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APPLICATION OF INNOVATIVE RISK ASSESSMENT METHODOLOGY FOR DAMAGE MECHANISMS IDENTIFICATION ON PART OF AMINE REGENERATION UNIT

PRIMENA INOVATIVNE METODOLOGIJE ZA PROCENU RIZIKA PRILIKOM ODREĐIVANJA MEHANIZAMA OŠTEĆENJA NA PRIMERU DELA REGENERATIVNOG AMINSKOG POSTROJENJA

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Abstract

When implementing the method for quantitative risk analysis, usually based on RBI (Risk Based Inspection), conditions which directly influence the identification of damage mechanisms are defined at the beginning of the analysis. Thus, conducted analysis applies to the exact parameters and very specific combinations of conditions and damage mechanisms. The question arises as to whether such an analysis and its results may represent initial data for some subsequent analysis that can be carried out in the following period, regardless of the reasons for the implementation. The extension of the methodology from the one shown in the ASME PCC 3 standard is to identify both active and passive/potential damage mechanisms and the conditions under which passive can be activated. This addition to the methodology is successfully applied in case of a Middle East refinery, and as a representative example, a typical amine regeneration unit present in all modern gas or oil refineries, specifically the part of the unit with lean amine, is shown.

Izvod

Prilikom sprovođenja metoda za kvantitativnu analizu rizika, zasnovanih na RBI (Ispitivanje zasnovano na riziku), na početku analize definišu se uslovi koji direktno imaju uticaj na identifikovanje mehanizama oštećenja. Tako sprovedena analiza važi za tačno te parametre i samim tim za vrlo konkretne kombinacije uslova i mehanizama oštećenja. Postavlja se pitanje da li jedna takva analiza i njeni rezultati mogu da predstavljaju početne podatke za neku narednu analizu koja može da se sprovede u narednom periodu, nezavisno od razloga za sprovođenje. Proširenje metodologije od one prikazane u standardu ASME PCC 3 jeste da se prilikom koraka identifikovanja mehanizama oštećenja identifikuju i aktivni ali i pasivni/potencijalni mehanizmi i uslovi pod kojima bi oni mogli preći u aktivne. Ovako definisan dodatak metodologiji već je uspešno primenjen na slučaju rafinerije na Bliskom istoku, a kao reprezentativni primer prikazano je tipično postrojenju za regeneraciju amina, prisutno u svim modernim rafinerijama, konkretno na delu postrojenja sa siromašnim rastvorom amina.

INTRODUCTION

Risk analysis and application of an RBI (Risk Based Inspection) methodology in oil and gas industry is becoming more and more complex due to constant improvement of processes itself, process parameters, materials used for the production of components, vessels, pipelines, additional equipment and similar. To support this claim, a constant revision of standards and recommended practice (RP) documents from an area of research is observed, mainly ASME PCC-3 /1/, API 580 /2/, API 581 /3/, API 571 /4/, or completely new ones are being published, like API (970) /5/. In addition to previously mentioned documents there are other documents which some oil and gas companies, such as Shell, QP, or classification societies like DNV GL are developing independently, but nevertheless are following the same methodology, rules and standards.

As shown in API 580 /2/, API 581 /3/, calculation of risk involves determination of a Probability of Failure (PoF) combined with the Consequences of Failure (CoF). Failure is defined as a termination of the ability of a system, structure, equipment, or component to perform its required function of containment of fluid (i.e. loss of containment) which can result as a leakage of fluid into the atmosphere or full rupture of pressure component. The aim of this paper is to demonstrate the application of a modified methodology for damage mechanisms identification and that damage mechanism factor is part of the equation for PoF calculation. More on the method for calculating the PoF shall follow.

