	>1000	>€ 1,000,000	€ 1,000,000	>1 month
High	11-100	101 – 1000	€ 100,001-1,000,000	€ 100,001-1,000,000	1 week to 1 month
Medium	0-10	11-100	€ 10,001-100,000	€ 10,001-100,000	1 day to 1 week
Low	0	1-10	€ 1-10,000	€ 1-10,000	>1 day
None	0	0	0	0	0



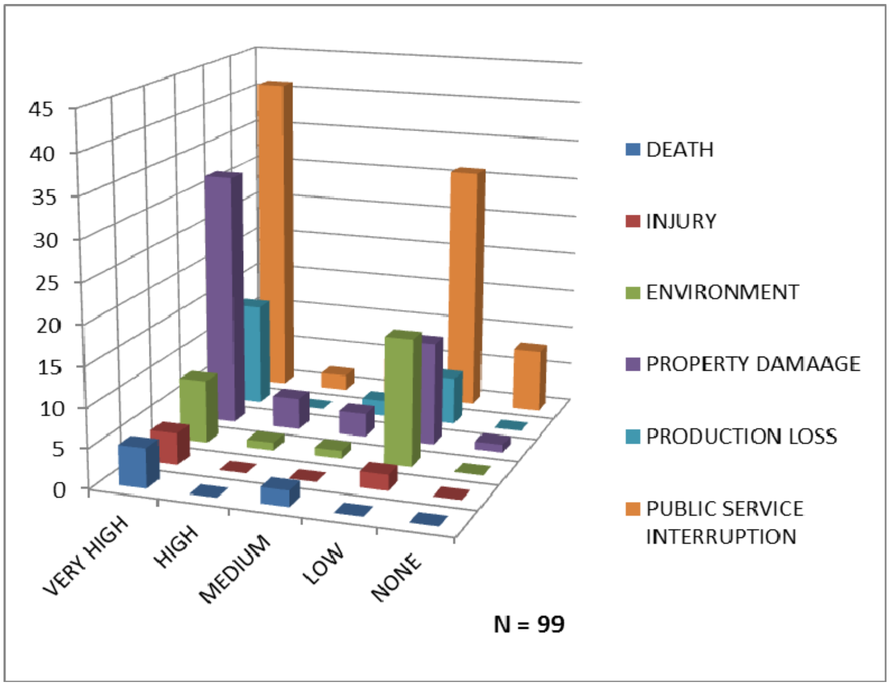
SOURCE	VERY HIGH	HIGH	MEDIUM	LOW	NONE/UN KNOWN	GRAND TOTAL
ARIA	17	1	3	21	5	47
CSB	3	0	1	0	0	4
EMARS	21	2	1	5	0	29
JST	6	2	1	8	1	18
LDEQ	0	0	0	2	1	3
LEES'	4	0	0	0	0	4
MARSH	3	0	0	0	0	3
MHIDAS	2	0	0	1	0	3
ZEMA	4	0	1	0	0	5
GRAND TOTAL	60	5	7	37	7	116

FIGURE 8. DISTRIBUTION OF EVENT TYPE FOR EACH TYPE OF FAILURE[10]

From Figure 8 above, it can also be observed that some sources focused more exclusively on high impact accidents, in particular, the Marsh and CSB reports. On the other hand, accidents reported within ARIA, JST and ZEMA include also accidents with lower impacts, based on criteria other than damage severity, e.g., release volume or event duragion. EU Member States must report major accidents at Seveso sites (which includes all petroleum refineries) using the severity criteria in Annex VI of the Directive. Therefore, eMARS is generally associated with predominantly higher consequence accidents reviewed in this study that occurred in the EU.[11] Accidents in eMARS occurring in France and Germany were also recorded in ARIA and in ZEMA (starting in 1993), respectively.

[10] Some accidents were reported or described by more than one source so the number of source citations exceeds the number of accidents studied.
[11] Some EU accidents reported in other databases (e.g., ARIA, ZEMA) may be associated with high impacts in this study even though they were not required to be reported to eMARS. The study used an additional criterion (production loss) with respect to eMARS to evaluate severity. In addition, the study used clean-up and restoration costs rather than area to estimate environmental impacts.

Public service interruption and property damage were the dominant consequences overall. (See Figure 9 below.) Taking into account production loss as well, 57% of the accidents studied were projected to have a significant ("very high") economic impact. Notably, sixteen OECD/EU accidents resulted in shut down of entire production units or entire refineries for weeks or months. Twelve accidents (12%) reported that the refinery was partially or completely shut down for a period. (Note that this consequence is likely to be underreported.) As noted in Table 6, estimates of shutdown times ranged from 10 days to approximately 240 days. In one report a shutdown of the hydrocracker, desulphurization, and hydrogen processing units for approximately 7 months (~210 days) resulted in a 30% reduction in production generating a business loss estimated at about €90,000,000 for the refinery [7].



LEVEL OF IMPACT	DEATH	INJURY	ENVIR	PROP DAM	PROD LOSS	PUB SRVC
VERY HIGH	5	4	8	32	13	41
HIGH	0	0	1	4	0	2
MEDIUM	2	0	1	3	2	5
LOW	0	2	16	13	6	31
NONE	0	0	0	1	0	8
Grand Total	7	6	26	53	21	87

FIGURE 9. LEVEL OF CONSEQUENCE VS. TYPE OF CONSEQUENCE[12]

[12] There may be more than one type of dominant consequence per event. For 8 accidents it appeared that minimal or no consequences resulted.

While less than one third of accidents studied involved death and injuries, potential health impacts remain high. For example, two accidents account for the majority of deaths and injuries recorded for the accidents studied. As shown in Table 6 on the next page, in total the number of deaths reported, on and off-site, equals 67, or 0.68 deaths per accident. The number of injuries totaled 219 or 2.21 per accident. Evacuation numbers were reported less frequently, but in total 7500 people were reported as evacuated across the 99 accidents.

Although there have been no deaths and only 19 injuries recorded in corrosion-related accidents in refineries since 2000, potential for catastrophic human health effects from any type of chemical accident in a refinery cannot be discounted. There have been several fatal accidents (related to other causes than corrosion) occurring in refineries in the EU and OECD in the last 10 years (and even in the last two), many of them in plants several decades old. The potential for a corrosion failure to cause a human disaster appears to be undiminished.

Environmental damage was reported for nearly a third of accidents and mainly associated with toxic releases to water. Six out of 14 accidents in which clean-up and restoration costs were provided or could be calculated, the environmental costs (usual soil or surface water contamination) were fairly high**.** One accident alone accounted for environmental clean-up and restoration costs of approximately €624,000,000. Eight accidents were estimated to cost under €50,000 and the five remaining accidents ranged from €300,000 to €32,000,000. (See Table 6 on the next page.)

TABLE 6. CUMULATIVE TOTALS OF CONSEQUENCE FIGURES FOR ALL ACCIDENTS

Category	# of accidents	Total reported
Total fatalities reported	8	67
Onsite fatalities	8	67
Offsite fatalities	0	0
Total injuries reported	18	219
Onsite injuries	16	193
Offsite injuries	5	27
Total reported population evacuated	5	7450
Total material costs of accidents reported[13]	42	€ 748,386,332
Onsite property damage	10	€ 172,712,786
Offsite property damage	2	€ 8,235,999
Operating losses	6	€ 165,164,253
Estimated environmental restoration and clean-up costs	14	€ 698,615,706
Estimated time of full or partial shutdown[14]	10	1036 days

[13] The ”total material costs” represent the sum of property damage, on and offsite, and operating losses. In many cases, accident reports did not provide a breakdown of these costs. Therefore, the “total material costs” category is much greater than if one adds up the totals of the subcategories (e.g., onsite property damage). The subcategories represent only the total figure for cases where this breakdown was provided.

14 Temporary shutdown was managed as a consequence in 12 cases but 2 did not specify a time frame.

CHAPTER 2 ANALYSIS OF THE POTENTIAL CONTRIBUTION OF PROCESS AND EQUIPMENT CONDITIONS

Corrosion represents a particularly relevant risk to petroleum refineries because refineries typically have several high risk factors because of the type of substances and processes involved in refinery operations. Other local conditions may also contribute to an acceleration in the corrosion rate, including physical location of equipment and the climate. Moreover, certain operating conditions in a refinery, both normal and abnormal, by their nature are particularly likely to present favourable opportunities for a corrosion failure to initiate a chain of events leading to a major accident. The accidents reviewed in this study consist of several cases where typical conditions conducive to a significant corrosion failure were somehow overlooked or if recognized, sufficient measures were not applied to avoid an accident. This chapter summarizes the study findings in the context of the process and equipment conditions with known risk potential, highlighting in particular those which were identified as relevant in analyses of the cases studied.

Corrosion can appear as either uniform corrosion or localized corrosion. Uniform corrosion is also known as general corrosion and is the classic form of corrosion in which the entire surface area, or a large fraction of the total area, is affected by a general thinning of the metal. In chemical processing uniform corrosion is considered the least dangerous form of corrosion because it is easily visible long before it is degraded enough to fail. Nonetheless, uniform corrosion may sometimes be a cause of accidents, for example, in pipelines that are in remote locations, underground, or otherwise, not viewed frequently, general corrosion may continue for a long time undetected.

Conversely, there are numerous types of localized corrosion that are far more difficult to detect without targeted effort. Thus, consequences of localized corrosion can be more severe than uniform corrosion as failure occurs without warning and often after only a short period of use or exposure. Typically, localized corrosion occurs between joints (crevice corrosion) or under a paint coating or insulation. Stress corrosion cracking and hydrogen-assisted stress corrosion are also forms of localized corrosion. They are often grouped together with hydrogen embrittlement and stress embrittlement, even though these are not corrosion phenomena, because the conditions and the resulting failure mechanism (cracks in the metal) are remarkably similar. As such, it is not necessarily easy to determine which phenomenon caused such a failure following an accident; hence, by necessity, analyses of accidents involving corrosion-related failures generally include both phenomena.

Generally speaking refineries are vulnerable to corrosion both due to internal process conditions as well as other factors. In the majority of cases studied for this report, it was possible to identify some of the causal factors and have a general knowledge about which ones were likely to be dominant. The following sections, present the results of the analysis of corrosion conditions that may have been responsible for equipment failure in these cases.

2.1 Process conditions contributing to corrosion in study cases

Refineries are most vulnerable to corrosion due to internal process conditions. Ironically, despite the existence of several corrosion references and standards, a uniform approach to describing and organizing corrosion types does not exist. The American Petroleum Institute Recommended Practice 571 (API 571) lists over 25 common corrosion damage mechanisms to industrial activity plus 11 addition types that are specific to refineries.[17] In addition, studies of aging facilities may classify corrosion effects into different groupings on the basis of characteristics such as failure mechanisms (e.g., wall thinning, cracking and fracture, physical deformation), common causal factors (e.g., stress-driven damage, metallurgical/environmental damage) or other commonalities. Table 7 on pages 33 and 34 shows examples of some typical corrosion phenomena in refineries as classified in API 571 by damage mechanism.[15] The table shows only a portion of the vast number of corrosion phenomena identified.

In 53 cases process conditions were identified as contributing to the corrosive conditions preceding the accident. The most commonly cited contributor was the substance (46). Flow (either high, low, turbulent or unequal) was cited in ten cases, and temperature (mostly high, but in a few cases, low) and pressure (mostly high) were cited as contributors in 11 and 7 cases respectively. In eight cases other exacerbating process conditions were present, including operation outside design parameters and variation across process cycles.

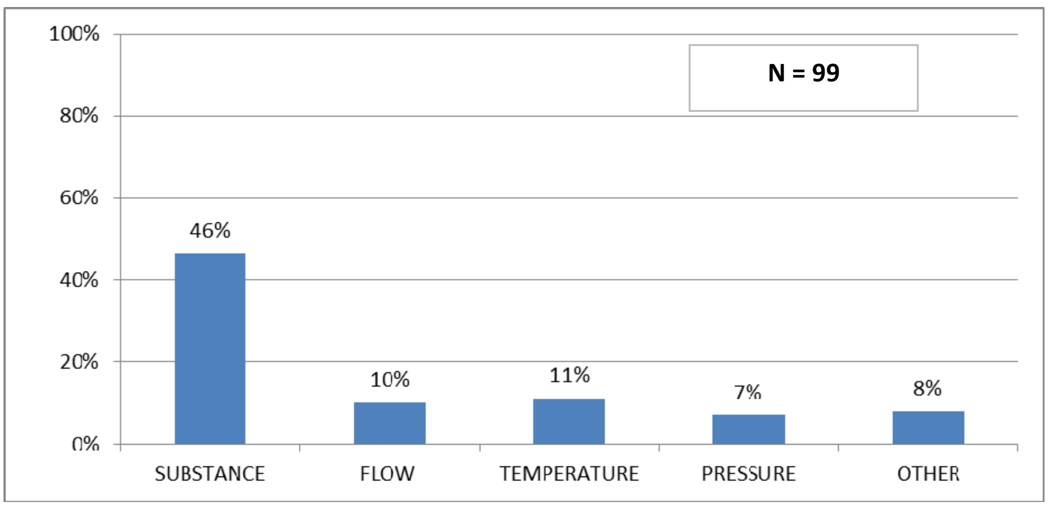


FIGURE 10. PROCESS CONDITIONS CITED AS CONTRIBUTING TO CORROSIVE CONDITIONS ACCIDENTS STUDIED (53 CASES IN TOTAL)

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[15] Note that erosion/corrosion is included because it is so strongly associated with corrosion. However, several other mechanical and metallurgical failures not listed here are accelerated by corrosion phenomena (e.g., creep and stress rupture).

TABLE 7. EXAMPLES OF STRESS CORROSION CRACKING DAMAGE MECHANISMS PROPOSED BY API 571 [17][16]

Damage Mechanism	Velocity, Temperature and pH Influences	Substances Involved	Other Influences	Processes Affected
Mechanical and Metallurgical Failure Mechanisms				
Erosion-corrosion	High velocity, High Temperature, High, Low pH	Varied	Particularly occurs in pockets, elbows and similar configurations.	Affects all types of equipment exposed to moving fluids, gas-borne catalytic particles.
Uniform or Localized Loss of Thickness (Generic)				
Galvanic corrosion		Varied		
Atmospheric corrosion	Low temperature		Cyclic: Fluctuation between ambient and < or > temperature.	
Cooling water corrosion	Low velocity, High temperature	Fresh or salt water, potential chlorides		
High Temperature Corrosion (Generic)				
Sulphidation	High temperature	Sulphur concentration		FCC, coker, vacuum distillation, visbreaker and hydro-processing
High temperature H2/H2S	High temperature	H_2 and H_2S		Desulphurizers, hydroprocessing , hydrotreaters, hydrocracking
Nitriding	High temperature	Nitrogen compounds		

[16] This table is by no means a complete list. It only shows a number of examples of some typical refinery corrosion phenomena classified and described in API 571. For more information please consult the reference document.

Damage Mechanism	Velocity, Temperature and pH Influences	Substances Involved	Other influences	Processes Affected
Uniform or Localized Thickness Phenomena (Refinery Specific)				
Amine corrosion	High velocity/temperature	Ammonia, H_2S and HCN	Higher turbulence	
HCL corrosion	Low pH	HCL when water is available (presence of oxidizing agents)		Crude unit, hydroprocessing unit, catalytic reforming units
Hydrofluoric acid corrosion	High velocity/temperature	HF concentration + O_2 and sulphur, higher presence of water to HF concentration	Higher turbulence	HF alykylation, deadlegs
Naphthenic acid corrosion	High velocity/temperature low pH	Naphthenic acid, sulphur content	Two-phase flow (liquid and vapou), High turbulence	Crude and vacuum heater tubes and lines, cokers, piping systems
Phenol carbolic acid corrosion	High temperature	Sulphur and organic acids and very dilute phenol solutions		
Sour water corrosion	High temperature, low pH	Higher concentrations of H_2S, Oxygen		FCC and cokers
Phosphoric acid corrosion	Low velocity and pH	Solid phosphoric acid catalysts, free water, contaminants		Polymerization units
Environmentally-Assisted (Refineries)				
Polythionic acid stress corrosion cracking		Sulphur acids & oxygen		heat exchanger tubes, hydroprocessing, crude and coker units, FCC units, boilers
Chloride stress corrosion cracking	High temperature, pH > 2	Chloride content, oxygen	Cyclic flux between wet-dry conditions, tensile stress	

2.2 Analysis of cases in association with specific process conditions

The study also analysed the cases to identify what types of substances, process units and equipment were associated with the accidents. As noted in Section 2.1 above certain substances have properties that may cause them to be corrosive agents. Table 8 on the next page highlights some typical substances that have notable influence on corrosion rates in various refineries depending on the crude oil inputs and types of processes present In addition, different processes and equipment have greater or lesser tendencies to be associated with a corrosion-related incident. For these reasons, it was considered interesting to determine the prevalence of various categories of substances, processes and equipment in association with the accidents. Although trends identified could not be considered conclusive, because of the non-representative nature of the data, it is still worth noting how frequently some typical associated causal factors appear in the data. A fundamental ingredient of corrosion is exposure to a corrosive agent via a refinery process, that is, a substance that under certain processing conditions acts upon the metal and weakens it. These corrosive agents are in effect oxidizing substances, which may include water, a variety of acid compounds introduced or generated in the process as well as the crude oil and final and interim products, such as coke and kerosene. As noted in Table 7 in the previous pages, some substances have unique corrosion "signatures", that is, the corrosion produced is characterized by a particular specific visual or textural pattern, reacts with specific metal compounds, and frequently occurs in the same types of locations. Figure 11 on page 36 indicates the frequency with which various types of substances were cited in the accident reports as potential agents which may have accelerated corrosion rates ultimately leading to equipment failure. Out of 96 cases, 49 (51 %) identified the process substances that were most likely to be responsible for accelerating the corrosion rate of the equipment involved.

Substances cited most commonly were sulphur and sulphur compounds and water (14 cases each) followed by hydrogen sulphide (11 cases), along with crude oil (8 cases), as noted in Figure 11. The substances identified in Figure 11 from the accidents studied are normally present in the highest volumes and in a variety of processes throughout a refinery site. Carbon is another common corrosive agent with an important presence in refineries but it was not mentioned as being involved in any of the accidents studied for this report.

TABLE 8. TYPICAL PROCESS SUBSTANCES ASSOCIATED WITH REFINERY CORROSION

Substance	Role and Significance
Crude oil	Crude oils consist of many different hydrocarbon compounds and vary considerably depending on their source. Crude oils range in consistency from water to tar-like solids, and in color from clear to black. An "average" crude oil contains about 84% carbon, 14% hydrogen, 1%-3% sulphur, and less than 1% each of nitrogen, oxygen, metals, and salts. [18] The refining industry differentiates crude oils in a number of ways in relation to their predominant properties. For example, they can be generally classified as paraffinic, naphthenic, or aromatic, based on the predominant proportion of similar hydrocarbon molecules. They are also often classified as "sweet" or "sour" on the basis of sulphur content. Refinery crude feed stock often consists of mixtures of two or more different crude oils and the stock is largely influenced by regional economics, in particular, where the closest sources of crude oil are located.
Naphthenic acid	Naphthenic acid is the generic name used for all of the organic acids present in crude oils and this type of acid can be highly corrosive. Naphthenic acid corrosion occurs primarily in high-velocity areas of crude distillation units in the 220 °C to 400 °C (430 °F to 750 °F) temperature range. When combined with high temperature and high velocity, even very low levels of naphthenic acid may result in very high corrosion rates. The presence of naphthenic acid and sulphur compounds considerably increases corrosion in the high temperature parts of the distillation units. [6]
Sulphur compounds	After carbon and hydrogen, sulphur is typically the most available element on a refinery site. Sulphurs may be present in crude oil as hydrogen sulfide (H_2S), as sulphur compounds, such as mercaptans, sulphides, disulphides, thiophenes, and polythionic acids, or as elemental sulphur. In fact, all high temperature sulphidation is caused by hydrogen sulphur and the rate of corrosion via sulphidation depends on the degree to which all the sulphur compounds in the crude feedstock decompose to H_2S. Over the years the average concentration of sulphur in the crude feedstock in OECD-EU refineries has been rising for at least a decade and this trend has contributed to potential increase in corrosion risk. Hence, regardless of the types of processes hosted by the refinery, most refineries are vulnerable in varying degrees to one or more form of corrosion associated with sulphur throughout the plant.
Hydrogen	Hydrogen is plays a particularly important role in the removal of impurities, most notably in the hydrotreating and hydrocracking processes. The processing of heavier crude oil and stricter environmental regulations has increased the use of and demand for hydrogen in refineries in recent years. According to one source, as recently as 2008 petroleum refineries accounted for approximately 90% of global hydrogen consumption. [19] At elevated temperatures and pressures, hydrogen can have a corrosive effect on carbon and low-alloy steels. Typical corrosion phenomena resulting from pipeline exposure to hydrogen under intense process conditions includes galvanic corrosion, high temperature hydrogen attack, chemical reactions of metal with acids, or with other chemicals as in sulfide stress cracking. Although hydrogen embrittlement and blistering are not corrosion mechanisms, they may create similar weaknesses in the metal leading to material failure. Expert knowledge is often necessary to distinguish the specific hydrogen damage mechanism(s) responsible for a particular equipment failure.
Water	Water is associated with corrosion as a conductor of potentially corrosive agents but also as a catalyst for generating corrosive agents. The presence of the chloride ion in the crude oil (from briny water), cooling water that has been recycled and picked up various oxidizing agents or that that has been pre-treated with chlorine (e.g., from the public water supply). The corrosivity of the water therefore varies greatly depending on its origin. Water is also associated with the formation of corrosive agents such as hydrochloric acid and accelerating their corrosive behavior.
Hydrofluoric acid	The aqueous solution of hydrogen fluoride (hydrofluoric acid) is a weak acid as the high strength of hydrogen-fluorine bonds do not allow complete dissociation with water. Hydrofluoric acid is used as the catalyst of refinery alkylation which facilitates the reaction of low olefins (typically butene) and isoparaffins (typically isobutane) to form higher isoparaffins.
Ammonia and ammonia compounds	A small percentage of crude oil consists of nitrogen compounds as well as ammonia chlorides. These products are generally extracted and processed to produce ammonia. Ammonium chloride and ammonium sulphates are corrosive, as gas, as solid, or in solution and are of particular concern (but not limited to) distillation, hydrotreating, hydrocracking, catalytic reforming, and catalytic cracking processes.
Carbon and carbon dioxide	Carbon dioxide is found in trace amounts in crude oil and also in condensate and produced water. It is released from crudes typically produced in CO_2-flooded fields and crudes that contain a high content of naphthenic acid. When combined with water, carbon dioxide produces carbonic acid (H_2CO_2), which is highly corrosive with steel and other metallurgies. Conditions also exist in refineries (high temperatures, ample carbon sources) that are conducive to carburization and decarburization.

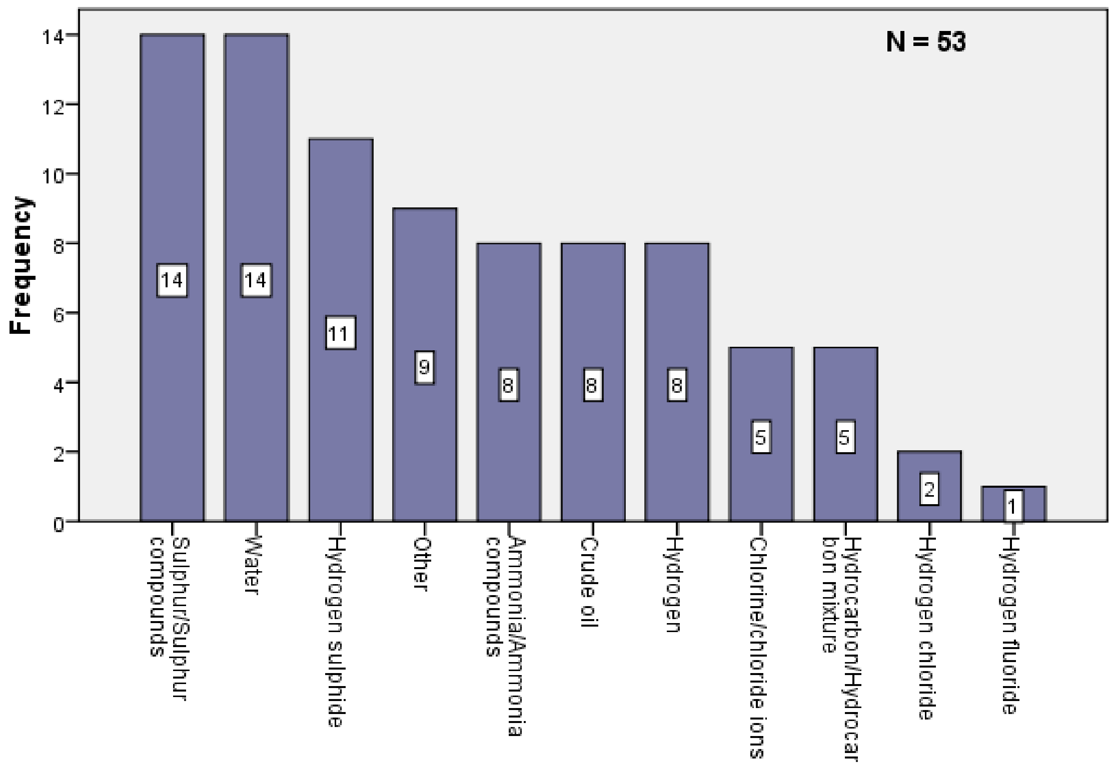


FIGURE 11. PROCESS-RELATED SUBSTANCES CITED AS CONTRIBUTING TO CORROSION FAILURES[17]

Ammonia and ammonia compounds, chlorine and chloride ions, and hydrogen were each cited in eight cases as a potentially dominant corrosive agent influencing the equipment failure, mainly in the distillation and storage units. Hydrogen chloride was reported as the corrosive agent in two of the accidents studied. Only one accident studied identified hydrofluoric acid as a contributing factor. Many refineries do not use hydrogen fluoride for alkylation and hence, this risk is not necessarily present in all refineries. Other process-related substances cited in the accidents included recycled content, phosphoric acid and nitrogen and nitrogen compounds.

[17] One accident could include more than one process substance as a contributor to corrosion. Hence, the total frequency of all substances added together exceeds the number of cases where this phenomenon was noted. Water was only cited as a contributing substance if it was introduced into or generated by the process. Where water was introduced by the external environment (e.g., rain, marine climate), it was not counted as a process substance contributing to corrosion.

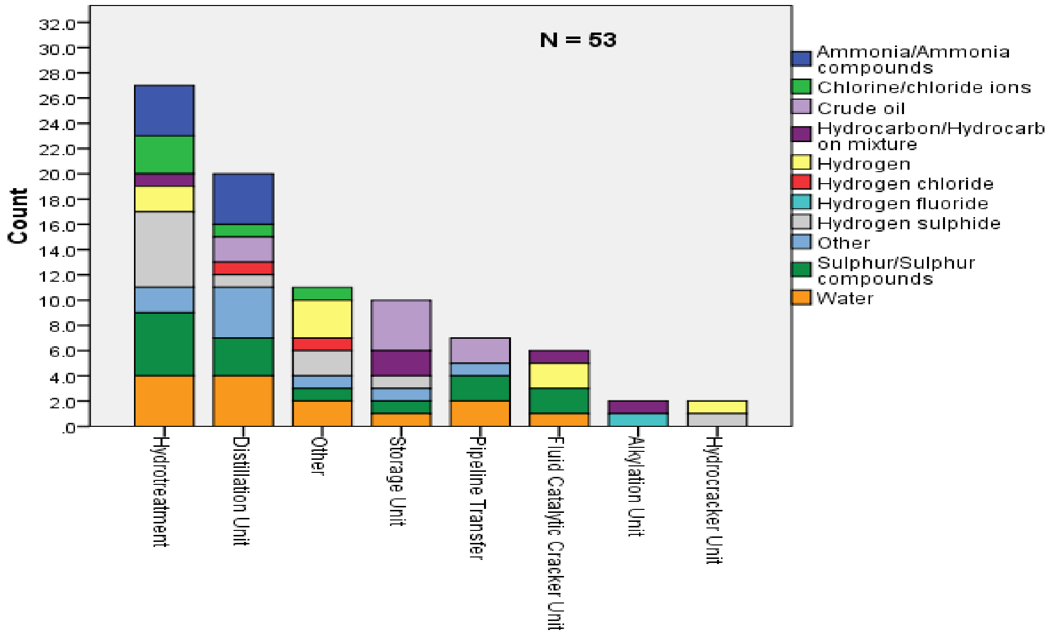


FIGURE 12. PROCESS SUBSTANCES CONTRIBUTING TO CORROSION FAILURE IN ASSOCIATION WITH THE PROCESS UNIT OF ORIGIN[18]

Figure 12 above shows which process units were identified as the origin of the accident in association with process substances indicated as contributing to the corrosion failure. Although some substances are cited slightly more frequently than other, the frequency is not high enough in any one unit to indicate dominance of a particular substance. Rather, this figure illustrates the wide diversity of substances throughout refinery production that can accelerate corrosion rates.

The accidents studied highlighted a variety of conditions that appeared to contribute to accelerated corrosion rates leading to the equipment failure, including:

- A corrosive agent was formed by a reaction between process fluids
- Process conditions cause decomposition of the corrosion inhibitor
- Corrosion was induced by the presence of sulphur and sulphur compounds
- Corrosion was induced by the presence of hydrogen
- Corrosion was induced by the presence of hydrogen sulphide
- Corrosion accelerated through corrosive agents in process water

Examples of these conditions are given in Figure 12 on the next page.

[18] One accident could include more than one process substance as a contributor to corrosion. Hence, the total frequency of all substances added together exceeds the number of cases where this phenomenon was noted.

FIGURE 13. OBSERVATIONS ON PROCESS CONDITIONS RELATED TO ACCIDENT OCCURRENCE

Corrosive agent formed by reaction between process fluids

"An analysis conducted on the process waters showed that in normal conditions this medium is lightly corrosive to steel carbon, but strongly corrosive during the period when the catalyzer is being circulated. The transition phase of recirculation is characterized in effect by a diversion of the content to be replaced by recirculation of the catalyzer. An injection of torch oil keeps the catalyzer at a certain temperature. The combustion of sulphur in the torch oil releases vapours of sulphur trioxide of which a part passes by the reactor to end up at the top of the principal fractionating column. In contact with the process waters, the SO3 forms an acid (H2SO4) that is particularly corrosive. This corrosion is accentuated by a mechanism of corrosion-erosion at the elbow joints (drip phenomenon). The repetition of recirculation phases led to the eventual formation of the leak. " [Case 79]

"The cause of corrosion of the heat transfer tube was assumed to be hydrogen chloride. In addition, the following fact was proven as a result of a flow analysis in the heat exchanger. At both right and left sides of the upper stage of heat transfer tubes in each pass in the heat exchanger, the quantity of washing water decreased. Therefore, washing water, which had been condensed once, was reheated and part of the solved ammonium chloride was re-evaporated and hydrogen chloride was generated. In this heat transfer tube, the lower part in which liquid remains becomes an intensely corrosive environment." [Case 62]

"An oval opening of 130 × 90 mm was caused in by-pass piping of the hydrogen sulfide absorption tower for re-circulation gas at the atmospheric fuel oil hydro-desulphurization unit. Internal fluid spouted, and a fire occurred. Ammonium hydrosulfide was formed by a reaction of ammonia in the crude oil with hydrogen sulfide in the by-pass. The flow of internal fluid was unique due to piping in a cold district, no heat insulation for the flange, and a vertical dead end, etc. The environment with active corrosion by ammonium hydro sulfide was partially created by drops of water." [Case 69]

Process conditions cause decomposition of the corrosion inhibitor

"The operator observed corrosion on the inside of the injection pipe and its carbon steel manifold. The temperature conditions and the injection flow were such that an unexpected decomposition of the inhibitor, containing phosphorus compounds, led to formation of concentrated phosphoric acid, a substance that is both very hot and very corrosive in particular to Hastelloy B2 alloy of which the injection pipe was made." [Case 64]

Corrosion induced by the presence of sulphur and sulphur compounds

" … the rupture was caused by four types of deterioration, the effects of which had cumulatively led to a reduction of thickness to a point below that at which the tube could withstand operating pressure….
- aggression supposedly due to exposure to polythionic acids: These acids form when the sulphurised constituents of the load are in contact with oxygen. …
- reduction of thickness by oxidation/sulphuration: In the grooves formed by the polythionic acid aggression, the material (austenitic stainless steel) had lost its unoxidizable character, leading to a reduction of thickness …
- the presence of sigma phase (an intermetallic compound causing very marked fragility of the metal) in a low proportion, which may have facilitated the development and penetration of the intergranular attack.
- loss of intergranular cohesion entailing slow creep … which generates fissuring in the outer skin of the tube: this … could be explained by poor heat exchange due to a deposit of coke on the inside of the tube. [Case 74]

Corrosion induced by the presence of hydrogen

"The decompression of a depropanisor and the head spherical tank, through the opening of a pipeline, caused an unconfined vapour cloud explosion in a fluid catalytic cracker … Corrosion of an elbow pipe of 8" in carbon steel located at 15m high on the pipeline of the depropanisor from hydrogen blistering was suspected as the origin of the accident." [Case 18]

Corrosion induced by the presence of hydrogen sulphide

"The ruptured buffer drum had been operated in a wet hydrogen sulfide gaseous environment for a long time. Stress corrosion cracking gradually proceeded due to the hydrogen sulfide environment, and a rupture occurred under usual operation pressure." [Case 41]

Corrosion accelerated through corrosive agents in process water

"It is desirable to avoid treatment using water with a high chloride concentration. Industrial water was used to dilute the polythionic acid. Therefore, the chloride concentration was high in the polythionic acid aqueous solution that accumulated in the drain valve nozzle. In addition, the chlorine was concentrated by the evaporation of water due to high temperature after starting operation, and SCC occurred. Water management using industrial water is a basic factor, though there was a possibility of SCC due to chlorine. The stress was generated by thermal expansion at the gusset supporting drain piping by a temperature rise after starting operation." [Case 9]

2.3 Corrosion risk associated with chemical refining processes

Refinery processes generally consist of either refining or treatment processes. Figure 14 below is a simplified diagram of the refinery process showing what are more or less the basic units hosted by most refineries, although the technologies applied may vary. The composition of process units is unique to every refinery. While several process steps are fundamental, such as distillation, cracking, and removal of impurities and byproduct, the technology applied to the same processes can vary considerably across refineries. The composition of process downstream from distillation is also determined by the refinery's chosen product lines. Some typical refinery processes are described in Table 9 on the next pages.

Refining processes, such as distillation and thermal cracking, breakdown and manipulate the molecules in the crude oil feedstock to convert it into marketable products. Treatment processes remove impurities and byproducts from the feedstock and refining output. As much as possible these "unwanted' substances are either recycled into the refining or treatment process (e.g., hydrogen) or sold as products in their own right (e.g., sulphur).After desalting, the crude feedstock is fed into the distillation unit, the first main processing operation. The distillation process results in output of heavier and lighter fractions of petroleum product.

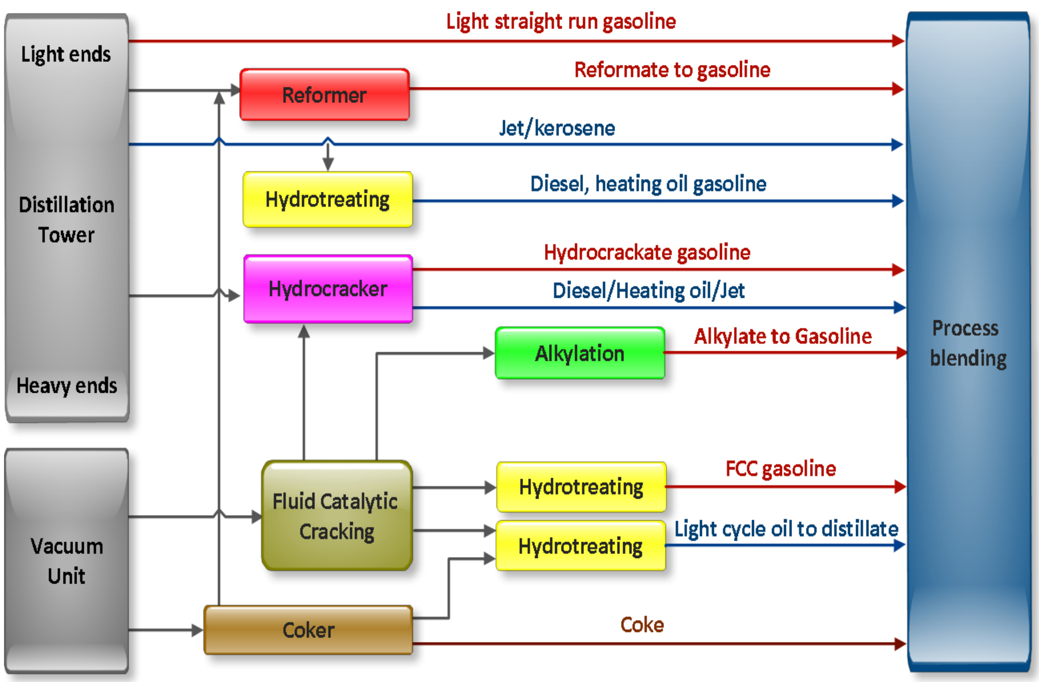


FIGURE 14. SIMPLIFIED DIAGRAM OF A REFINERY PROCESS
(SOURCE: U. S. DEPARTMENT OF ENERGY) [4]

TABLE 9. TYPICAL REFINERY PROCESSES

Process	Role and Significance
Atmospheric and vacuum distillation	Distillation (fractionation) of the crude feedstock is the start of the refining process. Since it receives untreated crude oil, it is exposed to all potential corrosive agents and their precursors in the feedstock. Notably, more than one fifth of the accidents studied started in the distillation unit. In a study of corrosion failures in an Israeli oil company from 2001-2004, 15% of 210 corrosion failures over that period were recorded in distillation units. [21] Like many refinery processes, distillation is heat intensive. Temperatures at the bottom are generally around 350ºC to 400ºC and gradually decrease as vapour rises in the column. As the vapour rises and cools, it separates into layers of product with the heaviest at the bottom (lubricating oil, paraffin wax, fuel oils) to lighter products (middle distillates, kerosene) and lighter products (naphthas), as shown in Figure X. Residue and heavy oils at the bottom of the column are further distilled via vacuum distillation at a reduced pressure and high temperature. According to the US OSHA Technical Manual, vulnerable areas within the distillation process include the preheat exchanger (HCl and H_2S), the preheat furnace and bottoms exchanger (H_2S and sulphur compounds), the atmospheric tower and vacuum furnace (H_2S, sulphur compounds, and organic acids), the vacuum tower (H_2S and organic acids), and the overhead (H_2S, HCl, and water). [18] The top section of the atmospheric distillation tower is highly vulnerable to corrosion. The most common substances released as a result of a corrosion failure in the distillation failure tend to be hydrocarbons, including crude oil and various distilled products.
Hydrotreating	Hydrotreating is a catalytic reaction occurring in the presence of hydrogen at elevated temperature and pressure. It removes objectionable materials from petroleum fractions by selectively reacting these materials with hydrogen in a reactor at relatively high temperatures at moderate pressures. These objectionable materials include, but are not solely limited to, sulphur, nitrogen, olefins, and aromatics. [22] There are a number of hydrotreating processes used in refineries, one of the most common being desulphurisation and denitrogenation. Hydrotreatment units can experience a number of corrosion phenomena.
Storage facilities	Most refinery storage tanks fall into the following categories: atmospheric storage, pressure storage, and heated storage. All the storage tank accidents studied in this report originated in atmospheric storage tanks. All atmospheric storage tanks are open to the atmosphere, or are maintained at atmospheric pressure by a controlled vapor blanket. [23] In Groysman's study, 22% of the corrosion failures cited originated in storage facilities. [21] Potential consequences of atmospheric storage tank failures can be particularly high due to their large capacity. Storage tanks have generally been involved in some of the most severe accidents in EU and OECD countries, most often because they have led to sizable fires sometimes requiring a number of days to extinguish. However, the majority of storage tank accidents studied involved predominantly environmental impacts, due to leaks or ruptures at the base of the tank.
Alkylation	The primary commercial alkylation processes are hydrogen fluoride and sulphuric acid alkylation. In general corrosion in both types of units can occur if the vulnerabilities are not controlled. Notably, hydrogen fluoride is highly corrosive to most materials. Carbon steel is generally less vulnerable to corrosion via sulphuric acid, but high concentrations of the substance and the breakdown of sulphuric acid esters, or where caustic is added for neutralization, may accelerate the process. [6] [24]