Two methods of calculating PoF are shown in API 581 /3/; the generic failure frequency (GFF) method, Eq.(1), and a two-parameter Weibull distribution method. The GFF method is used to predict loss of containment probability of failure from pressure boundary equipment, while the Weibull distribution method is used to predict probability of failure for pressure relief devices and heat exchanger bundles.

$$P_f(t) = gff \cdot F_{MS} \cdot D_f(t), \qquad (1)$$

where: PoF is a function of time $P_f(t)$ and is determined as the product of generic failure frequency gff, management system factor F_{MS}, and damage factor $D_f(t)$.

This analysis shall not include factors gff and F_{MS}.

Damage factor $D_f(t)$ is determined based on the applicable damage mechanisms relevant to the materials of construction and the process service, the physical condition of the component, and the inspection techniques used to quantify damage, and it is the only factor that is a function of time, therefore, the damage factor represents an expected condition and expected damage rate. In other words, it can be said that the damage factor modifies the industry generic failure frequency, gff, which is specific for component/equipment/unit and makes it specific for the component/equipment/unit under evaluation. The management systems factor, F_{MS}, is an adjustment factor that accounts for the influence of the facility's management system on the mechanical integrity of the plant equipment and as such is not time dependent nor dependent from the change in operating conditions. The basic function of the damage factor, as given in API 581 /3/, is to evaluate the amount of damage that may be present as a function of time in service and the effectiveness of the inspection activity to quantify that damage. Means and number of identified damage mechanisms have direct correlation to the value of PoF and therefore on the quantified value of the final risk.

FINAL TREATMENT OF OIL PRODUCTS

Primary but also secondary products that are obtained in the process of atmospheric distillation of crude oil or in the thermal and respectively catalytic processes, due to the number of undesirable and harmful components, are not suitable for final use, nor can they be used as raw material in standard refining processes. Some of the compounds are toxic, corrosive, chemically unstable or they can form deposits during prolonged storage. Because of all this, most of these products have to be refined to a certain quality level. The origin of some of the compounds in crude oil and in its products is natural, while others form due to oil processing. For a further analysis in this paper, the following compounds are of interest:

Hydrogen sulphide (H_2S) is found in sour crude oil, but the largest quantities are made in the process of decomposing organic sulfuric compounds through oil distillation, thermal and catalytic cracking, hydrocracking, reforming, hydrodesulphuration and other forms of oil and gas processing and treatment.

Elemental sulphur is frequently found in oil. Usually it is formed by oxidation of hydrogen sulphide that is in contact with oxygen from air during the prolonged storage of oil products.

Water, as a free water, comes together with oil from the well. Free water is separated in the process of oil preparation for atmospheric distillation. Water in oil products originates from the bottom of the storage reservoir, where it accumulates over time as a condensate of moisture that enters into the reservoir with air through the exhaust system.

Carbon dioxide (CO_2), in variable quantities is found in natural gas. In liquid products it can be found as a product of catalytic cracking.

AMINE REGENERATION UNIT

One of the challenging units for risk assessment in oil and gas industry is the unit for amine regeneration. Amines are organic compounds that contain one more basic nitrogen atoms and they are considered to be derivates of ammonia due to structural similarities. What is important to mention in regard to amine physical properties is that amines have excellent water solubility. The gas treating process, specifically amine gas treating, also known as amine scrubbing or gas sweeting, refers to a process that uses amine-water solution to remove hydrogen sulphide (H_2S) and carbon dioxide (CO_2) from sour gas stream. Both H_2S and CO_2 are categorized as acid gases and hence are corrosive to carbon steels, where CO_2 is the stronger acid of the two. In smaller quantities, sulphur, as chemical element, and in this case as a chemical compound H_2S, can have a protective role in a way that it forms a protective film of iron sulphide on the surface of the material. A typical amine treating unit is shown in Fig. 1, and is fully taken from API 571 /4/ with suggested damage mechanisms.