TABLE 9: TYPICAL REFINERY PROCESSES (CONTINUED)

Process	Role and Significance
Cracking	This term is given to those processes that convert heavy oil (usually fuel oil or residues) into lighter product stock such as LPG, naphtha, and middle distillates by applying only heat to the feed over a prescribed element of time. There are a number of types of cracking technologies including thermal cracking, hydrocracking and catalytic cracking. There are also a number of catalytic cracking technologies, including fluid catalytic cracking (FCC), moving-bed catalytic cracking, and Thermofor catalytic cracking (TCC). Of these fluid catalytic cracking is the most common. The FCC is one of the largest downstream units and one of the few units whose size is relatively consistent with the size of the distillation tower across refineries. FCCs tend to be from 35-40% of the distillation tower. The FCC and the alkylation units, combined, supply close to one half of the gasoline volumes in refinery operations. Hydrocracking is the oldest cracking process and operates normally at very high pressures, typically around 2,000 psig. As such, it tends to be rather costly in comparison and its use in refineries has declined over time in favour of the FCC. [20] [22]
Pipeline transfer	The sheer volume of the pipeline network in a refinery makes it inevitable that failure in pipeline transfer due to corrosion is high. Process and utility piping distribute product, process inputs, steam, water, and other process fluids throughout the facility. Their size and construction depend on the type of service, pressure, temperature, and nature of the products. Vent, drain, and sample connections are provided on piping, as well as provisions for blanking. [18] For pipeline networks, process conditions are not necessarily the dominant contributor to corrosive conditions. In particular, exposure to wet climate, weather, acid rain, and soil may be greater contributors in some cases than internal process conditions. Severe accidents involving pipeline transfer are often associated with loading and unloading involving the transfer of large volumes across the pipeline in a short period of time. As recently as 2008 a spill of 478 metric tonnes of heavy fuel into a major water body occurred when the pipe leading to the oil tanker failed as a result of corrosion.
Isomerisation	Isomerization converts straight-chain molecules to their branched-chain counterparts primarily to provide additional feedstock for alkylation units and to produce higher octane molecules for gasoline blending. Corrosion potential can be elevated when acids happen to be present in the feedstock.
Coking	Coking is considered to be the most severe process, involving a number of intense physical subprocesses, including frequent heating and cooling cycles, necessary to break up the long chain hydrocarbon residue from the bottom of the distilling column. The coking unit has been noted as a frequent cause of refinery fires, especially as sulphur and metal content of residues increase and accelerate corrosion. Notably, many refineries do not have coking units. [20] [26]
Catalytic reforming	The catalytic reformer plant aims to upgrade low octane naphtha to a high octane product that meets "anti-knocking" for blending into motor gasoline fuel. As with cracking, catalytic processes have overtaken thermal processes as the process of choice in the industry as the more cost-effective option. Catalytic reforming unit consists of a series of several reactors (e.g., cracking, polymerization, dehydrogenation). The catalytic reformer may operate at low or high pressures (50-200 psi) and can be continuous or non-continuous (up to 1000 psig). The reformer is also a major gasoline-producing unit, providing about 1/3 of the gasoline volume that a refinery produces. [20]

The distillation process is followed by a number of conversion processes depending on the product. These processes include:

- cracking processes (e.g., thermal and catalytic) which result in decomposition of the product
- unification, e.g., through alkylation and polymerisation, in which smaller hydrocarbons are to make larger ones (unification)
- alteration processes, such as isomerization and catalytic reforming, which rearrange the molecules essentially modifying the molecular structure to create or improve product. [18]

Conversion is then followed by treatment, formulating and blending. Treatment removes unwanted substances from the product, such as impurities and contaminants. Formulation and blending are finishing processes which improve and alter product properties to meet various quality or performance criteria. Other refinery processes also exist for recovery and treatment of process effluent and to recover catalysts and substances extracted from the product for other uses.

Figure 15 below shows the processes most often cited at the origin of the accident in the cases studied. It highlights typical units where important corrosion failures may occur. Out of 99 cases, the highest percentage (23%) started in the distillation unit, followed closely by hydrotreatment units (20%). In the cases studied there were substantially fewer cases involving such units after 2000 compared to prior years. Conversely, the number of cases involving the pipeline transfer network is proportionally somewhat higher after 2000. The "Other" category includes units for sulphur recovery, solvent extraction, saturated gas, olefin manufacturing and oil gasification. The study does not show any pattern linking specific units with accident consequences of a particular level of severity (see Figure 16 on the next page).

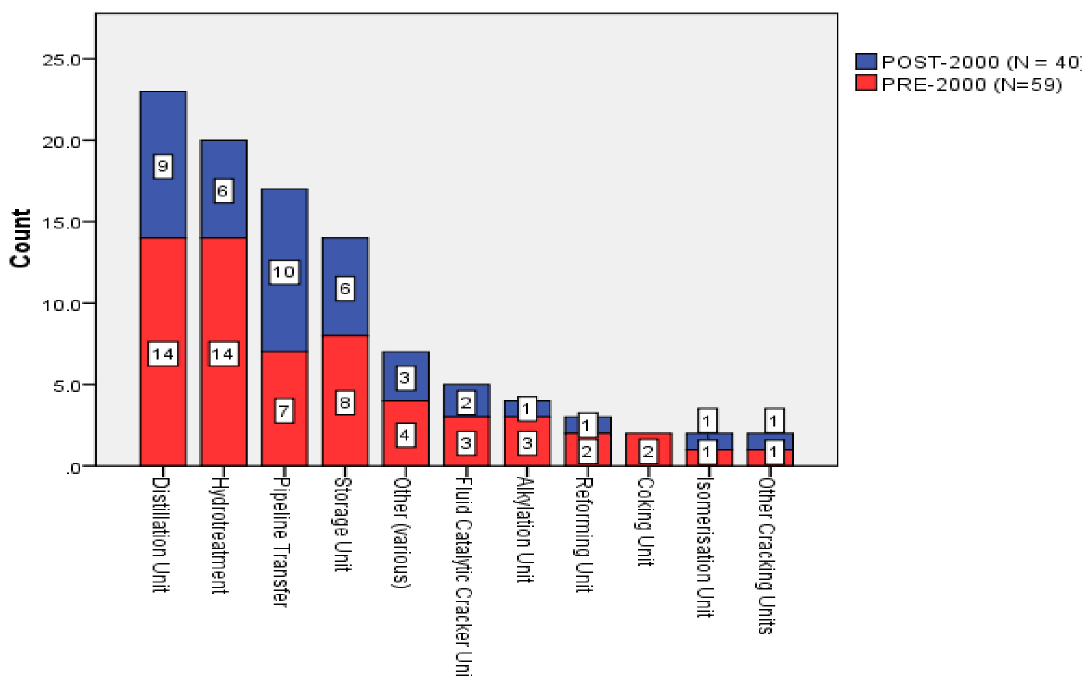


FIGURE 15. UNIT OF ACCIDENT BY ORIGIN OF CASES STUDIED

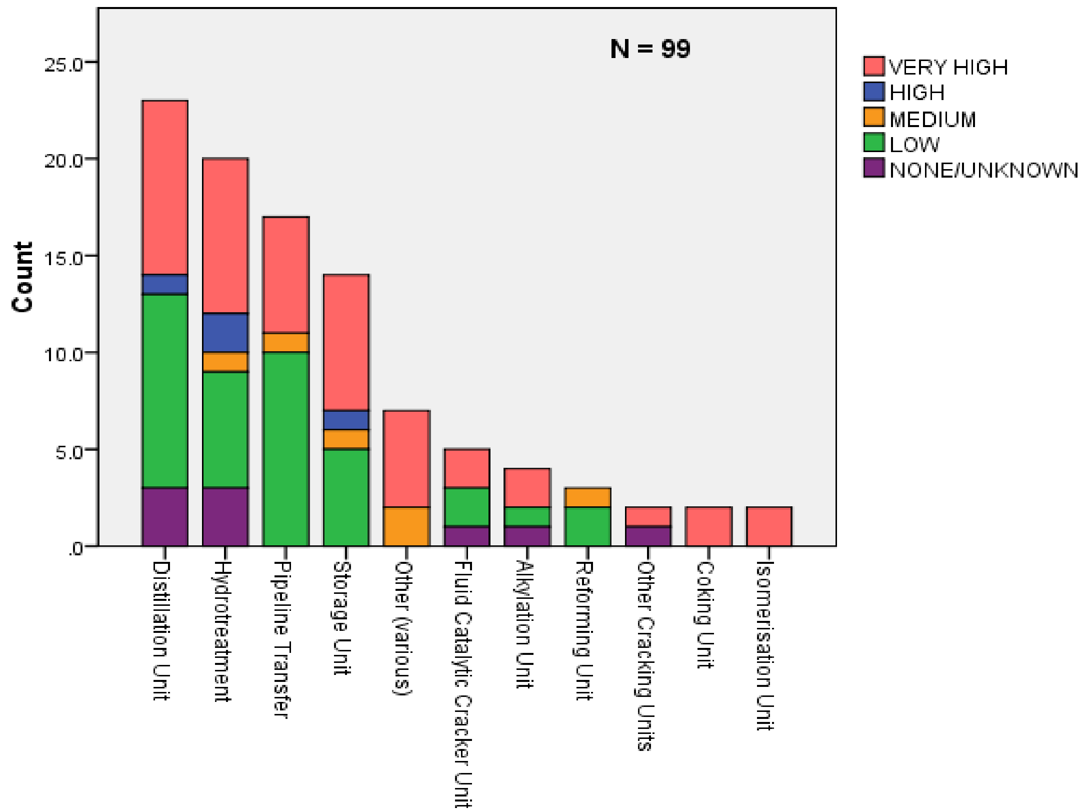


FIGURE 16. SEVERITY OF CONSEQUENCES ASSOCIATED WITH UNIT OF ORIGIN OF ACCIDENTS STUDIED

In addition to these processes, the refinery also has additional support units, many of which exist off-site or distinctly apart from the main processing operations. Major units often located off-sited include storage, product blending, road and rail loading, jetty facilities, waste disposal, and effluent water treating. Tank farms and transport pipelines to remote locations are generally most associated with recurring corrosion problems. Notably, pipes and equipment located in marine environments may be exposed to salty air exacerbating the corrosion process from the outside.

In the context of corrosion, the financial impact of loss of production is a significant factor in the risk management of corrosion in refineries. Therefore, when large units such as the FCC are taken out of service for some time, the refinery may have to run distillation and other units at lower rates. The physical connections between different refinery units, storage limitations, and distribution system limitations for moving intermediate feedstocks into and out of a refinery results in downstream effects affecting total production. For example, inputs to the distillation tower may be reduced when the FCC unit is down in order to reduce the amount of FCC feedstock being generated. In addition, reduction in distillation tower runs will affect coking unit inputs unless coking unit feedstock is not readily available for purchase. [20]

2.4 Involvement of refinery equipment in corrosion-related accidents

The magnitude of a petroleum refinery unit and the complexity of the processes are such that a wide variety of equipment types can be subject to corrosion depending on the process.[19] In general, the pipeline infrastructure and the pipework associated within a particular unit and/or piece of equipment are quite vulnerable. Storage tank failures can also occur due to corrosion and generally have high risk profiles due to the volumes that they may contain. Corrosion can also occur in other equipment components such as trays, drums and towers. As illustrated in the RIMAP study of equipment vulnerabilities in European process and power plants (see Table 10 on the next page), some equipment types are more vulnerable to corrosion, or to certain types of corrosion, than others usually due to their role in the process, the design of the pipework, or physical location on the site. Sometimes faulty repairs or process re-design can increase corrosion vulnerability. Hence, equipment design and maintenance practices are critical to controlling refinery corrosion.

Figure 17 on page 47 shows the equipment components cited in the accident cases studied. As illustrated, corrosion failure originated predominantly in pipe works, causing 71% of the accidents studied. Fifty percent of accidents involved the internal pipework of the equipment. As noted in the previous section, 17% of the original failures took place in the pipeline infrastructure of the plant for transfer between units and to and from transport modes, and 4% took place in tubes associated with heat exchange and cooling units. Fifteen percent of the accidents occurred in storage tanks. Two accidents started in the reactor vessel and the remaining accidents resulted from corrosion failures in a variety of components including a pressure vessel, a flare, a chimney, and a drum. In a few cases the equipment component was not clearly specified.

Various factors make some equipment components more vulnerable to the acceleration of the corrosion rate than others. Configuration and design of equipment play a particular role in creating opportunity for corrosive deposits to accumulate. Function and location can also determine the level of exposure to corroding agents. Integrity of corrosion protection and repair are applications that can alter the character of the equipment with an impact on its vulnerability to corrosive factors. These factors apply equally to any piece of refinery equipment (assuming they all have metal parts).

Failures due to equipment design and composition are also often linked with aging plant infrastructures. A significant body of technical standards has evolved for modern design and construction of process equipment and pipelines for petroleum and petrochemical products, providing detailed guidance on how to optimize resistance to various stress factors. However, many of these standards may not have been in place when the process unit was originally built. In addition the equipment may not have been built for the same process conditions and often it is not clear what process assumptions were used in the original design.

[19] Note that this section only discusses the tendency for elevated rates of corrosion failure in equipment and equipment components. It does not take into account criticality of equipment and equipment components in terms of potential accident consequences.

TABLE 10. CLASSIFICATION OF TYPE OF DAMAGE VS. SYSTEMS/COMPONENTS IN PROCESS PLANTS FROM THE RIMAP PROJECT [27]

Type of damage	Damage specific mechanisms	Where to look for it in process plants
I. Corrosion/erosion/environment related damage, equated to or leading to:		
I.A. Volumetric loss of material on surface	I.A1 General corrosion, oxidation, erosion, wear solid particle erosion	Heat exchangers, pipes, bends, pumps reactor vessels
	1.A2 Localized (pitting, crevice or galvanic) corrosion	Heat exchangers, reactor vessels, pipes, water tubes
I.B.	I.B1 Stress corrosion (chloride, caustic, etc.)	Stainless piping, reactor vessels
	I.B2 Hydrogen-induced damage (including blistering high temperature hydrogen attack)	Crackers, columns, reformers
	I.B3 Corrosion fatigue	Dissimilar welds
I.C	I.C1 Thermal degradation (spheroidization, graphitization, etc. including incipient melting)	Heat exchangers, reformers, crackers, pipes, reactor vessels
	I.C2 Carburization, decarburization, dealloying	Reformers, crackers
	1.C3 Embrittlement (including hardening, strain aging, temper embrittlement, liquid metal embrittlement, etc.)	Forgings, hot vessels and piping
II. Mechanical or thermomechanical loads related or leading to:		
II. A	Sliding wear, cavitational wear	Pumps, valves, condensers
II. B	Overloading, creep, handling damage	Hot piping, nozzles, T-Y configurations (pipes)
II. C Microvoid formation	Creep, creep-fatigue	Hot piping, reformer tubes, reactor vessels
II. D Microcracking, cracking	Fatigue (HCF, LCF), thermal fatigue, corrosion fatigue, thermal shock, creep, creep-fatigue	Rotating machinery
II. E Fracture	Overloading, brittle fracture, foreign object damage	Vessel failures, pipe bursts, reformer tubes

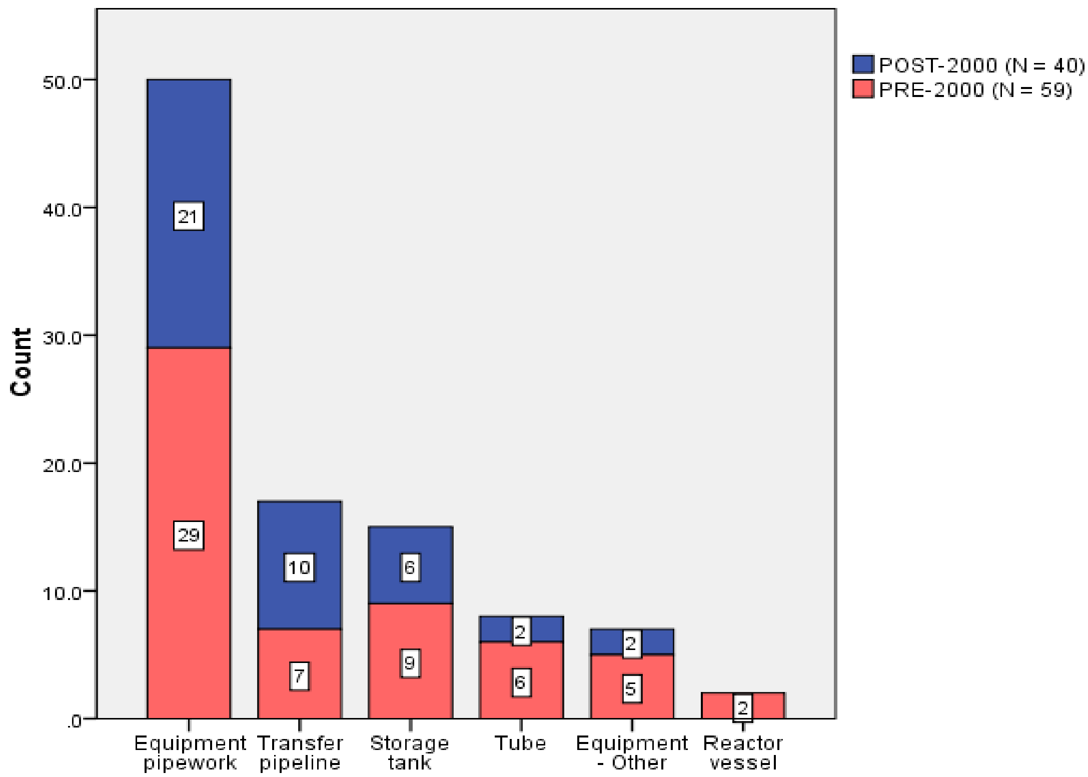


FIGURE 17. ACCIDENT ORIGIN BY EQUIPMENT COMPONENT

However, in any refinery, there will usually be points at which the pipework fails to meet the necessary design standards for a number of reasons. These reasons include age, process change, design change, risk assessment errors, and poor repair and maintenance. Notably, this list contains some of the most important technical challenges faced by refinery operators over the life time of a site and not surprisingly, these vulnerabilities are common causal factors for other mechanical integrity failures besides corrosion.

A few types of equipment, notably the heat exchanger (a necessary component of many process units) and the storage tank, are also highly correlated with corrosion. A study performed by the British government agencies responsible for plant safety identified pumps, compressors, furnaces, orifice plates, injection points, poorly supported small bore pipework, pipework/ equipment under lagging, and buried pipelines, as particularly prone to ageing mechanisms such as corrosion, erosion and fatigue. [31] Groysman calculated that about 60% of total such failures were associated with heat exchangers, condensers, pipelines and tanks in his study of Israeli refinery sites. [21] Table 11 on the next page provides a number of additional insights on possible factors contributing to corrosion failures in equipment from a number of studies of corrosion and aging in refineries and process plants.

TABLE 11. FACTORS CONTRIBUTING TO CORROSION AND AGING EQUIPMENT FAILURES IDENTIFIED IN VARIOUS STUDIES [28] [29] [30]

- No reinforcement of mounting plates
- Removable covers for charging purposes
- Retention areas, areas that emerge from insulation (drains, purge points)
- Expansion compensators
- Welds that are complex or likely to be a home to stress concentrations,
- Heterogeneous welds or major or specific tapping points
- Low points, e.g., lower end of the radius, bends, bases
- Segments that are representative of circular and longitudinal welded joins.
- Specific points where there is a lack of continuity
- Supports and ends
- Outdated materials
- Welding quality, welding defects and repairs
- Design fatigue life/corrosion allowance utilized
- Corrosive environments
- Predictable deterioration
- Change of service (function, rate, etc.)
- Failure of cathodic protection systems or lack of records
- Poor condition of paint and surface coatings
- Repairs

Source: INERIS [28] [29] [30]

TABLE 12. CORROSION AND AGING FAILURES ASSOCIATED WITH PIPEWORK [29] [30] [31]

General

- Complex welds
- Nozzles of diameter greater than 50% of the diameter of the device
- Supports or attachment points on equipment subject to vibration or cycles fatigue
- Tap bases and supports
- Impurity concentration areas
- Taps, purges, drains and dead legs

pes – internal to the site

- Defective or missing internal lining
- Internal corrosion that is dependent on the fluid
- Erosion, especially downstream injection points or changes in cross section or in tight elbows

es –external to the site (i.e., connecting to transport vessels or distribution networks)

External corrosion

- Dripping from a pipe located above, or dripping via supports (racks or pipe supports)
- Corrosion under insulation (CUI), corrosion under the paint (paint joints)
- Underground piping or ones that are in sheaths and are hard to inspect.
- Corrosion under protection other than anti-corrosion coating (e.g., heat, cold or fire insulation)
- Corrosion at ground/air interfaces, or supporting areas that may cause lining damage by friction (e.g., gravel) and areas that are hard to access and as such, the linings may be less effectively applied

Internal corrosion

- Under deposits in dead legs. Dead legs are sections of process piping that have been isolated and no longer maintain a flow of liquid or gas
- Along slop lines. Slop lines consist of "off-spec" fuel that is usually reprocessed into the plant. Off-spec fuel is an output that has failed to meet product specifications. As such its composition varies considerably and often unpredictably.

Sources: INERIS [28] [29] and the UK Health and Safety Executive [31]

Pipework. Pipes are present in abundance throughout a refinery site as basic components of equipment infrastructure as well as the chief transport conveyance between refinery units and to remote sites, external from the main processing area, and as a delivery mechanism connecting to external pipelines delivering the product to distribution points and customers. Constructed of metal, often a variant of carbon steel, pipes are more or less naturally vulnerable to corrosion processes. Hence, pipes are the vast majority of corrosion victims in refineries whether they function as a component of a piece of equipment or of a unit, or service multiple units or the refinery at large.

Technically similar in composition to pipework, tubes are highlighted here in 8 cases (9%) separately from pipework to highlight the particular nature of some accidents originating in heat exchangers, ovens or furnaces. In total 24 accidents, or one out of every four accidents, originated in either in the tube structure or in other associated pipework of heat exchangers, ovens or furnaces. The intensity of temperatures and temperature fluctuations in these elements are a factor that can accelerate the corrosion process in the presence of certain corrosive agents.

Table 12 on the previous page highlights typically vulnerabilities contributing to corrosion and aging failures associated with pipework in the chemical process industries.

Storage tanks. While not as prevalent as pipework failures, storage tanks of hazardous substances are well-represented in major accidents in the process industries, including corrosion-related accidents. Both atmospheric and heated storage tanks are used extensively in refineries. Atmospheric storage tanks generally contain fuels and other products with low vapor pressure. Common products stored in insulated and heated tanks include acid and solvents, benzene, naphtha, liquid sulphur, sour water, and asphalt and related products. Both types are vulnerable to corrosion. Table 13 on the next page highlights findings from studies by the UK Health and Safety Executive and the French government research institute for industrial risk on factors contribution to corrosion and aging failures associated with atmospheric storage tanks.

In particular, the construction of such tanks is deceptively simple and old tanks accordingly remain in service for a long time. The longer that a tank is in service the more likely that factors associated with age, including original design and construction, and undetected or uncorrected wear and tear, or the storage of incompatible substances can undermine tank integrity. As such, less than rigorous inspection is sometimes considered a major cause of corrosion failures in storage tanks. [32] Exterior corrosion, whether general or localized at crevices, is very easy to detect with an external inspection. Internal corrosion from exposure to corrosive agents in the product in the vapour or liquid phase is generally monitored via a number of measurement technologies detailed extensively in the relevant literature.

TABLE 13. FACTORS CONTRIBUTING TO CORROSION AND AGING FAILURES ASSOCIATED WITH ATMOSPHERIC STORAGE TANKS [28]

- Corrosion between steel sheet and wall with which the steel sheet was in contact
- Corrosion on fixed tank roofs (by condensation) which may require a change in the roof
- Rainwater drains (should they develop holes, hydrocarbons leak into the dike)
- External corrosion (possibly under insulation)
- Foundation settling (water collects under the tank)
- External corrosion at the bottom of pan and bottom of pan
- Corrosion of the solder-coat bottom
- Corrosion on both sides of the floating roof
- Leaking roof drains
- Leaking joints of floating roof
- Cracks caused by fatigue on floating roofs

Source: INERIS [28]

INERIS studied a number of accidents associated with storage tanks in the processing industries and concluded that tanks of crude oil are victims of more aggressive corrosion forces than other refinery products. [28] In particular, crude oil storage tanks should be designed with special materials to prevent corrosion resulting from sulphur content. Key factors from this INERIS study are summarized in Table 13 above. Figure 18 below provides some examples of from the study of types of corrosion damage that contributed to accidents involving storage tank failure.

FIGURE 18. FIGURE 18. DESCRIPTIONS FROM CASE STUDIES OF CORROSION FAILURES IN STORAGE TANKS

"A circumferential fissure in the bottom plate has been observed after cleaning. This fissure has a length of about 10 m and is situated at about 2 m from the tank wall. Samples of the bottom plate have been taken for further investigation. This incident further shows that in the bottom of storage tanks gutters can be formed. In those gutters corrosive products can accumulate, and can result in local, uniform corrosion." [Case 77]

"Corrosion of vessel floor resulting in a hole of approximately 20cm^2. Oil sand base of the tank was washed out by escaping oil. The company had anticipated pinhole leaks would appear. It failed to attempt to measure the extent of pitting corrosion or its rate of progression. Tank examination/inspection scheme did not anticipate the rate of corrosion which was encountered." [Case 58]

"There was a leak of kerosene from the base of a large storage tank into the ground and groundwater beneath the tank and the site … Movement of a small water drain pipe against a sump wall caused the surface protective coating on the sump to be eroded. The bare surface then corroded and formed a 10 mm hole, through which the 660 tonnes of kerosene leaked." [Case 78]

Pressure vessels and other equipment. Pressure vessels are used mostly in process industry, refinery and petrochemical plant to carry or hold liquid, gases or process fluids. They are typically subjected to pressure loading and internal or external operating pressure different from ambient pressure. A number of refinery processing units, including crackers, cokers and reformers, include pressure vessel equipment. Pressure vessels as well as other vessels such as drums and reactors also are vulnerable to a number of failure mechanisms including corrosion. Nonetheless, only a small number of the cases studied involved these types of equipment. Table 14 below highlights conditions that make pressure vessels vulnerable to corrosion and other mechanical integrity failures according to the Safety Assessment Federation (SAFed).

TABLE 14. PRESSURE VESSELS SUBJECT TO POTENTIALLY RAPID DETERIORATION
▪ Contents which cause rapid corrosion/erosion ▪ Potentially corrosive external environment ▪ Vessel subject to significant vibration ▪ Vessel subject to significant cyclic pressures, cyclic temperatures and/or thermal shock ▪ Safety valves or other protective devices susceptible to blockage ▪ Riveted seams ▪ Inwardly dished ends

Source: SAFed [33]

2.5 Frequency that various equipment vulnerabilities were cited in the accidents studied

Figure 19 on the next page shows the frequency with which various types of conditions associated with the equipment were cited in the reports, individually or in combination with other factors, as potentially contributing to an accident event. The study grouped these conditions in the following categories of vulnerability:

- Material composition of the component
- Configuration
- Function
- Location
- Adequacy of anti-corrosion protection
- Welded parts

Most of these vulnerabilities were associated with corrosion failure in pipework but factors such as equipment configuration adequacy of anti-corrosion protection, and welded parts were also associated with other types of equipment as highlighted by various observations in the reports studied. (See Figure 20 on page 53.) Many of the factors cited are commonly referenced in the scientific literature as potentially contributing to acceleration of the corrosion rate under particular conditions. For more information on why these factors are more vulnerable to corrosion forces, there are numerous scientific references and articles in the literature on corrosion

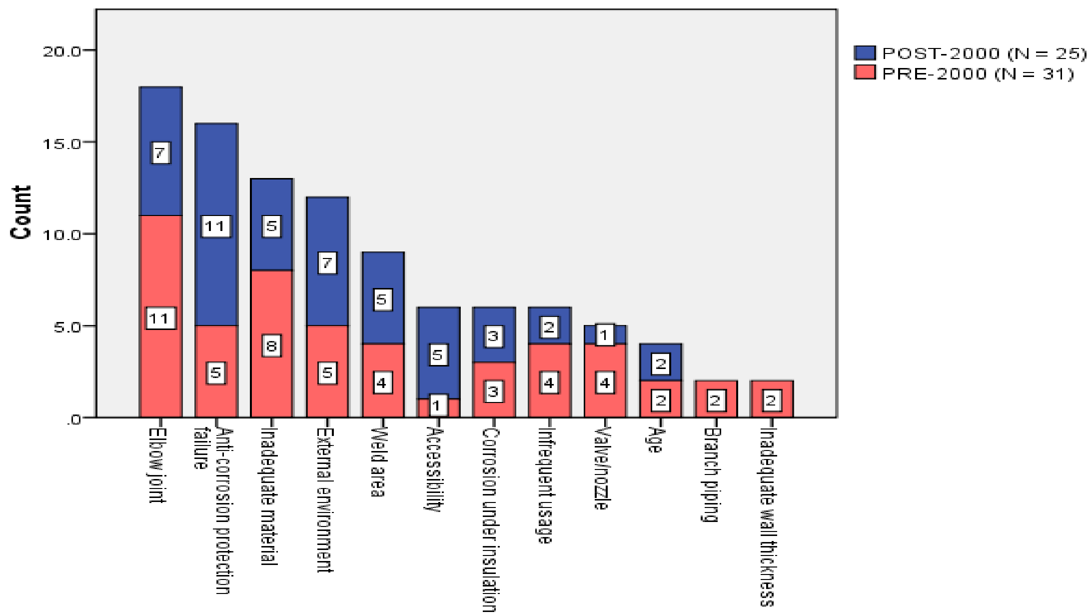


FIGURE 19. TYPES OF VULNERABILITIES SITED FOR PIPEWORK AND PIPELINES CONTRIBUTING TO CORROSION ACCELERATION OF EQUIPMENT INVOLVED[20]

that explain the particular properties and circumstance that may result in a potential acceleration in the corrosion rate (some of which are included in the list of references in this report).

The study revealed that in nine cases, the inadequacy of the material composition in design or repair of the pipe component was considered a contributor factor to the corrosion failure. Six cases indicated that infrequent use may have resulted in a reduction in the frequency of monitoring and maintenance of an equipment component. Overall failure of the anti-corrosion protection was cited in 16 of the accidents studied. Corrosion failure was attributed to potential welding error in nine of the cases studied. Only four cases mentioned the age of the equipment as a contributing factor, although in several reports there were also references to the advanced age of the equipment involved in the accident without citing it explicitly as a contributing factor.

- **Material composition.** Corrosion is a natural process that occurs in chemical processing because unstable materials, i.e., the refined metals used to contain process liquids and product, want to return to a more stable compound. In nine cases, the inadequacy of the material composition in design or repair of the pipe component was considered a contributor factor to the corrosion failure. Pipe wall thickness was also cited in two cases (2%). In reality, choice of material composition is suspected to be a much higher factor in the accidents studied, but this is one of many causes that tends to be under reported in corrosion-related accident reports. In these cases, either the investigation did not explore this element or the accident summary neglected to include this causal factor (in which case, many other details are usually also missing).

[20] In some cases more than one deficiency was cited. Hence, the total frequency of all substances added together exceeds the number of cases in this figure.

FIGURE 20. OBSERVATIONS FROM CASES ON RELATED EQUIPMENT CONDITIONS

Presence of an elbow joint

"The line had been pierced at a part of an elbow at the 135◦C point following an elbow of 90◦C. Subsequent inspection showed that the presence of the elbows caused a turbulence which in turn created a localised depression. This configuration was conducive to the formation of deposits (in particular following stoppages of the water flushing pump). Corrosion under the deposits developed and eventually formed a hole in the line. The elbow at 90◦C was checked but not the one at 135◦C". [Case 51]

"According to preliminary examinations, it seemed that the particular pipe configuration (2 elbows in succession of 3 different dimensions) were involved in the incident of this section, exacerbated by the presence of a corrosive product (H2S), provoking the formation of an atypical corrosion zone." [Case 52]

"An ordinary steel pipeline had been put into place in 1960 with a thickness of 11 mm and in 1972 the line was inspected and a thickness of 8.5 mm was measured. The reduction in thickness was attributed to corrosion. The rupture took place in a straight portion of the pipe between two elbow joints where, after the accident, a thickness of 0.8 mm was measured."[Case 7]

"A slow flow velocity at the U-figured piping partially separated hydrogen sulfide which stayed in the upper part of the U-figured piping section. It is assumed that the free hydrogen sulfide at a high temperature of 350°C corroded the piping area, and the hydrogen sulfide that leaked from the opening ignited." [Case 63]

"Examination of the ASME A106 (8" bore) x 8mm grade 13 steel pipe revealed that a plug of rust and sludge (containing 9.9% FeF_2, 8.1% FeF_3 and 37.5% Fe_2O_3) accumulated in base of a shallow bend. The retention of HF in this plug caused accelerated internal corrosion in a localized zone around the surface of the plug." [Case 16]

Corrosion affected by presence of welding

"The rupture zone was located near an elbow, not far from the compressor discharge. After examination, it was noted that the pipeline had signs of internal corrosion, notably in the lower generator. The hole occurred in a zone affected thermally by welding. Measurements of thickness at various points revealed that certain areas were less than specified." [Case 59]

"Preliminary NBS [National Bureau of Standards] test results indicated that the subject plate material (ASTM A516, Grade 70 carbon steel) of the amine absorber was susceptible to hydrogen-induced cracking. Furthermore, repair welds that were done in the field, and that had not been stress relieved, were especially sensitive to amine-induced corrosion and cracking. Taking all of these findings into account, it can be concluded that this failure occurred because the welding procedure used when replacing a section of the vessel caused the formation of a hard microstructure in the weld. This hard region was susceptible to hydrogen assisted cracking resulting in growth of large cracks in the vessel. The uncracked material in the vicinity of the existing cracks had low toughness due to hydrogen embrittlement and failed at the COTD [crack tip opening displacement] in the vessel arising from the operating pressure and residual stresses associated with the weld." [Case 15]

"The piping was remarkably thin due to corrosion from inside and outside. Scale adhering to the surface was detached because a water seal and a welding repair were carried out repeatedly. Therefore, the opening suddenly expanded and LPG blew out." [Case 30]

Corrosion at a valve intersection

""In an atmospheric distillation unit in normal operation a fire broke out in the distillation column. The fire occurred at a valve on the naphtha stripper. The stripper was insulated up to the valve location. The naphtha escaped through a leak and spread into the insulation which ignited." [Case 6]

Corrosion at a little used section of pipe

"Example of corrosion of unnecessary piping left for a long time. Leakage of water contaminated with crude oil from a corroded part of piping during removing operation of unnecessary piping left for a long time. Crude oil leaked on removing unnecessary piping at an oil refinery. The piping was used for transfer to a refining unit from a crude oil tank. It had not been used for about two and a half years." [Case 27]

"The peripheral part of the system is not considered to be so important, and inspection and management are apt to be inadequate. This might be a cause of the accident. The vent piping was hardly maintained during operation management because it had not been considered to be so important." [Case 11]

In general, the choice of the material composition of the pipe is an important design and repair decision when there is a likelihood that the pipework could be exposed to experience a higher corrosion rate due to process location or location on site. These considerations also should take into account other conditions that could create the potential for an elevated corrosion rate, particular the external atmosphere. There also can be a potential for elevated corrosion rates when dissimilar metals are placed adjacent to each along a pipeline. Corrosion potential may be exacerbated because of intrinsic incompatibilities between the metals.

Wall thickness, or “corrosion allowance”, may also be added to the design when a component may be exposed to excessive corrosive conditions. There are standard calculations for calculating the allowance in accordance with particular conditions and the expected corrosion rates for various types of equipment, materials and configurations. The absence of a proper allowance for certain corrosive conditions, particular in relation to the process or regular exposure to potentially corrosive fluids, can be considered an error in design that may potentially elevate the risk of material failure.

- **Function.** Function is largely covered in the previous section related to process. However, a related factor can be frequency of use. Six cases (6%) indicated that infrequent use may have resulted in a reduction in the frequency of monitoring and maintenance of an equipment component. These cases usually involved pipework that was no longer used due to a process change or by design its service was required infrequently.

- **Configuration.** Configuration of the pipework plays a strong role in the corrosion process. Some design features create weak points in the system that are particularly vulnerable to potential stresses, including corrosion. The accidents studied identified the following specific equipment types of subcomponents with this tendency: elbow joints, valves, nozzles and branch piping.

  - ***The elbow joint.*** The elbow joint is the most common geometric configuration involved in a corrosion-related failure in the study, noted in 19% (18) of all cases as the original site of corrosion. Elbow joints have practical and engineering advantages but they also are vulnerable to certain types of stresses, particularly erosion/corrosion, low of uneven flow, vibration, and external pressure from natural forces such as wind and floods. A slightly higher proportion of the pre-2000 cases cited an elbow joint as the origin of the corrosion failure.

  - ***Valves, nozzles and branch piping.*** In total 8 different cases (8%) referred to valves or branched piping as the original location of the corrosion failure. Valves, nozzles and branched pipework all represent pipe intersections that are joined to the system by various mechanisms, including welding. While the construction and design of these components varies considerably, it can generally be said that the process of making an intersection creates a weak point in the pipe system. Corrosion may be one of several types of stresses (e.g., thermal fatigue, vibration) on the intersection that eventually loosens the join or the fit of the connection, or causes deterioration in the wall thickness of the subcomponent, both of which may lead to an eventual loss of containment. Corrosion failures originating at valves and nozzles was only reported in accidents occurring before the year 2000.

- **Location.** Aside from process location, other location factors also may affect corrosion vulnerability. In this study two additional location issues were highlighted in 13 separate cases (13%): exposure to the external environment and accessibility. In one case a section of equipment pipework was poorly accessible for routine inspection. Seven cases (7%) concerned pipes that were on the ground or underground, 4 of which were considered also fairly inaccessible for routine inspection. Pipeline standards generally recommend that buried and submerged metallic equipment should have adequate protective coating. Five (5%) cases concerned pipes submerged in water.

Also, the inaccessibility of underground and submerged pipes also contributes to potential for corrosion failure. As in three cases (3%) studied for this report, pipes may also be inaccessible due to placement behind other bulkier pipes or equipment parts. Although inherent risk may not be higher in their particular location, pipes that are less accessible may be monitored infrequently. They cannot benefit from even the occasional visual check and routine monitoring can be costly.

- **Adequacy of anti-corrosion protection.** In addition to material and wall thickness, another method of corrosion protection includes protective coatings. Protective coating sometimes may be a simple coat of paint properly applied. Zinc coatings, also called galvanizing are often applied to steel to improve resistance to atmospheric exposure. Other methods of corrosion protection include anodic or cathodic protection, adding a metal lining to the pipe, or adding a corrosion inhibitor to the corrosive environment (for example, to process fluids). Each of these methods failed in at least one of the cases studied with insulation and coating cited most often in this regard. [34] Overall failure of the anti-corrosion protection was cited in 16 (12%) of the accidents studied and was the second highest type of equipment vulnerability cited as a contributing cause to an accident.