Process description

Hydrogen sulphide is a gas naturally present in larger quantities in crude oil which is better known as sour crude, but also in a greater number of natural gas sources. In addition to natural occurrence, H_2S is produced as by-product during the oil and gas treating processes which aim to produce low sulphur refined products. H_2S is removed from refinery gas and product streams using a circulating amine solution in the amine treating unit primarily because this sulfuric compound is extremely harmful to human health, and secondly because limiting sulphur emissions from the refinery can satisfy process requirements and comply with environmental regulations. During the process, heated refinery gas is pushed through the column where it is mixed with liquid amine solution whereby, H_2S and CO_2 respectively, are being stripped out from the gas stream. Both gases are then removed from the amine solution in the amine regeneration unit, and are sent as a concentrated acid gas stream to the other part of the refinery where it is converted to elemental sulphur to be disposed of as a refinery by-product. There are many different amines used in gas treating, but in this particular case it shall be regarded that a solution of methyl diethanolamine (MDEA) with 45 % wt. is used (depending on the amount of H_2S/CO_2, MDEA can be used in the concentration range of 30-55 %). The unit is designed to keep the lean amine acid gas at or below 0.008 mol(H_2S/mol(MDEA)) based on a rich amine loading of 0.41 mol(H_2S)/mol(MDEA). MDEA is

chosen as a product for acid gas removal due to the fact that is gives a better composition for raw material for further processing and treating. The amine treating unit consists of the following sections:
• Rich amine feed section
• Amine regeneration section
• Lean amine cooling section
• Amine drain section
• Lean amine filtration section
• Chemical injection/Flare KO drum section
• Common lean amine storage section

Being that the unit consist of several sections and that it is noted in the process description that there are several different types of operating fluids due to the concentration change of hydrogen sulphide in the amine solution (according to an RBI methodology, when a significant change occurs in the process or chemical parameters, it is then considered to be a different operating fluid in question), identification of the damage mechanisms shall be oriented only to the part of the unit with lean amine solution, Fig. 2,

marked with green lines. Results of this analysis can also be used for other parts of the refinery where there are same or similar enough combinations of operating conditions and operating fluids.

For the material from which the equipment and piping are made, it shall be regarded that it is carbon steel suitable for operation in a corrosive environment and with the corresponding corrosion allowance for the operating conditions. The specific choice of material depends on the operating conditions and the corrosivity of the operating fluid, which changes depending on the concentration of hydrogen sulphide and carbon dioxide. For such piping sections and equipment, use of stainless steel as well as duplex steel with corresponding corrosion allowance for the operating conditions is considered.