  The three cases involving corrosion under insulation (CUI) were also counted as failure of anti-corrosion protection. CUI can be caused by the ingress of water due to poor installation or subsequent damage. Sometimes the insulation material itself may contain corrosive agents such as free chlorides. Other conditions such as high temperature flow may also increase the risk of an elevated corrosion rate. CUI may be particularly difficult to detect since it is not often visible and controlling for it may be expensive. [35]

  As highlighted in Figure 21 on the next page the cases studied provided a number of examples where anti-corrosion protection was deemed inadequate, including:

  - Lack of protective coating on an underground section of pipeline
  - Poor application of anti-protective coating
  - Deterioration of original protective coating
  - Protective coating washed away by water injection upstream
  - Protective coating washed away by water leak from overhead pipe section
  - Corrosion under insulation
  - Anti-corrosion coating on one section elevates risk of corrosion on the adjacent unprotected section

Welded parts. Corrosion failures related to deficiencies in welding repairs are also cited frequently as contributing causes to refinery accidents. Weldments can be incorporated in the original design or be used for repair of all types of equipment. Corrosion failure was attributed to potential welding error in nine (9%) of the cases studied in association with equipment

Figure 21. Observations from cases on inadequate anti-corrosion protection

Lack of protective coating on an underground section of pipeline

"According to the operator, this situation was probably due to the lack of a protective sand bed around the pipeline. Small pebbles were in effect in direct contact with the pipeline wall and even pierced the pitch coating. A repair was undertaken involving installation of anti-leak collars in the zones most affected and in establishing a new coat of pitch." [Case 68]

Poor application of anti-protective coating

"The branch piping for mounting a pressure gauge was installed in 1973. Afterwards, it was not replaced although external corrosion was advancing due to splashes of sea water. The branch piping was checked by removing paint. On re-painting after the check, surface treating such as rust removal before painting was inadequate. For this reason, corrosion advanced and it seems that a lump of rust peeled off by pressure at the time of loading, and a hole opened." [Case 37]

Deterioration of original protective coating

"As the waterproofing of the hot insulation of the piping was inadequate, sea water invaded. The piping which was not coated with corrosive protection paint corroded. Scale adhered to the piping about a maximum of 10 mm thick, and is regarded to have separated due to the increase in the internal pressure. 30 years had passed since construction of the heat insulation." [Case 28]

"It is likely that the localization of the fissure, with respect to the point where it formed, is linked to one or more of the following factors:

- localized damage in the original pipe coating
- material defect in the original pipe coating
- critical operative conditions (of the pipe section in which the fissure occurred) linked to the placement of the pipe near the ground and its exposition to atmospheric events (sea air)." [Case 83]

Protective coating washed away by water injection upstream

"The extent of the thinning was mapped and shown to be localized to the elbow and to a slight degree the neighbouring sections of pipe. The pattern of thinning appeared to be directly associated with the water injection position and the downstream flow path of the water from the injection point and around the outside of the elbow. The metallurgical examination revealed that the uncorroded sections of the pipe were internally coated with black iron sulphide. This is known as a 'passivation' layer and once it has formed it serves to protect the carbon steel wall material from further corrosion. However, when the water injection was in operation it washed away the protective coating, leaving it open to attack by corrosive agents in the gas stream." [Case 66]

Protective coating washed away by water leak from overhead pipe section

"The origin of the break in this pipeline seems to be linked to another breach of water pipe located above the fuel pipe. The perpetual leaking of water onto the fuel pipe would have led initially to the slow degradation of the insulation protecting the pipe from corrosion." [Case 17]

Corrosion under insulation

"The incident was primarily caused by a structural failure of a 200mm NB Carbon Steel feed pipe to the dehexanizer column on Unit 35. The pipe was insulated and the external surface of the pipe wall beneath the insulation had corroded at a region where water had been collecting. The corrosion had reduced the pipe wall metal thickness to a level that could not support the internal pressure of the process fluids and a major process release occurred." [Case 89]

"The break of a 6 inches Ø pipe was the cause of the accident. An external corrosion process, under the insulating material, affected, seriously and in a localized position, the inner face of an elbow in the aerial pipe rack. [Case 97]

Anti-corrosion coating on one section elevates risk of corrosion on the adjacent unprotected section

"Preliminary findings indicate that the pipeline was rusted out lengthwise. Measurements taken of the air came up negative for hydrocarbons. The pipeline was modified in June 1997 in order to provide greater protection. A half-shell of resin was provisionally painted on the pipe. The opposite effect occurred with creation of an area of corrosion preference that led to the rupture." [Case 61] pipework (4), storage tanks (2), the pipeline transfer network (1), a pressure vessel (1) and a flare (1). Studies confirm that weldments experience all the classical forms of corrosion, but they are particularly susceptible to those affected by variations in microstructure and composition.

Corrosion susceptibility generally stems from the nature of welding, and the welding process. The nature of welding is such that the character of the welded component is altered in some way, so that the material composition and often the surface texture are altered, usually becoming more heterogeneous, and thereby creating greater opportunity for corrosion. Moreover, the process of welding itself is invasive and errors in miscalculation in procedure can also increase corrosion vulnerability of the weld. Skilled welding professionals are generally required to minimize the risk of committing serious error leading to corrosion failures, and potentially catastrophic events, due to welding.

- **Aging.** A number of studies on corrosion and aging plants have reported recurring problems associated with the aging of specific equipment or equipment components. In this study, only four cases (4%) mentioned the age of the equipment as a contributing factor, although in several reports there were also references to the advanced age of the equipment without indicating it as a causal element. While corrosion is often associated with aging, it is not often considered the main contributor to a corrosion failure. In particular, process conditions rather than aging contribute to a vast amount of corrosion failures in refineries as evidenced by this study. Moreover, corrosion due to aging is not inevitable but passage of time can elevate the risk. In the absence of any other aggravating factors, timely inspection and maintenance can be effective in minimizing this risk.

CHAPTER 3 ANALYSIS OF THE POTENTIAL CONTRIBUTION OF RISK MANAGEMENT FAILURES

Due to the complexity and size of most refineries, it is not likely that operators of such sites can eliminate the presence of corrosion-related hazards. Given these circumstances, every refinery is expected to have an appropriate risk management strategy to minimize the risks with adequate layers of protection supported by an effective safety management system. It was clear that a failure in risk management was a contributing cause to the vast majority of accidents studied.

Due to the variation in reporting detail and style across the cases studied, it was not possible to analyse the risk management failures associated with the accidents in a systematic way. In particular the analyses of the causes in reports are always subjective, tending to vary on the basis of the author’s knowledge (competence as well as availability of information) and the perceived purpose and audience of the report. For example, while one report may emphasize the contribution of the poor process design, a different report of the same accident may focus on the lack of frequent inspections.

However, it can still be very useful from the point of view of lessons learned to identify how many times certain types of risk management failures were cited in association with the cases reviewed. Because of the limitations already cited, such observations will be quite broad. The study was able to summarize potential risk management failures in terms of five general categories:

- Inadequate awareness or attention to known corrosion hazards
- Inadequate risk analysis at design and construction stage
- Inadequate risk analysis prior to change, which is essentially a lack of or failure in the management of change process
- Failure to identify or address process risks in planning inspections
- Inadequate identification of hazards and risks for other purposes, such as safe performance of repairs and establishment of detection and mitigation systems

The findings, while quite broad, give very strong support for a robust risk management programme guided by adequate risk assessment at appropriate points in the process. Many cases illustrate that there were not adequate layers of protection, both in terms of the process and equipment design but also mitigation and detection. There is also substantial evidence that an inadequate or malfunctioning safety management system was a large contributor to the fact that a corrosion failure occurred as well as, in several cases, the magnitude of its consequences.

3.1 Inadequate awareness of or attention to known corrosion hazards

A question often asked in the process safety community is "Why do we continue to repeat the same mistakes?" Considerable progress has been made in the last three decades since Bhopal in understanding, identifying and quantifying risks and technology has equally made strides in providing solutions. For refineries a partial explanation is simply that significant hazards are present in site consisting of a vast and complex network of interconnected processes. Moreover, many refineries in the EU and OECD countries are old; the ownership has changed hands at least once in recent years and crucial knowledge about process risks has been lost.

Nonetheless, under the same conditions, different refinery sites may be quite disparate in terms of safety performance. In general these differences are attributed to refinery management and specifically, the operator's approach to risk management. Not all accident investigations will raise the possibility of a management failure, especially investigations conducted with the main purpose of understanding the technical causes. More than half of the cases studied for this report focused the causal and lessons learned analysis (when provided) on purely technical factors contributing to the accident and there was no indication of a management role (see Figure 22 below). However, remaining reports contained hints of management involvement. Of these, it was implied, and sometimes clearly stated, that an inadequate awareness or attention of management to known corrosion hazards was a contributing factor to the accident occurrence in 23% of the cases.

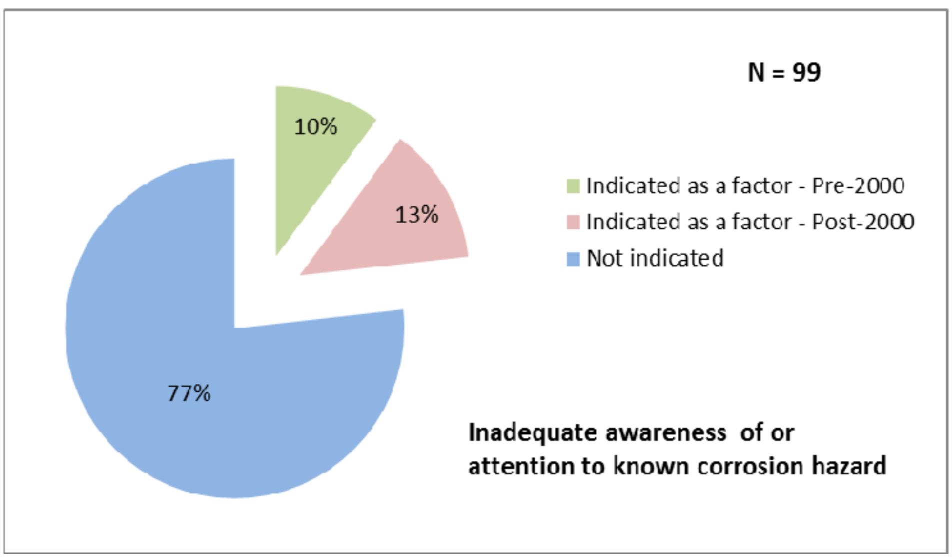


FIGURE 22. PERCENTAGE OF ACCIDENTS WHERE AN INADEQUATE AWARENESS OR ATTENTION CONCERNING A KNOWN CORROSION HAZARD WAS INDICATED

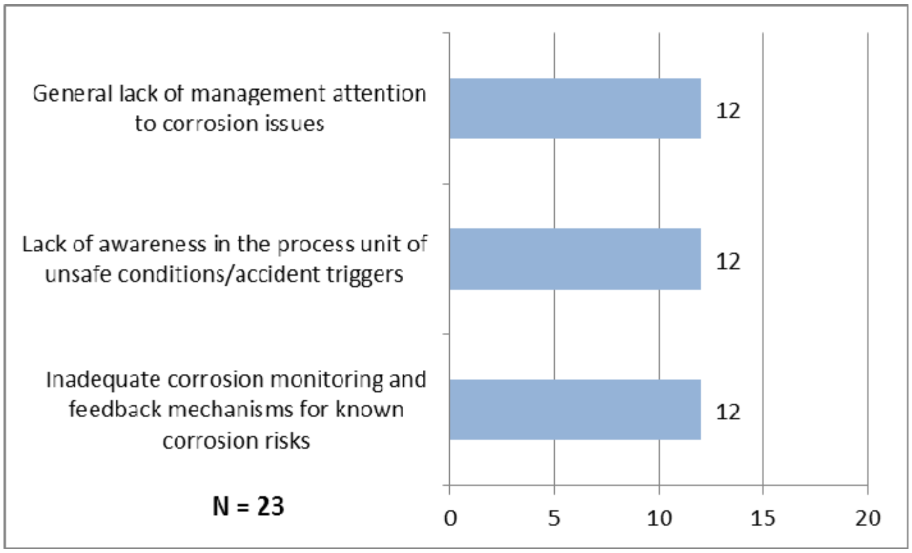


Figure 23. Indications of a management failure in cases studied[21]

The potential influence of a management failure was flagged in cases where one or more of the following conditions appeared to exist according to the observations found in the accident report:

- General lack of management attention to corrosion issues
- Lack of awareness in the process unit of potentially unsafe conditions and accident triggers
- Inadequate corrosion monitoring and feedback mechanisms for known areas of elevated corrosion risk

Descriptions from case reports highlighted in Figure 24 (on the next page) illustrate how this can be relevant to an accidental occurrence.

Figure 23 above illustrates the number of times such situations were cited in the cases and which were counted by the study as an indication of a management failure belonging to one of these categories. Each factor was cited in 50% of the cases where it was indicated that a management failure was a factor. It was also noted that in some cases the condition occurred due to a low prioritization of safety issues by the management. However, in other situations, it was not clear that the management was negligent, but simply that the management, or the unit in question, did not have the proper competence to identify the presence or the extent of the corrosion hazard or the knowledge of the proper measures that were necessary to take in order to control the risks. In some

[21] An accident could have more than one indication of a management failure. Therefore, the total of indications noted exceeds the number of accidents where this factor was implied.

Figure 24. Observations from cases studied indicating potential inadequate awareness of or attention to known corrosion hazards

General lack of management attention to corrosion issues

"The effects on the design plant of a productivity increase were not adequately analysed because of a wrong attitude of management towards safety." [Case 31]

"The company was well aware that the water concentration in Hydrogen Fluoride (HF) should not exceed 2% weight to limit the corrosion of carbon steel. On recommissioning after the hydrotest, there would have been a relatively high concentration of water in the HF in the line. There is therefore nothing new to be learned with regard to this particular issue." [Case 71]

"[The operator] did not have an adequate mechanical integrity management system to prevent and address safety and environmental hazards from the deterioration of H2SO4 storage tanks. [The operator's] engineering management and MOC [Management of Change] systems inadequately addressed conversion of the tanks from fresh to spent acid service. 3. The [operator's] hot work program was inadequate." [Case 67]

"The partial distillation unit was very old and had already presented problems before, but nevertheless it had not been meticulously checked. After an interruption of six months it was put into operation the night before the accident." [Case 35]

Lack of awareness in the process unit of potentially unsafe conditions and potential accident triggers

"The persons related to the tank did not understand that a tank could be easily corroded by semi-finished kerosene including hydrogen sulfide. From this fact, it was well known that an overhaul inspection of such a tank is important …" [Case 8]

"Two significant communication failings contributed to this incident. Firstly the various changes to the frequency of use of the water injection point were not communicated outside plant operations personnel. As a result there was a belief elsewhere that it was in occasional use only and did not constitute a corrosion risk. Secondly, information from the injection point inspection, which was carried out in 1994, was not adequately recorded or communicated, with the result that the recommended further inspections of the pipe were never carried out.

These failings were confirmed in a subsequent detailed inspection of specific human factors issues at the refinery. Safety communications were found to be largely 'top-down' instructions related to personal safety issues, rather than seeking to involve the workforce in the active prevention of major accidents" [Case 66]

"Corrosion was caused by …
- lack of knowledge of the degradation mechanism; the correct non-destructive techniques were not used.
- Information of the condition of the terp material was present within the organization, but not with the department concerned (inspection/maintenance)" [Case 75]

Inadequate corrosion monitoring and feedback mechanisms for known areas of elevated corrosion risk

"External corrosion is easily generated at a specific part. We know those places. For example, the inside of thermal insulation, where trapped water can hardly come out, and the places with poor surface treatment on painting. Management or specifications of paint work was inadequate. In 1993, when the accident occurred, external corrosion of piping had already become a topic of maintenance. Why did the external corrosion of branch piping near the seashore remain? Due to a discrepancy in information-gathering, the preservation plan may have been too late. As corrosion of piping advances to the inside of piping unexpectedly, preservation repair work might require much time and man-power." [Case 37]

"[The operator] educated personnel and advocated for identification and control of damage mechanisms, including sulphidation corrosion. However, [personnel] had limited practical influence to implement their recommendations. These individuals did not participate in the crude unit Process Hazard Analysis (PHA) and did not affect decisions concerning control of sulphidation corrosion during the crude unit turnaround process." [Case 99] cases employee training and awareness may not have been sufficient to enable members of the workforce to recognize corrosion hazards or to encourage them to take action when various types and areas of degradation had been observed. While aware of and concerned about corrosion risks, it is also is conceivable that cost considerations may have motivated management in some cases to forego a layer or layers of protection, particularly on the detection and mitigation side. For this reason in many cases monitoring and feedback mechanisms have been inadequate for equipment exposed to potentially elevated rates of corrosion risk.

3.2 Failure to conduct an adequate hazard identification or risk assessment for life cycle planning and events

The remaining four categories of risk management failure identified in the study can be traced to a failure associated with hazard identification or risk assessment at an important stage in the life of the equipment. Most major accidents imply at least a partial failure in the identification and risk assessment of a major hazard resulting in an inadequate evaluation of the hazard and associated risk. For corrosion hazards, risk is normally expressed as the product of the probability of a corrosion-related failure and the consequences of such a failure. The outcome of the assessment has implications for downstream decisions associated with design, operation and maintenance of the process. According to a study by the Health and Safety Executive (United Kingdom) a corrosion hazard should be assessed on the basis of each of the following threat categories [36]

- internal corrosion threat
- external corrosion threat
- safety/hazard threat
- environmental threat
- operability threat

Figure 25 on the next page shows an example of a typical risk assessment of a corrosion hazard using an event tree approach.

The outcome of the risk assessment then influences whether or not additional control measures are necessary as well as what kind and how many. A barrier analysis is sometimes another type of risk assessment used to evaluate the effectiveness of control measures selected, including detection and mitigation measures. Figure 26 and 27 on page 64 show the generic framework that could be used to assess barrier effectiveness measures for reducing risk associated with two typical potential failure scenarios one of which is corrosion.

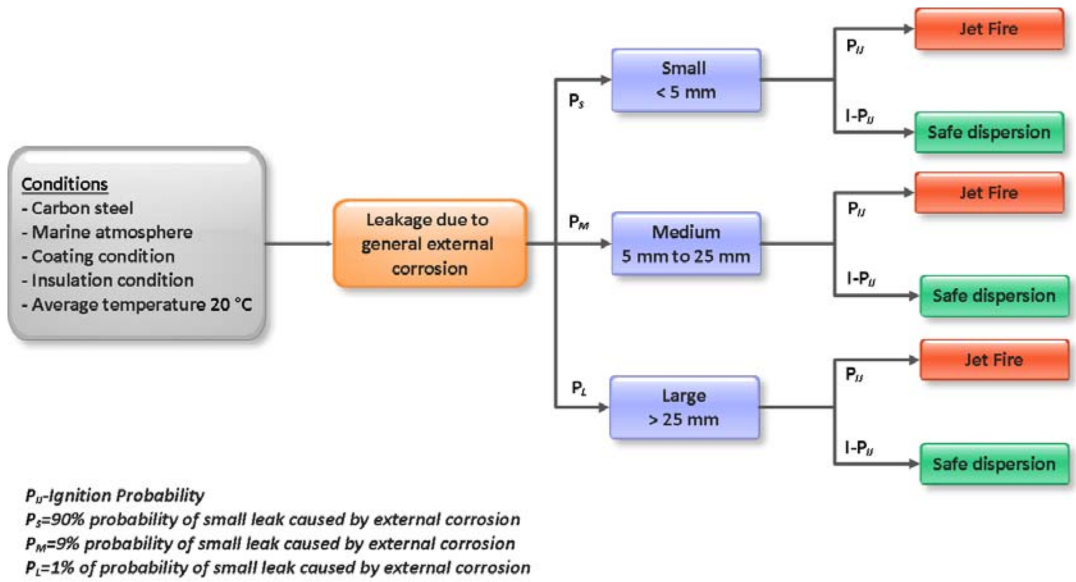
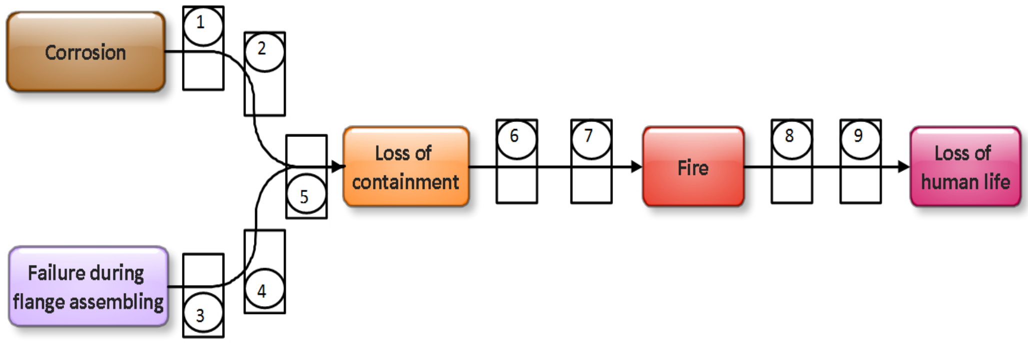


FIGURE 25. EXAMPLE OF CONSEQUENCE EVENT TREE - CARBON STEEL PIPE CONTAINING LPG EXPOSED TO EXTERNAL CORROSION
(SOURCE: STEINBEIS ADVANCED RESEARCH TECHNOLGIES) [37]

It could be deduced from numerous accident reports studied in this analysis that an inadequate risk assessment of the process at a critical operational phase was a contributing cause of the accident. Usually the risk assessment was inadequate for a number of reasons, including:

- The hazard was not identified and a risk assessment for that hazard was never performed at a critical point in the safety life cycle
- Critical information about the hazard and potential risk was available but omitted from the risk assessment.
- Critical information about the hazard and potential was not fully available for the risk assessment



1. Condition monitoring to reveal corrosion
2.Inspection to reveal corrosion
3. Self control of work to reveal failure
4. Third party control to reveal failure
5. Leak test to reveal failure
6. Process shutdown to reduce size of release
7. Disconnection of ignition sources to prevent ignition
8. Deluge activation to extinguish fire
9. Escape ways for evacuation

FIGURE 26. ILLUSTRATION OF BARRIERS INFLUENCING A PROCESS INCIDENT
(SOURCE: S. SKLET) [38]

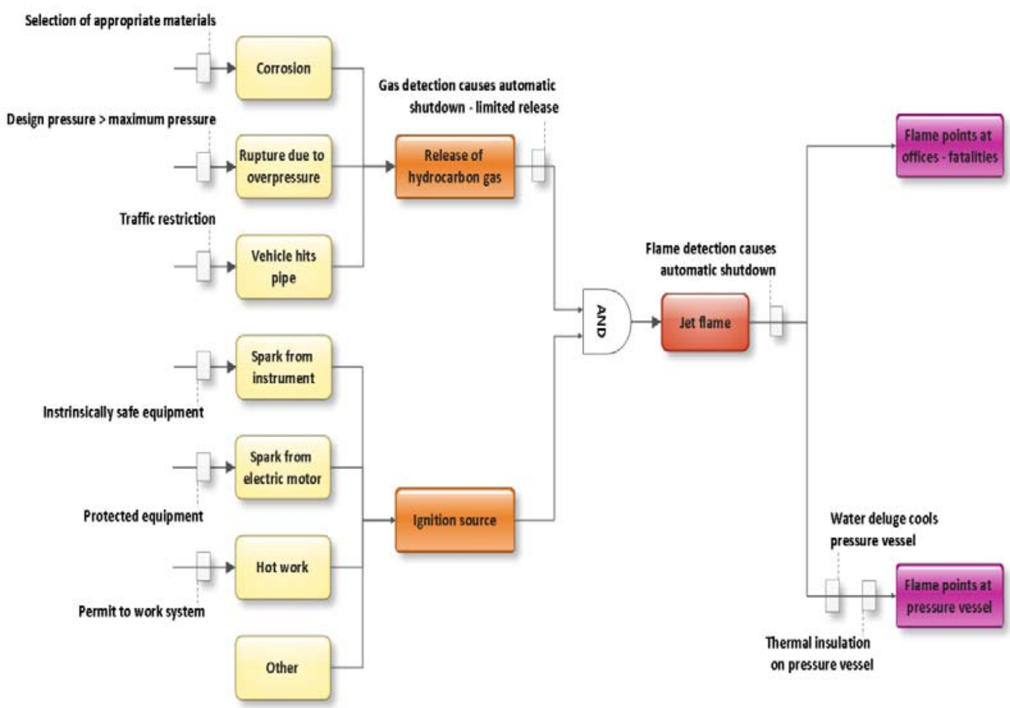


FIGURE 27. BASIC SAFETY BARRIER DIAGRAM
(SOURCE: UK HEALTH AND SAFETY EXECUTIVE] [39]

Moreover, several other safety management components depend on the accuracy and completeness of the risk assessment, as will be discussed in other parts of this section. Figure 27 illustrates how a risk assessment focusing on corrosion hazards may influence other choices related to inspections, monitoring, detection, and emergency response.

From the accident reports studied, it cannot be determined whether or not a risk assessment was performed at a certain point of the life cycle and why, if the assessment was performed, it did not adequately characterize the risk. However, many of the reports contained detail that suggested that a risk assessment should have occurred at a particular point in the life cycle, and that at the time it was either not performed or it was insufficient in identifying the corrosion hazard and/or its associated risk potential. Just over 60% of the accidents indicated that a risk assessment was not adequate at some point in the life cycle. Since a number of accidents, particularly pre-2000, failed to provide any causal information related to risk management, it is somewhat likely that this figure grossly underestimates the role of a failure in the risk assessment process.

This study found that these inadequacies into four different categories according to their occurrence in the safety management process, as follows:

- Inadequate risk analysis at design and construction stage
- Inadequate risk analysis prior to change, which is essentially a lack of or failure in the management of change process
- Failure to identify or address process risks in planning inspections
- Inadequate identification of hazards and risks for other purposes, such as safe performance of repairs and establishment of detection and mitigation systems

Of this list, the first two categories are closely aligned with the classic process hazard analysis and risk assessment that is the basis for the risk management strategy of an operation. The remaining two types of risk analyses are more specific to a particular operational function. The following sections describe each category in more detail with some excerpts from accident reports for illustration purposes.

3.3 Inadequate risk analysis at design and construction stage

This type of error refers to accidents where it appears that the presence of a particular hazard or level of risk was not recognized when the process was designed. It also covers accidents stemming from failures to recognize the impacts of a design change after the process is operating. It should be noted that this risk assessment in original design is closely aligned with the risk assessment needs prior to a design change, that is, when the equipment or process are deliberately changed to improve or renovate the original design and construction.

Taking into consideration the conditions that create a significant corrosion hazard, the chemical and physical process design the potential risk posed by the presence of this hazard. Modern technology offers a large variety of solutions and selection and implementation are largely dependent on process and equipment characteristic, risk analysis outcomes, and cost considerations. Recommended technical measures tend to focus on process and equipment adjustments that either reduce exposure of equipment to corrosive agents or reduce vulnerability of the equipment to the corrosive agents. As such measures for corrosion control in design are more often protection measures against corrosion (e.g., inhibitors, equipment upgrades) rather than process changes, such as chemical substitution, but in many cases, opportunities for the latter also exist Table 15 below gives examples of design principles that can be used to minimize corrosion and associated challenges from the UK Health and Safety Executive .

Figure 28 on the next page shows that overall the risk assessment prior to original design or a later equipment design change may not have been adequate in just over 25% of accidents, according to the reports. Some of the reports were not entirely clear whether a design error was the result of a decision in the original design of the process or was part of a change to process equipment at a later stage. As a practical matter, the study assumed that, if change was not mentioned, the error was part of the original design; however, this choice could not be fully verified.

TABLE 15. EXAMPLE OF GUIDANCE FOR DESIGNING TO MINIMIZE CORROSION AND CHALLENGES IN MONITORING AND MAINTAINING CORROSION VULNERABLE AREAS
• Explicit treatment at the earliest stages of concept design to eliminate, where possible, hazards associated with corrosion damage that combine with operational loads to produce failures.
• Design assessments should look for sites of probable corrosion and consider the use of corrosion resistant materials or another effective method of corrosion control.
• Design to minimize corrosion damage to safety critical items and systems.
• Ensure that key support structures for equipment have a high reliability and resistance to failure. This is important in areas exposed to marine environments and subject to wash down or regular deluge from tests of firewater mains.
• Selection of locations, configurations and orientations that minimize threats to the integrity of equipment, e.g., design detailing of impingement/wear plates, drainage, and removal of deadlegs where corrosive conditions develop or chemical treatments are ineffective.
• Design to survive local or component failure by maximizing redundancy, e.g., backup injection pumps for inhibitor injection systems.
• Design to allow more reliable and effective inspection, ensure adequate access for inspection/monitoring equipment.
• Design for maintainability – easy removal of pumps, motors, valves.

Source: UK Health and Safety Executive [40]

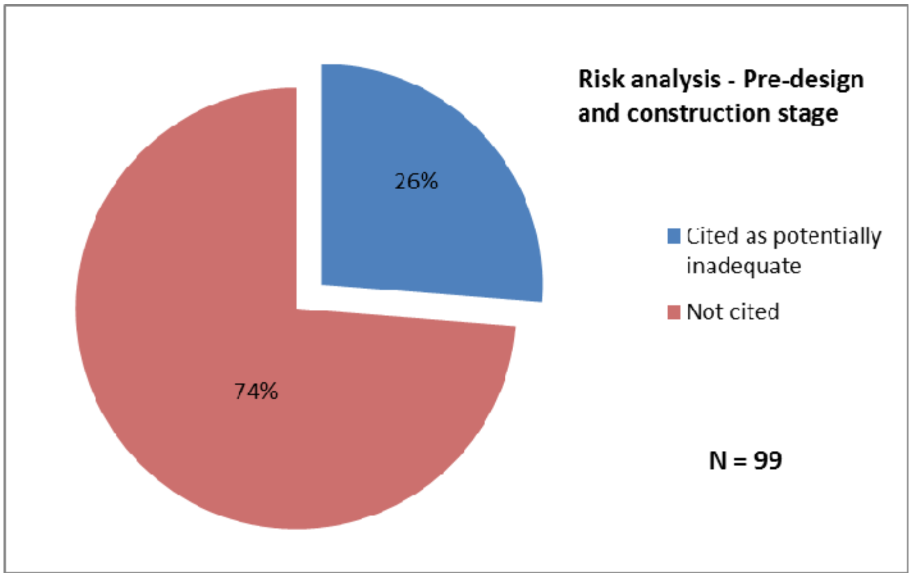


FIGURE 28. PERCENTAGE OF ACCIDENTS WHERE RISK ANALYSIS PRIOR TO DESIGN AND CONSTRUCTION WAS CITED AS POTENTIALLY INADEQUATE

In general as is evidenced in this report there are many known conditions that can contribute to an accelerated corrosion rate. Figure 29 on the next page provides a number of examples from the report where an inadequate risk assessment prior to design and construction was a contributing factor to the accident event. These cases include those where the report implied that a significant corrosion failure had occurred despite efforts of a competent and safety-aware operator. In other words a failure to identify an elevated risk associated with the process cannot always be attributed to negligence or incompetence (though it is often the case). Setting aside costs, identification and monitoring of corrosion risks inherent in oil production processes (i.e., corrosive combinations of flow content, intensity, temperature and pressure) remains a challenging area of corrosion management.

Even if process risks are known, the available science may not always be sufficient to identify precisely which equipment components may be subject to the highest risk and the degree to which the corrosion rate may be elevated. One source noted that in the past the impact of corrosion observed in the field has not sufficiently filtered to the design disciplines, such as flow modeling, although this may be changing. Results of studies that indicate more precisely how process design features can influence corrosion rates may eventually also help to justify the added expense that may be associated with anti-corrosion design measures. [41]

As illustrated in Figure 29 on the next page, a number of failures could be attributed to an inadequate risk assessment in the accidents studied, including:

- An adequate risk assessment was not conducted prior to starting operations
- Process risks were not foreseen in the original risk assessment
- Equipment as constructed did not adhere to recommended design specifications and norms
- A flaw in material was introduced in the construction phase and was ignored
- There was a failure to anticipate corrosive effects of the external environment
- Cost and convenience criteria had greater weight than potential risk

FIGURE 29. OBSERVATIONS FROM CASES ON INADEQUATE RISK ASSESSMENT PRIOR TO DESIGN

AND CONSTRUCTION

An adequate risk assessment was not conducted prior to starting operations

"It is necessary to check piping materials, standardize the exchange cycle of the piping, and prepare manuals including the above. Selection of the correct material is vital. The life of piping of a plant widely differs depending on its service conditions and flowing material. Points with a high probability of corrosion were not fully studied before the accident. The event shows how important a prior study is when installing a new plant as well as remodeling." [Case 63]

"Just as for each process equipment with risks for major accidents, the phenomena which can lead to a degradation of the containment, in this case the storage tank, should be identified and analysed. This accident indicates the possible risks as a consequence of the presence of nonmixable phases which can settle out. An investigation of the possible presence of such phases should form a part of the identification of possible corrosive phenomena. If necessary chemical analyses should be performed to determine the corrosive behaviour of these phases (chemical composition, pH, etc.)." [Case 77]

"The leakage was caused by the failure of the air cooler due to erosion/corrosion because of productivity increase of the unit. The effects on the design plant of a productivity increase was not adequately analyzed …" [Case 31]

Process risks were not foreseen in the original risk assessment

"An environment in which corrosion progresses partially very high seems to be created by the distribution and the history of temperature in piping and the movement of internal fluid, etc. The estimation and analysis of phenomena in piping with a dead end are difficult. A written report of the company states that it was impossible to foresee this accident because it was a special case. It is a unique accident with condensation at dead-end piping combined with the behavior of the flow in vertical piping." [Case 69]

Equipment as constructed did not adhere to recommended design specifications and norms

"A vent of a pump usually has a 1/2-inch plug hole. When 3/4-inch piping is connected, it is common sense to support it sufficiently. Why was the support insufficient?" [Case 11]

"This 6-inch diameter elbow was made of carbon steel instead of the 5 percent chrome alloy steel required by the design specifications since some of the pipes in this unit area reach temperatures up to 900°F An investigation indicated that the piping on each side of the ruptured elbow, which was fabricated and installed in 1963, was of the proper alloy steel." [Case 56]

A flaw in material was introduced in the construction phase and was ignored

"The investigation found that the rupture occurred due to low temperature embrittlement initiated at a flaw in the tank shell base metal, about 20 cm up from the bottom. The flaw had been created by an oxyacetylene cutting torch and had been there since the initial fabrication." [Case 21]

There was a failure to anticipate corrosive effects of the external environment

"According to studies, several factors contributed to the corrosion of the line. The site consists of fill clay with many sharp pebbles (flint), some are imprinted in the coating causing primary corrosion at each occurrence. The pipes are mounted on steel bars, which are susceptible to premature degradation of the coating. Soil samples show a very low concentration of chlorine and significant presence of sulfate and phosphate ions which increase considerably the conductivity of soil. Finally, the ruptured line and those nearby were subject to the cathodic protection of other pipelines in the vicinity, increasing the rate of corrosion to locations where the pipe is exposed (torn or punctured by flint)." [Case 25]

Cost and convenience criteria had greater weight than potential risk

"Individual decisions on piping material must be made taking into account operating environment and conditions. The positions at which piping material is changed must be determined from basic conditions such as presence of a corrosive medium, temperature, and pressure. Even if the change point does not match the piping shape, it should not be set at a convenient position such as a valve or a flange. High-grade material should be used up to a safer position even if it is more expensive. It is regarded as an error in piping material selection or application of the piping selection standard … One of the causes is considered to be the fact that changes in piping material selection often set flanges as a boundary. It seems that the designer of this piping selected carbon steel to cut cost because there were no suitable flanges downstream from the check valve." [Case 29]

3.4 Inadequate risk analysis prior to a change

Changes and modifications to processes and process equipment are a natural part of a refinery plant life cycle. A core element of any safety management system is a properly functioning management of change process. According to the Seveso Directive, management of change is the “adoption and implementation of procedures for planning modifications to, or the design of new installations, processes or storage facilities” [42] and includes “identification and analysis where appropriate of any safety implications of the change proposed.” [43] Management of change is also a core element of U.S. process safety regulations. [44] [45]

Failure in the management of change process has often been cited as an important element in the sequence of events leading to a serious chemical accident. The 1974 Flixborough explosion is perhaps the most well-known catastrophe associated with a failure in the management of change process. Eight accidents investigated by the U.S. Chemical Safety Board between 1998 and 2012 also were associated with failure to manage a process or equipment change. In this study 11% of accidents were cited as potentially resulting from a failure in the management of change process. (See Figure 30 on the next page.)

For a number of reasons, an operator may fail to conduct an adequate risk assessment before a change event, including the failure to recognize that a particular change requires a risk assessment. Effective corrosion management requires particular attention to the various kinds of changes that can make a process or equipment more susceptible to corrosion failure. As noted by Chosnek, the most common problem with the management of change is lack of a management of change process. The second most common problem is poor performance of the safety analysis resulting in an added risk to the process. (Chosnek also mentions that the third most common problem is a poor technical description of the change resulting in a different change than the one intended, but this element was not mentioned in the accident reports studied.) [46]

A change in the source of the raw material, crude oil, may in and of itself be considered a significant change to a refinery process. Processes will be changed to adapt to technology or the addition of new product lines may cause changes in other parts of a site, such as storage and waste treatment. In addition, older refineries will have undergone numerous changes of equipment for a number of reasons, particularly age, breakdown and process changes. In many cases, particularly processes with known risks such as corrosion, even a seemingly minor change in the equipment or process may alter the risk profile (for which reason screening criteria may be used to identify which changes have risk implications).

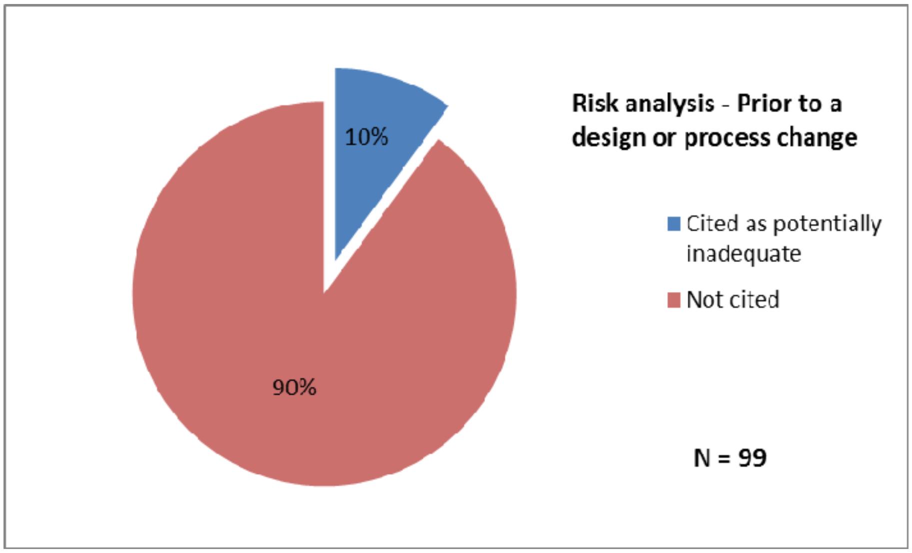


Figure 30. Percentage of accidents where risk analysis prior to a design or process change was cited as potentially inadequate

Cases studied in the report highlighted a number of deficiencies in the management of change process that may have contributed to the accident occurrence. Areas of weakness identified included the following:

- The management of change process existed was launched but not adequately performed
- Poor design choices were made for changes to equipment exposed to known corrosion risks
- Effect of a significant change in productivity of unit on mechanical integrity was not thoroughly analyzed
- Effect of a change in the source of crude oil on mechanical integrity was not analysed
- Impact of a process change in one unit was not considered for a downstream unit

Figure 31 provides a number of examples from the report of potential deficiencies of this nature as contributors to the accident occurrence. In some cases more than one event may involve this type of management of change failure.