For the operating fluid, it shall be regarded that it is a liquid with characteristics displayed in Table 1. Table 1 also provides additional information regarding the operating fluid and the example of the conditions in which a part of the unit operates.
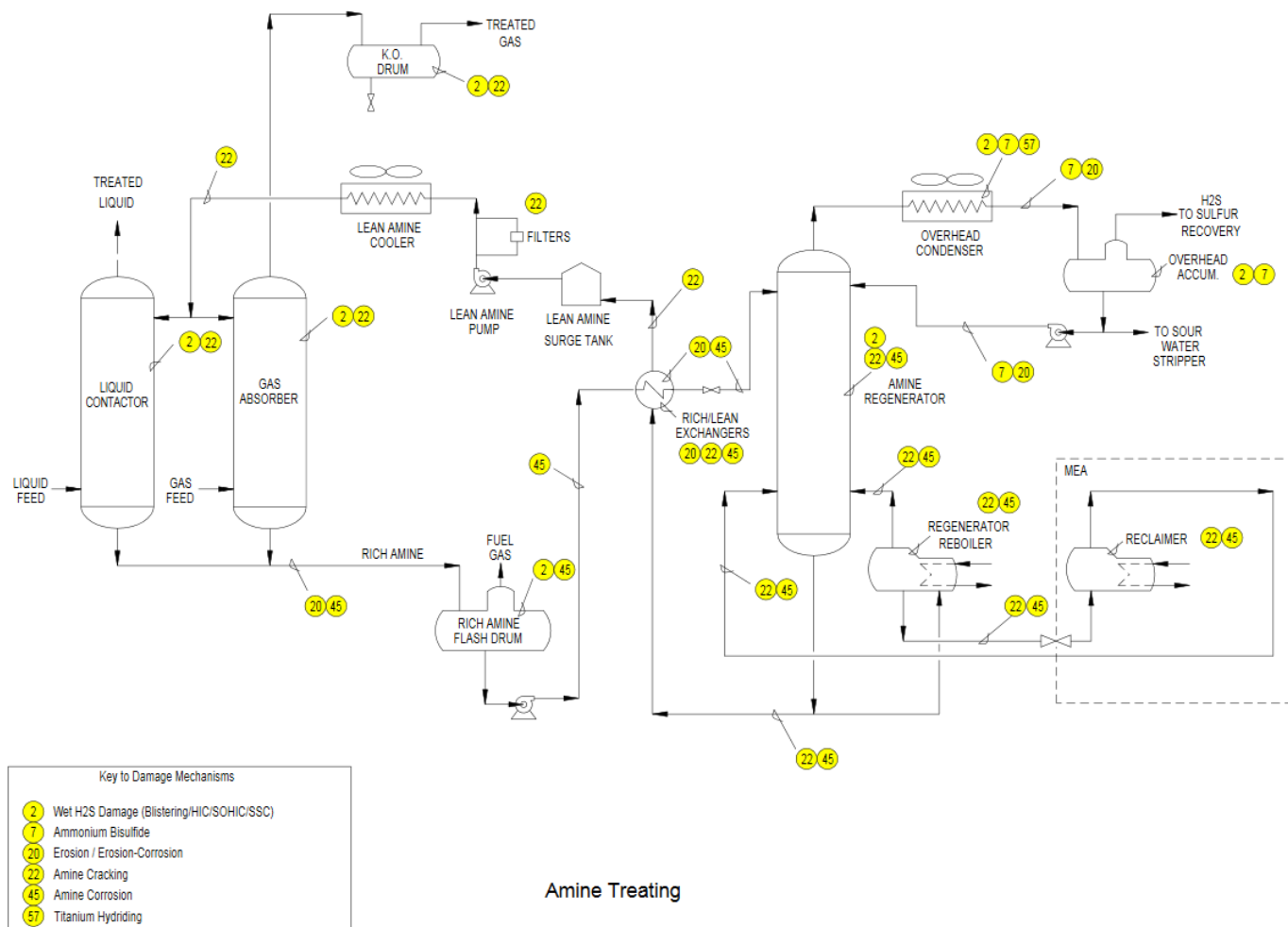

Figure 1. Typical amine treating unit per API 571.

Figure 2. Part of the amine regeneration section with the lean amine section marked, adapted from API 571.

Table 1. Example of operating characteristics of the working fluid at intake to the lean amine reservoir.

Working fluid	H₂O/MDEA solution	
Phase	Liquid	
MDMT*	°C	-3
Operating temperature	°C	96
Operating pressure	bar	13
Design temperature	°C	150
Design pressure	bar	19,3
Possible free water during normal operation	Yes/No	Yes
Wet sour service	Yes	
If YES, severity	High	
Crack and corrosion inducing agents		
H₂S in sour water	ppmw	1050
Amine	wt%	45
CO₂	mol%	0,005 (max)

* Minimum design metal temperature

CRITERIA FOR DAMAGE MECHANISM IDENTIFICATION

As per API 584 /6/ process parameters that influence mechanical integrity and/or reliability of the component, equipment or unit, fall into two categories: chemical and physical. Chemical parameters are those that relate to the chemistry and fluid content of the process and can include: pH, water content, acid gas loading, sulphur content, salt content, inhibitor concentration, oxygen content and etc. Physical (mechanical, operational) parameters are those that are not chemical in nature, but include all other aspects of a process design that are vital to maintaining control within established design parameters and can include: various pressure and temperatures such as design, operating, partial pressures, dew points, dry points, flow rates, vibration, heating and cooling rates, delta pressure, etc. With that in mind, damage mechanism will be identified based on those parameters and type of material used for the construction of the observed part of the system as per standard ASME PCC-3 /1/, recommended practices API 571 /4/ and API 970 /5/, list of selected criteria per API 970's Annex B /5/, which correspond to operating and process conditions shown in Table 2, and as well as defined process variables that are specific to typical amine regenerator units: amine type, load, filtration, chloride content, CO₂ content, H₂S