Figure 31. Observations from cases on inadequate risk assessment prior to a change

Management of change process existed was launched but not adequately performed

"In February 2000 an MoC [Management of Change] form was completed to increase the orifice size in the water feed line to the P4363 injection point in the overhead system. This intervention actually resulted in a reduction of the water flow rate due to confusion about the original orifice size, but the opportunity was not taken at this time to re-evaluate the effect that the water injection could have on downstream pipework ... Using an existing vent valve to connect the water into P4363 was expedient, and meant that there would have been little or no downtime required for this modification. This perception of a 'quick fix' is supported by the failure to implement the MoC system in operation at the time that would have required a technical memorandum to be raised covering the modification." [Case 66]

"In 1985, the addition of a heat exchanger and rearrangement of heat exchangers at the outlet of the reactor were carried out to rationalize energy recovery. Therefore, the concentration of corrosive substances at the heat exchanger outlet increased. According to general opinion at that time, no one believed the wall thickness at the part would be reduced by corrosion, so the part was not selected for wall thickness measurements … It is a fact that if you do not make a very careful study, safety aspects might be disregarded, even if the initial purpose of remodeling is achieved." [Case 23]

Poor design choices for changes to equipment exposed to known corrosion risks

"A hole opened due to corrosion. The heating furnace outlet temperature was 360 °C, and this high temperature caused high-temperature corrosion considering the properties of crude oil. Therefore, the material used should be 5Cr-1/2Mo steel. However, different materials were mixed at the time of reinforcement of a production capacity in 1974, and improper 1/2Mo steel was used. As a result, it is presumed that corrosion progressed more than expected and a hole was opened … Usually, before piping is erected, a piping list for construction is prepared for all conditions including material corresponding to application conditions. There might have been mistakes in the list or incomplete management of piping materials. It is uncertain what happened." [Case 48]

"Tank 393 was one of four tanks originally designed for fresh H_2SO_4 that had been converted to store spent acid. Spent H2SO4 normally contains small amounts of flammable materials. Light hydrocarbons in the acid can vaporize and create a flammable atmosphere above the liquid surface if sufficient oxygen is present. To guard against this hazard, [the operator] installed a carbon dioxide (CO_2) inerting system and a conservation vent with flame arrestor. However, the system was poorly designed and did not provide enough CO_2 flow to prevent the formation of a flammable atmosphere in the vapor space of tank 393. Because of the holes in the tank and an ineffective inerting system, tank 393 exhibited severe localized corrosion beyond that considered normal in concentrated H_2SO_4 service." [Case 67]

Effect of a significant change in productivity of unit on mechanical integrity was not thoroughly analyzed

"The leakage was caused by the failure of the air cooler due to erosion/corrosion because of a productivity increase of the unit. The effect on the design plant of a productivity increase was not adequately analyzed." [Case 31]

"The processed crude oil has an increased content of sulphur which was taken into account by using steel of higher quality for the pipework. When the steel was replaced, it was not done at a small part seldom used for maintenance. This part corroded and leaked, the released crude oil caught fire." [Case 82]

Effect of a change in the source of crude oil on mechanical integrity was not analyzed

"The oil type had been changed to Arabian heavy crude oil two years before, which has a high chlorine content compared to other kinds of crude oil. … Despite the change of the oil type, impurity levels such as chlorine were in the range of the licenser's manual. However, attention should have been paid because the chlorine level increased." [Case 62]

Impacts of process change in one unit was not considered for a downstream unit

"In June, 1972, stored oil was changed to kerosene. … Some part of kerosene was being received from the oil water separator of the odor water treatment unit after the kerosene had been used for extracting odor components such as hydrogen sulfide in odor waste water. The corrosiveness of the kerosene was much stronger than that of normal kerosene. It corroded the tank over long-term use … The importance of follow-up after starting operation of in-house developed equipment is shown. The developer should pay attention not only to his own … tasks, but also follow up influences on related facilities." [Case 8]

3.5 Inadequate risk analysis for planning inspections

The estimated corrosion risk associated with a process or piece of equipment should be a leading factor in scheduling routine inspections of equipment integrity. A more detailed risk assessment may also be warranted to identify specific degradation threats, the remaining life of the equipment and to feedback information into the overall risk assessment and control system. [36] The initial corrosion risk assessment should identify also points in the life cycle when the corrosion risk assessment should be upgraded.

The risk assessment may also be used to assign priorities for corrosion monitoring and as input into a Risk Based Inspection (RBI) scheme. RBI methodologies are interesting to examine since they provide some insight into some of the criteria that experts use to determine inspection frequencies on a site.[22]

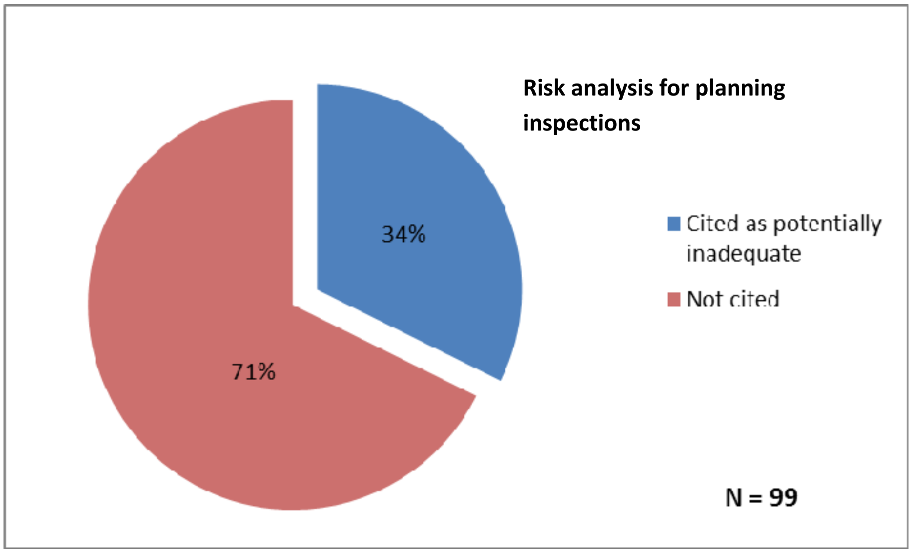


FIGURE 32. PERCENTAGE OF ACCIDENTS WHERE RISK ANALYSIS FOR PLANNING INSPECTIONS WAS CITED AS POTENTIALLY INADEQUATE

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[22] Risk Based Inspection (RBI) is a technology process whereby failure likelihood is combined with estimated severity of consequences in the event of equipment failure to rate the criticality of the equipment and thereby identify appropriate inspection frequencies. When correctly implemented, it is used to formally optimize the inspection efforts for each equipment item of plant within the boundaries of appropriately defined integrity operating limits, while minimizing equipment failure risks caused by the relevant damage mechanisms. [47] Experts usually favour the application of RBI methodologies to some or all parts of refinery sites. While such a recommendation is usually valid, RBI will not necessarily lead to the right inspections solutions if it is applied without sufficient resources, data or competence.

TABLE 16. EXAMPLES OF CRITERIA USED TO DETERMINE INSPECTION FREQUENCY FOR PRESSURE AND PIPE EQUIPMENT IN VARIOUS RBI METHODOLOGIES

Failure likelihood was usually based on a number of inputs, including:

- operating pressure and temperature
- diameter and length
- material
- thinning factor
- stress corrosion cracking (SCC) factor
- H2 partial pressure
- service life
- number of past inspections
- inspection effectiveness
- corrosion rate
- corrosion allowance
- online monitoring
- expert judgment

Generic standards were used when in-house data were inadequate or not available. One participant also applied a management factor "based on guidance in API 581 Appendix D and covering areas including leadership and administration, management of change, operating procedures, safe working practices and training."

Consequence analysis could be based on a variety of factors as well, including:

- fluid characteristics, hazard contents and pressure
- process stream, stream phase, toxic percentage, temperature, pressure, inventory and material density
- presence of detection and isolation systems
- impact on production, personnel and equipment
- impact on safety, health and environment
- impact on business issues and equipment costs
- the number of potential outage days together with generic cost data

Source: UK Health and Safety Laboratories [48]

FIGURE 33. OBSERVATIONS FROM CASES ON INSPECTION DEFICIENCIES

Inspections hardly took place at all

"Corrosion is caused at a place that is not visible and is not noticed. On the other hand, it can be prevented by careful watch. Defects in facility management resulting from insufficient information gathering or safety consciousness are considered to be the cause. External corrosion had already become a problem in oil refineries and petrochemical companies in 1990, the time of the accident. This company left it for ten years after a check in 1980. That is, sufficient maintenance was not performed on external corrosion. [Case 28]

Inspections were not adequately thorough to detect areas of weakness or accelerated deterioration

"The cause was not a welding defect, but a late-generated base material crack. This crack grew with a long-term use or the change of temperature and pressure at turn-around shutdowns/start-ups, etc. Although the base material conformed to the standard, the Charpy impact value was partly low. Breaking strength fell due to the above factor. The Dye Penetrant Test was carried out on the whole weld line until the internal overhaul inspection at a turnaround shutdown in 1971. However, for nine years until the accident, as inspection was partial, the crack was not found …

Corrosion and cracks must always be checked. A fundamental factor is a long-term use and omission of inspection. However, annual execution of the whole inspection is difficult, considering time and expense of drawing off and re-loading a lot of catalysts. At least, sufficient inspection every several years would be required." [Case 14]

Inspection intervals were not planned in conformance with accepted criteria

"The intervals between internal inspections have to be defined based on the estimated corrosion velocity. This is a general principle that can be found in de API 653 standard "Tank Inspection, Repair, Alteration and Reconstruction". Normally the corrosion velocity of the bottom plates is the most important one. In the case of major local corrosion, it will be this higher, local corrosion velocity which is determinative for the inspection interval." [Case 77]

"Accidents at fuel oil desulphurization units occur very frequently. One of the causes is the presence of a corrosive material. This unit should be inspected with top priority in a refinery." [EX056]

"[The company] failed to implement an effective system for the inspection of pipework on the Saturate Gas Plant (SGP), to complement that in place for process equipment. The system fell far below recognized industry good practice at the time. In addition they failed to use knowledge and experience from other sections of the plant that should have identified the need for more inspection of the SGP pipework. Over time sufficient pipework condition data should have been obtained, and entered into an inspection database, to verify the believed integrity and inform assessments of future inspection requirements. Without this both the system and the assessments were inadequate." [Case 66]

A sound risk-based inspection methodology was used but did not identify an elevated risk of corrosion

"The rupture of the tube that started the fire was a consequence of certain types of deterioration (coke deposit, attack by polythionic acids), which were not identified when the inspection plan was drawn up with the aid of the RBI software program used by the Group. Further development of this tool would thus seem necessary so that it includes the modes of deterioration mentioned above and to take the age of the equipment into account in the criticality calculations." [Case 74]

"In 1993, when the accident occurred, external corrosion of piping had already become a topic of maintenance. Why did the external corrosion of branch piping near the seashore remain? Due to a discrepancy in information-gathering, the preservation plan may have been too late. As corrosion of piping advances to the inside of piping unexpectedly, preservation repair work might require much time and man-power. Planned and detailed checks are important." [Case 37]

An inspection frequency was recommended in line with existing standards; the recommendation was ignored

"The design and implementation of the … tank inspection program was inadequate. [The] plan was to inspect its tanks at intervals prescribed by American Petroleum Institute (API) Standard 6539 (i.e., every 5 years for external inspections and 10 years for internal inspections). However, API 653 notes that inspection frequencies must be modified based on the corrosivity of the stored material. [Company] inspectors recommended revised frequencies, but the inspections did not occur." [Case 67]

Inspection frequency was reduced for budget reasons

Pipes of this type have not been maintained for many years to reduce costs, leading to the partial disposal of certain sections by progressive subsidence of the land. Soil moisture has probably accelerated the phenomenon of external corrosion. [Case 94]

In 2002 the UK Health and Safety Laboratories conducted a study of RBI methodologies involving seven different organizations including three refinery operators. Table 16 on page 73 provides a number of factors used to evaluate failure likelihood of equipment. Notably, a number of methodologies combined technical indicators (equipment dimensions and process characteristics) with operational factors (e.g., number of past inspections) and qualitative judgment. [48]

Over a third of the accidents reviewed in this study might have been avoided with appropriate planning of inspections on the basis of such criteria. (See Figure 32 on page 72.) In most cases the inspection frequency appeared to be inadequate taking into consideration vulnerabilities associated with the equipment involved (e.g., age, location, process intensity, etc.). In a few cases the inspections simply were not thorough enough to detect that corrosion was developing and could develop into a critical hazard with significant accident potential. There were also observations indicating that the assessment conducted by the operator had not identified an elevated risk of corrosion failure. Various deficiencies highlighted by these reports included:

- Inspections of the equipment in question hardly took place at all
- Inspections were not adequately thorough to detect areas of weakness or accelerated deterioration
- Inspection intervals were not planned in conformance with accepted criteria
- A sound risk-based inspection methodology was used but did not identify an elevated risk of corrosion
- An inspection frequency was recommended in line with existing standards; the recommendation was ignored
- Inspection frequency was reduced for budget reasons

Figure 33 on the previous page uses excerpts from various reports in regard to these particular aspects.

3.6 Inadequate identification of hazards and risks for other purposes

Several reports also highlighted other situations where a risk analysis might have been used to avoid a potential accident. In six cases it was reported that adequate assessment of conditions was not conducted prior to repair work, notably for hot work on corroded equipment. Hot work is a term used to describe heat and spark producing operations such as welding, flame cutting and grinding. It is a well-known hazard and is part of the permit-to-work procedure, standard good practice to control both occupational and process safety hazards. The U.S. Chemical Safety Board has noted that hot work is one of the most common causes of worker death in all the investigations it has covered. A bulletin that it issued on the topic identifies seven lessons learned from such accidents including identifying the hazards prior to the work and if possible use alternatives to avoid the work altogether when high risks are identified. Furthermore, once the hazards are identified, other precautions should be followed if the work is then to be carried forward.

FIGURE 34. OBSERVATIONS FROM CASES ON INADEQUATE HAZARD EVALUATION PRIOR TO REPAIR WORK

"There was a lack of awareness of the impact of changing conditions at the hot work site. Although combustible gas testing prior to the start of hot work early in the morning indicated that vapors were not present, gradual warming could make the presence of combustible vapors more likely." [Case 44]

"On the day of the incident, the piping contained approximately 90 gallons of naphtha, which was being pressurized from the running process unit through a leaking isolation valve. A work permit authorized maintenance employees to drain and remove the piping … As the line was being drained, naphtha was suddenly released from the open end of the piping that had been cut first. The naphtha ignited, most likely from contacting the nearby hot surfaces of the fractionator, and quickly engulfed the tower structure and personnel … Although the hot process equipment was close to the removal work, [the operator's] procedures and safe work permit did not identify ignition sources as a potential hazard. The permit also failed to identify the presence of hazardous amounts of benzene in the naphtha. The naphtha stripper vessel level control bypass valve was leaking, which prevented isolation of the line from the operating process unit. As a result, the running unit pressurized the naphtha piping … [The operator's] job planning procedures did not require a formal evaluation of the hazards of replacing the naphtha piping." [Case 55]

"The piping was remarkably thin due to corrosion from inside and outside. Scale adhering to the surface was detached because a water seal and a welding repair were carried out repeatedly. Therefore, the opening suddenly expanded and LPG blew out. The gasified LPG was ignited by a welding spark. The first repair work did not stop the leakage, and the second and third attempts at repairing were made. This inappropriate work was also one of the causes." [Case 30]

FIGURE 35. OBSERVATIONS FROM CASES ON THE ABSENCE OF ADEQUATE DETECTION AND MITIGATION SYSTEMS

"Vessel design, integrity, and maintenance were inadequate. The vessels did not have fire protection capability and had no provision for either emergency venting or frangible roof seams. Following the explosion of vapors, the vessels failed along their corroded bottom seams, releasing their contents." [Case 44]

"Following the incident a number of deficiencies were noted, including the poor availability of water curtains, the failure to intervene using the multipurpose pump, the lack of access stairway to the isolation valves of the dryers and the absence of any broadcast alarm for the unit to alert the other units on the site as well as the absence of corresponding detectors in the control room." [Case 36]

"After the accident, the plant was shut-down and the reactor purged. Its contents were removed and the reactor was prepared to open it to allow an internal examination. It was found that the temperature indicators on reactor had maximum readings below expected temperatures. Besides, no high temperature trips were fitted." [Case 42]

"The leakage was due to corrosion of the pipe, which had not been changed since 1973. There was no automatic gas-control system, which currently exists in every refinery in the country. This system, when it works, causes the immediate interruption of function if the leaking of certain gases is detected." [Case 35]

"Investigations revealed that the leak was detected only after 5 hours, by which time 478 tonnes of fuel had been spilled, of which 180 tonnes flowed into the river … the estimate that the volume shipped to a vessel corresponds more or less to the volume of a storage tank proved too imprecise to serve as feedback for alerting the workers in charge of the loading operation of a problem … " [Case 90]

It appeared in the cases studied that at least a prior risk analyses would have also identified the existing corrosion defects in the part under repair. These damaged sections (or in two cases, the presence of leaked fluids) created the opportunity for the accident to occur. Figure 34 on the previous page provides excerpts from the cases studied highlighting an absence of an appropriate hazard evaluation prior to conducting repairs on equipment showing clear signs of corrosion and other potential deficiencies. In some cases the leak had already occurred before the work was performed but the site was not monitored prior to the work. In other cases the release occurred while the work was taking place. For example, work was performed in a weakened area of the equipment such that this area expanded and broke open during the repair intervention. In all cases the flammable substances found an ignition source resulting in a fire or explosion or both.

In seven cases there were observations in the associated report(s) concerning detection and mitigation mechanisms that could have prevented a release from becoming a serious accident if they had been in place. An effective risk management approach relies on assigning appropriate technical measures to reduce and eliminate the risks. In the classic layer of protection strategy, measures that prevent a loss of containment are considered first order controls and measures to reduce the impacts of a loss of containment are considered second order controls. The severity of consequences associated with some cases, for example, an accident occurring during a loading operation in which 478 tonnes of fuel were spilled, suggested that, in addition to measures to prevent loss of containment prevention, second order protection, such as sensors, alarms, automatic shut-off controls and/or other possible measures, could have significantly reduced the impact of the event.

Figure 35 on the previous page gives examples where the severity of the event could have been minimized with adequate detection and mitigation measures for equipment where conditions were known to be associated with higher corrosion rates.

CHAPTER 4 CONCLUSIONS

Petroleum oil refining is an essential industry and an important element of the economic infrastructure of many EU and OECD countries and the geographic regions they inhabit. It also has a large presence wherever it is located. Sites are usually fairly large compared to other industries because production and storage capacity were designed to support a volume sufficient to assure profitability. But it is a high hazard industry, dealing daily with considerable volumes of flammable substances, of which a large subset of these are also toxic to the environment and some are also toxic to human health. Hence, there is always potential that a loss of containment under certain conditions on these sites, if not prevented or controlled, may have serious consequences for the surrounding community and environment and sometimes the economy of the local region.

By and large refineries are able to manage their sites safely. It is generally refinery industry experts that are driving efforts for better control technologies and risk management strategies to reduce their major accident risks to a minimum. Professional organizations such as the American Petroleum Institute and the Energy Institute are leaders in the promotion of safety technology and standards.

Nonetheless, corrosion control remains a particularly challenging phenomenon in the effort to reduce refinery accident risks, further elevated in many EU and OECD countries by the aging infrastructure and variation in crude oil supply and market conditions. According to the eMARS database, corrosion failure is responsible for one out of five of each major refinery accident occurring in the EU alone since 2000. This analysis of 99 corrosion-related accidents occurring in refineries over the last 50 years is an effort try to help the expert community maintain a focus on conditions that may put critical refinery equipment at risk of corrosion failure.