content, oxygen content, HSAS (Heat Stable Amine Salts) content, water content in the solution, and etc., as shown in Table 1. Also, to keep a systematic approach, the analysed system will be divided into one or more subsections which, as per API 970 /5/, can consist of piping, equipment and components that are exposed to:
- common materials of construction;
- common design conditions;
- common operating conditions;
- common set of one or more damage mechanisms;
- common expected corrosion rate;
- common expected damage locations/morphology.

In this manner defined subsection is called a Corrosion loop or Corrosion Circuit (short CL) and it does not need to represent the physical subsystem of the analysed system. The following analysis is carried out for such defined CLs.

Table 1. Important criteria for damage mechanism identification as per operating and process conditions (/5/, Table B.1).

Low temperature (aqueous) corrosion and stress corrosion cracking damage mechanisms
b) Is there a potential for rapid corrosion at or downstream of injection or process mixing points due to heating/cooling, condensation/evaporation, reaction, between the injecting and mixing streams, etc.?
d) Is there a potential for rapid corrosion due to change in flow rates, changes in flow regime, e.g. vaporization, flashing, or other multiphase flow conditions?
e) Is there a potential for localized corrosion or cracking of austenitic stainless steels during shutdowns where polythionic acids (PTA) may be present?
h) Is there a potential for accelerated corrosion from precipitation of corrosive salts, e.g. amine/ammonium chlorides, etc.?
m) Can increase or decrease in pH (inadvertent or undetected) lead to increased corrosion or stress corrosion cracking?
q) Can solids be present causing increased erosion-corrosion (i.e. catalyst carryover, accumulation of corrosion products, etc.)?
s) Is there potential for increased corrosion in the inlet zone or at a vapor/liquid interface?
v) Is there a potential for inadvertent process contamination that could cause stress corrosion cracking? (e.g. wet H_2S, caustic, amines, chlorides, polythionic acids)?

For the identification of damage mechanisms, the following principles are applied:
1. categorize/classify equipment in CLs;
2. analyse fluid and operating condition;
3. analyse possible operating modes of the system (normal condition, upset conditions, downtime, etc.)
4. apply criteria for damage mechanism identification per ASME PCC-3 /1/ under conditions defined in previous points;
5. apply criteria for damage mechanism identification per API 970's Annex B /5/, Table 2.

Active damage mechanisms

Based on the above-mentioned principles, the following **active** damage mechanisms have been identified:
1. Sour water corrosion (presence of water and H_2S)
2. CO_2 corrosion (presence of CO_2 in the stream)
3. Amine cracking
4. Amine corrosion
5. Ammonium bisulfide corrosion
6. Corrosion under insulation (for insulated parts)
7. Atmospheric corrosion (for not insulated parts)
8. Sulphide stress cracking (SSC)

Conditions under which damage mechanisms occur are given in the following text and are fully taken from the referenced literature.

Sour water corrosion (presence of water and H_2S) /1/

Corrosion of steel due to acidic sour water containing H_2S at a pH between 4.5 and 7.0. Carbon dioxide (CO_2) may also be present. Sour waters containing significant amounts of ammonia, chlorides, or cyanides may significantly affect pH but are outside the scope of this section.

CO_2 corrosion (presence of CO_2 in the stream) /1/

Carbon dioxide (CO_2) corrosion results when CO_2 dissolves in water to form carbonic acid (H_2CO_3). The acid may lower the pH and sufficient quantities may promote general corrosion and/or pitting corrosion of carbon steel.