In this regard the following findings and conclusions are highlighted:

- Corrosion of equipment continues to be an important source of accident risk potential at EU and OECD refineries. The study identified 40 accidents occurring since 2000. Half of the accidents were estimated to have had very high consequences, particularly in terms of impacts on the environment and in terms of economic costs for the refinery itself as well as potentially the surrounding community.
- Generally, significant corrosion failures occur either because the hazard was not properly identified or the hazard was substantially ignored. There is an enormous variety of corrosion phenomena that can occur, yet the list of factors that may contribute to any corrosion failure, whatever type, is relatively short. The factors mainly involve the presence of various known corrosive agents, exposure to certain conditions, and equipment composition and configuration. Still it requires a certain level of competency, particular in regard to production processes (versus storage and transfer), to recognize that all the conditions are present to create a significant corrosion hazard. However, there appeared to be a number of cases studied in which the corrosion risk was quite obvious, and yet the management chose to ignore or underestimate it.
- The lack of an adequate hazard identification, or inadequate assessment of the associated risk potential, cannot be attributed to any one fundamental cause. It is sometimes a clear management failure in not having competence to make a good analysis, but not always. It appeared from the studies that experts sometimes overlooked how the various elements of a process could combine to create the conditions for accelerated corrosion. There is also a

question about how much experience specifically in mechanical integrity disciplines is available at some refineries to diagnose these properly.

- The study indicates that one of the most important challenges in managing refinery corrosion is also the element of change. Already changes to process design and equipment pose a challenge and need a certain competency to identify if a new corrosion risk has been introduced. However, other changes that can affect corrosion rates may go unrecognized and thus not be evaluated for an elevated risk. Particular changes of this nature could be a change in the source of crude oil or an increase in production rate, particularly if they are considered to be somewhat temporary.

  Inconspicuous changes can also create risk and in this regard, the refinery's greatest risk may be change over time. Loss of experienced personnel, lack of knowledge of the original process and equipment design (sometimes decades ago), and aging equipment all fall in this category. The industry is well aware of this kind of threat and there are numerous resources on how to work with such challenges. Strategies such as risk-based inspections, life-cycle management, and safety performance indicators, to name a few, are all good practices that can support risk management for this somewhat insidious changes that can greatly influence the level of risk. Corporate leadership and safety culture, areas of renewed emphasis following the accident at BP Texas City in March 2005, also offer promising conceptual frameworks for organizations to reinforce and sustain efforts at the operational level.

  There are also numerous developments that have taken place and targeted for the future in regard to control technologies. In particular improvements and innovations in detection systems and methods can help refineries with the inherent perils of scientific uncertainty associated with the corrosion process in the production units and storage tanks, as well as creeping effects of change over time.

- Neglecting to identify or manage corrosion hazards also continues to be a problem on some refinery sites. While there are many exemplary refinery operators with admirable risk management programmes, the evidence is clear that not all refinery operators are necessarily "good actors" who place an appropriate emphasis on risk management objectives. There is also probably a slightly different category of operators that intends to be a good actor but lack the management skills to establish a safety management system that works. In either case, some accident reports are quite clear that the lesson learned was less about the technical challenge of managing corrosion but simply about having an effective risk management program. The work of inspection authorities is most certainly challenging in these situations.

In essence this study provides some evidence to confirm concerns among experts in both government and industry that the risk of corrosion failures causing major accident remains a strong area of concern. In illustrating the kinds of decisions that may have led to certain accident, or the severity of their consequences, it is hoped that inspectors and refinery engineers who are looking to improve their awareness of corrosion risks will have gained some knowledge that will help them in their work. In addition, it is possible that the findings can also help key leaders in government and industry point out that corrosion remains a significant refinery hazard deserving serious and sustained management attention.

APPENDIX 1: LIST OF ACCIDENTS STUDIED

CASE	YEAR	COUNTRY	SOURCES[23]	SHORT DESCRIPTION
CASE 1	1965	France	ARIA 26620	A fire broke out in a vertical oven of a reforming unit recently placed in service.
CASE 2	1967	USA	Lees'	Catastrophic explosion in underground pipeline kills 7 and injures 13.
CASE 3	1969	France	ARIA 7320	A buried pipeline carrying acid gases containing hydrogen sulphide leaked at a weld.
CASE 4	1973	France	ARIA 26574	The upper part of a metallic chimney of an atmospheric distillation unit in normal operation detached and caused material damage in the vicinity of the installation.
CASE 5	1974	France	ARIA 26620	A fire took place in a vertical oven of a reforming unit following the rupture of a tube joining the radiation and convection sections.
CASE 6	1975	France	ARIA 26578	In an atmospheric distillation unit in normal operation a fire broke out in the distillation column.
CASE 7	1975	France	ARIA 26990	The rupture of the suction line at the bottom of the column in an atmospheric distillation unit in stable operation caused a limited fire because of the inflammation of the residuals.
CASE 8	1975	Japan	JST	Large-scale fire of an oil tank due to overlooking corrosive properties of distillate.
CASE 9	1977	Japan	JST	Leakage and fire of hydrogen caused due to stress corrosion cracking that originated from the influence of turnaround shutdown maintenance on a drain valve at hydrogen gas piping in a fuel oil desulphurization cracking unit.

[23] Sources are as follows:
ARIA = http://www.aria.developpement-durable.gouv.fr/
JST = http://www.sozogaku.com/fkd/en/index.html
ZEMA = http://www.infosis.uba.de/index.php/de/site/12981/zema/index.html
eMARS = https://emars.jrc.ec.europa.eu
CSB = http://www.csb.gov
Lees' = Lees' Loss Prevention in the Process Industries, 3rd edition [13]
MARSH = Marsh 100 Largest Losses, 20th edition, 1972-2001 [7]
MHIDAS = a database established by the U.K. Health & Safety Executive in 1986 (no longer available)
LDEQ = Louisiana Department of Environmental Quality

CASE 10	1978	France	ARIA 26534	Fire was fed by the rupture of the discharge pipe of the residue pump in the distillation unit.
CASE 11	1978	Japan	JST	Leakage and fire of heavy gas oil from an opening in vent piping of a reflux pump at a distillation column.
CASE 12	1978	Japan	JST	Outflow of all fuel oil from a tank caused due to breakage of a base plate of an outdoor oil tank from an earthquake.
CASE 13	1979	USA	ARIA 7279	In an alkylation unit of sulphuric acid, butane evaporated in the atmosphere creating a vapour cloud that engulfed the boiler of the neighbouring catalytic cracker.
CASE 14	1980	Japan	JST	Rupture of a reactor during an air-tight test of reactor at a catalytic hydro-desulphurization unit.
CASE 15	1984	USA	ARIA 7127 Koch et al.[50]	An amine absorber pressure vessel ruptured during welding work and released large quantities of flammable gases and vapors.
CASE 16	1986	United Kingdom	eMARS MHIDAS	Leak in the isobutane recycling unit
CASE 17	1988	France	ARIA 163	In a storage area during loading the seal of a fixed roof tank containing oil residues ruptured.
CASE 18	1988	USA	ARIA 324 Lees'	The decompression of a depropanizer and the head spherical tank through the opening of a pipeline, caused an unconfined vapour cloud explosion in a fluid catalytic cracker unit.
CASE 19	1988	Japan	JST	Fire caused due to erosion of a water injection nozzle connected to reactor outlet piping at a heavy oil hydrodesulphurization unit.
CASE 20	1988	Australia	MHIDAS	Tank rupture causes major spill of gasoline requiring evacuation of the surrounding community.
CASE 21	1988	USA	Lees' MHIDAS	Catastrophic rupture of 48 year old diesel tank on initial fill after it had been relocated and reconstructed.
CASE 22	1989	Japan	ARIA 106	A loss of hydrogen occurred in a distribution box of the thermal exchanger of a desulphurization unit, triggering an explosion and fire.
CASE 23	1989	Japan	JST	Leakage and explosion of hydrogen at outlet piping of a reactor in the hydrodesulphurization unit.
CASE 24	1989	Germany	eMARS	Material failure causes rupture in pipeline.
CASE 25	1990	France	ARIA 2257	An explosion occurred from a leak located at the level of an elbow of a buried pipeline exporting premium gasoline from the refinery.

CASE 26	1990	France	ARIA 26504	An air tube cooler (air cooler) ruptured in a unit for hydrotreatment/desulphurization of distillate.
CASE 27	1990	Japan	JST	Leakage of water contaminated with crude oil from a corroded part of piping during removing operation of unnecessary piping left for a long time.
CASE 28	1990	Japan	JST	Leakage of fuel oil into the sea from the corroded part under hot insulation of receiving pipe at a jetty.
CASE 29	1990	Japan	JST	Fire involving a vacuum residue that was leaked from the opening of a pipe due to corrosion in the bottom recycling line of a vacuum distillation unit.
CASE 30	1991	Japan	JST	A fire occurred during repair work at an LPG washing column of a gasification-desulphurization unit for vacuum residue oil in a refinery.
CASE 31	1991	Germany	eMARS ARIA 2631 ZEMA 9112	A pipe failure in the T-junctions area of a collector for an air cooler in the high pressure section of the hydrocracker unit resulted in a release of hydrocarbons and hydrogen, which subsequently ignited.
CASE 32	1992	USA	MARSH	An explosion occurred in the hydrogen processing unit occurred releasing a hydrocarbon/hydrogen mixture to the atmosphere.
CASE 33	1992	Belgium	eMARS ARIA 22229	A loss of process gas occurred at an elbow in the pipeline of a desulphurization unit. A flammable cloud was released to the atmosphere and exploded causing a fire.
CASE 34	1992	France	eMARS ARIA 3969	A breach in the transmission line feeding the gas plant released gas into the fluid catalytic cracker causing a violent explosion.
CASE 35	1992	Greece	eMARS ARIA 3912 Iliopoulou et al.[52]	An explosion was caused by the ignition of a vapour cloud of hydrocarbons that were most likely to have been released following the rupture of a pipe at the bottom of the naphtha stabilizer tower.
CASE 36	1993	France	ARIA 26186	A loss of propane, caused by the coming apart of a pipe purging a propane dryer, occurred in a refining unit.
CASE 37	1993	Japan	JST	Fuel oil leakage from the corroded part of branch piping for pressure gauge attachment at jetty loading equipment.
CASE 38	1993	USA	MARSH	A fire occurred during normal operation in the central unit of three delayed coker units.
CASE 39	1993	Germany	eMARS ARIA 19222 ZEMA 9310	A fire occurred in a coking unit resulting in a significant loss of product.

CASE 40	1994	France	ARIA 6011	A significant loss of gasoline was discovered from a pipeline in the refinery and an explosion cloud was formed near the railway.
CASE 41	1994	Japan	JST	Fire caused due to sudden rupture of a buffer drum of a compressor at a light fuel oil desulphurization unit.
CASE 42	1994	United Kingdom	eMARS	Rupture of reactor vessel following an exceedence of the design parameters
CASE 43	1995	Germany	ARIA 10347 ZEMA 9525	The gas recycling pipeline burst and the spilled contents ignited.
CASE 44	1995	USA	ARIA 7635 US EPA [53]	Abnormally high pressure led to rupture at the tank bottom weakened by corrosion.
CASE 45	1995	France	ARIA 7433	Leak of sulphurized hydrogen in the tank at the top of the amine regeneration column.
CASE 46	1996	France	ARIA 10400	A loss occurred in the reflux pipe (of the FCC pumphouse) downstream from an injection spout for superheated water.
CASE 47	1996	France	ARIA 8167	The loss from a thermal exchanger in a unit separating aromatic compounds from distillates led to the rejection, via the cooling water, of furfural into a nearby water body.
CASE 48	1996	Japan	JST	Leakage and fire due to corrosion of branch piping of a thermometer of an atmospheric distillation unit in normal operation.
CASE 49	1996	France	eMARS	Leakage of solvent due to corrosion of tubes in the heat exchanger.
CASE 50	1996	Germany	eMARS ARIA 14666	A separator exploded causing a release of hydrocarbon gases upon startup of the freezer installation.
CASE 51	1998	France	ARIA 23175	A leak occurred in a line connecting the hot separator to the cold separator of a gasoil desulphurization unit.
CASE 52	1998	France	ARIA 20356	Following the bursting of a 250 mm pipe, a mixture containing hydrogen, hydrogen sulphide, water and hydrocarbons was discharged into the atmosphere.
CASE 53	1998	France	ARIA 20355	Following the loss of containment of a pipeline located downstream from a flow meter, diesel used to clean a distillation column under vacuum pressure ignited.
CASE 54	1999	Japan	JST	Fire caused by diversion of naphtha to a corroded pipeline during an emergency shutdown.
CASE 55	1999	USA	CSB	Fire in a fractionating tower in normal operation as workers are performing maintenance on the unit.
CASE 56	1999	Greece	eMARS MARSH	A release and auto-ignition of light gas oil occurred due to a failure of an overhead line connecting a crude furnace to

				a reactor in the crude distillation unit.
CASE 57	1999	United Kingdom	eMARS	Uncontrolled release of highly flammable liquid from a leak at the base of a storage tank.
CASE 58	1999	United Kingdom	eMARS	Failure of crude oil storage tank due to pitting corrosion of the tank bottom.
CASE 59	2000	France	ARIA 19538	An 8" LPG pipeline burst in a crude distillation unit due to a hole in a zone affected thermally by welding.
CASE 60	2000	France	ARIA 19527	A gas leak occurred in the lower part of a process reactor and subsequently the unit was engulfed in flames.
CASE 61	2000	France	ARIA 19522	A loss of gasoline occurred in a trench near a pipeline.
CASE 62	2000	Japan	JST	A fire was caused due to unequal flow distribution between tubes in a fin-fan cooler at an outlet of the reactor at a fuel oil hydro-desulphurization unit.
CASE 63	2000	Japan	JST	Fire involving hydrogen sulphide that leaked from overflash piping of an atmospheric distillation column.
CASE 64	2001	France	ARIA 36581	A leak of gasoil, followed by self-ignition, occurred in an injection pipe fitted with a high temperature corrosion inhibitor.
CASE 65	2001	USA	MARSH Lees'	Three days after shutdown from a fire the distillation tower suffered a structural failure due to corrosion issues compounded by the fire.
CASE 66	2001	United Kingdom	eMARS HSE	A catastrophic failure occurred on a section of pipework on the Saturate Gas Plant at an elbow just downstream of a water-into-gas injection point.
CASE 67	2001	USA	eMARS CSB	Explosion in a sulphuric acid storage tank farm causes one death and 8 injuries.
CASE 68	2002	France	ARIA 23034	A stream of crude oil was observed along a pipeline in the refinery.
CASE 69	2002	Japan	JST	Leakage and a fire occurred due to corrosion of bypass piping for recirculation gas at a fuel oil desulphurization unit.
CASE 70	2003	France	ARIA 25346	During the unloading of pyrolysis oil at the jetty, there was a leak in an ensheathed pipe in the street underpass.
CASE 71	2003	United Kingdom	eMARS	Failure in a thermal relief line from a pressure relief valve (PRV) due to corrosion under insulation.
CASE 72	2004	France	ARIA 29518	Leak of gasoil in a distillation unit due to a hole worn by corrosion into 3 tubes of an open exchanger circuit cooled with water.
CASE 73	2004	France	ARIA 26978	A leak of gasoil from an internal pipeline spilled near the jetty.

CASE 74	2004	France	eMARS	A fire broke out in the pre-heating oven of the gas-oil desulphurization unit of the refinery.
CASE 75	2004	The Netherlands	eMARS	Leakage of reformate benzene from a storage tank.
CASE 76	2004	Germany	eMARS	Fire and explosion in a petrol desulphurization plant caused significant property on-site damage.
CASE 77	2005	Belgium	eMARS	Failure of a storage tank resulting in the release of all contents.
CASE 78	2005	UK	eMARS	A significant volume of kerosene was released from the base of a large storage tank into the ground and groundwater beneath the tank and the site.
CASE 79	2006	France	ARIA 36578	A leak occurred in an elbow section of a steel carbon pipe at the top of a primary fractionating column.
CASE 80	2006	France	ARIA 31370	Hydrogen escaped during a loading operation and spilled in the waterproof zone of the pumping station connected to a filtration pipe.
CASE 81	2006	Germany	ZEMA	Leakage in the atmospheric distillation column causes release of gas oil.
CASE 82	2006	Austria	eMARS	Leakage of crude oil pipe due to corrosion with subsequent fire.
CASE 83	2006	Italy	eMARS	A leak of liquid hydrocarbons from a pipeline resulted ina massive fire within 2 metres distance from the local subway.
CASE 84	2006	Austria	eMARS	Leakage of a heat exchanger and a pipe containing crude oil with subsequent fire.
CASE 85	2006	Italy	eMARS	A crude oil leak was detected in the bottom part of the shell of a floating roof tank.
CASE 86	2006	USA	LDEQ	Large volumes of sulphur dioxide, nitrogen compounds and hydrogen sulphide were released to the flare after failed attempts to stop a leak in the sulphur recovery plant.
CASE 87	2006	USA	LDEQ	A leak in an underground line of the catalytic reformer caused a release of 15 tons of corrosive waste and sludge.
CASE 88	2007	Germany	ZEMA	Because of incorrect air flow there was an iron sulphide fire in a flare pipe.
CASE 89	2007	United Kingdom	eMARS	A fire occurred in the isomerization plant (Unit 35) releasing a significant volume of naptha.

CASE 90	2007	USA	LDEQ	Internal corrosion of a pipeline resulted in a release of crude oil to the surrounding environment.
CASE 91	2008	France	eMARS MEEDDAT [55] ARIA 34351	During loading of a tanker, a leak occurred in a corroded pipeline and caused a spill of a high volume of heavy fuel which lasted over five hours, causing significant pollution of the nearby water body.
CASE 92	2009	France	ARIA 37681	Heavy aromatic hydrocarbons escaped from an insulated pipe located at the jetty and are released into the adjacent water body.
CASE 93	2010	France	ARIA 38503	A leak was spotted on an ethylene extra pipe located in a walkway on the downstream part of vapocracker.
CASE 94	2010	France	ARIA 39803	A leak of crude oil was detected at a water pipe connected to a storage tank.
CASE 95	2010	France	ARIA 38023	An explosion occurs due to failure of insulation in a section of the atmospheric distillation unit.
CASE 96	2011	France	eMARS ARIA 40173	An oil leak was detected in a desulphurization unit causing a release of hydrogen and hydrogen sulfide.
CASE 97	2012	Spain	eMARS	A fire occurred in the fluid catalytic cracking unit of an oil refinery due to a leak in a process pipe.
CASE 98	2012	France	ARIA 42801	A leak was detected in a hydrodesulphurization unit of a refinery probably due to corrosion from exposure to hydrogen sulphide.
CASE 99	2012	USA	CSB	The catastrophic failure of a pipe in the crude oil distillation unit released flammable substances and produced a large vapour cloud that spread to the off-site community.

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European Commission

EUR 26331 EN – Joint Research Centre – Institute for the Protection and Security of the Citizen (IPSC)

Title: Corrosion Related Accidents in Petroleum Refineries: Lessons learned from accidents in EU and OECD countries

Author(s): Maureen Heraty Wood, Ana Lisa Vetere Arellano, and Lorenzo Van Wijk

Luxembourg: Publications Office of the European Union

2013 – 92 pp. – 21.0 x 29.7 cm

EUR – Scientific and Technical Research series

ISSN 1018-5593 (Printed)

ISSN 1831-9424 (Online)

doi: 10.2788/37964 (Printed)

doi: 10.2788/37964 (Online)

Abstract

Petroleum refineries are generally acknowledged to be high hazard sites due to the nature of petroleum products and the processing technologies that produce them in the current era. For the most part, however, the risks are well-known and refinery operators have applied considerable knowledge and resources over the past decades to control and minimize risk potential. Nonetheless, major accidents in refineries tend to regularly occur with impacts not only on human health and the environment, but also in many cases on social and economic well-being. A recurring cause of accidents in petroleum refineries is well-known to be corrosion. This report studies corrosion-related accidents in refineries within the European Union (EU) and the Organization for Economic Co-operation and Development (OECD), comparing accident occurring before and after 2000 and with the view to providing insights into recent causal trends and identifying lessons learned that could influence prevention strategies in future. The report highlights process and equipment conditions and potential risk management failures that were cited in 99 different corrosion-related accidents occurring between 1965 and 2008. In particular, the study provides some evidence to confirm concerns among experts in both government and industry that the risk of corrosion failures causing major accidents in EU and OECD countries remains a strong area of concern. The aim of this analysis is to aid particular inspectors by providing a concise summary of refinery corrosion hazards and examples of how they have been manifested in past accidents. The findings may be also useful to operators in renewing aspects of their risk management strategy or training personnel on how to recognize and evaluate potential corrosion risks.

LB-NA-26331-EN-N

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Publications Office

ISBN 978-92-79-34652-1