Amine cracking /1/

Amine cracking is a common term applied to the cracking of steels under the combined action of tensile stress and corrosion in aqueous alkanolamine systems used to remove/absorb H_2S and/or CO_2 and their mixtures from various gas and liquid hydrocarbon streams. Amine cracking is a form of alkaline stress corrosion cracking. It is most often found at or adjacent to non-PWHT'd carbon steel weldments or in highly coldworked parts.

Amine corrosion /1/

Amine corrosion refers to the general and/or localized corrosion that occurs principally on carbon steel in amine treating processes. Corrosion is not caused by the amine itself, but results from dissolved acid gases (CO_2 and H_2S), amine degradation products, heat stable amine salts (HSAS), and other contaminants.

Ammonium bisulfide corrosion /4/

Aggressive corrosion occurring in the hydro processing reactor effluent streams and in units handling alkaline sour water.

Corrosion under insulation (for insulated parts) /1/

Corrosion of piping, pressure vessels, and structural components resulting from water trapped under insulation or fireproofing.

Atmospheric corrosion (for not insulated parts) /1/

The deterioration of metal caused by chemical or electrochemical reaction of a metal with its environment over a uniform area.

Sulphide stress cracking (SSC) /1/

Cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulphide.

Passive damage mechanisms

In addition to identifying the active damage mechanism, following **passive or potential** damage mechanisms, which can become active due to change in any number of observed

parameters or conditions (e.g. change in fluid composition, change in process parameters, change in material, etc.) have also been identified:

1. Carbonate stress corrosion cracking (SCC)
2. Wet H_2S damage
3. Erosion/erosion corrosion
4. Erosion – droplets
5. Brittle fracture

As in the case of active damage mechanisms, the condition under which passive damage mechanisms become active are given in the following text and are fully taken from the referenced literature.

Carbonate SCC /1/

Carbonate stress corrosion cracking (often referred to as carbonate cracking) is the term applied to surface breaking or cracks that occur adjacent to carbon steel welds under the combined action of tensile stress and corrosion in carbonate-containing systems. It is a form of alkaline stress corrosion cracking (ASCC).

Wet H_2S damage /4/

This damage mechanism represents an aggregation of four types of damage that result in blistering and/or cracking of carbon steel and low alloy steels in wet H_2S environments. Four types of wet H_2S damage can be found in literature: hydrogen blistering, hydrogen induced cracking (HIC), stress oriented hydrogen induced cracking (SOHIC) and sulphide stress cracking (SSC).

Erosion/erosion-corrosion /1/

Erosion is the accelerated mechanical removal of surface material as a result of relative movement between or impact from solids, liquids, vapor, or any combination thereof. Erosion/corrosion is a description for the damage that occurs when corrosion contributes to erosion by removing protective films or scales, or by exposing the metal surface to further corrosion under the combined action of erosion and corrosion. Damage intensity is directly correlated with flow rate, generation of turbulent flow and presence of undissolved solid particles in the fluid (e.g. salt, sand, corrosion products and similar). Damage can also occur when fluid flow is obstructed/stopped thus creating the condition for phase change.

Erosion – droplets /1/

Erosion accelerated by two-phase flow. This form of damage occurs whenever two-phase flow is present or when the possibility of occurrence of two-phase stream in combination with relatively high flow rate can lead to the creation of patches with turbulent flow. Damage can also occur when fluid flow is obstructed/stopped thus creating the condition for phase change.

Brittle fracture /1/

Brittle fracture is the sudden rapid fracture under stress (residual or applied) where the material exhibits little or no evidence of ductility or plastic deformation.

Identification of the passive damage mechanism was carried out by using *what if* analysis where realistic conse-quences of barrier failures, which are taken into account in order to prevent the occurrence or reduce the impact of active damage mechanisms, were observed. In other words, situations where changes in operating parameters created conditions for the appearance of such identified damage mechanisms were observed. The probability that the observed component, system or facility during its lifetime will operate in such operating condition is expectedly high, especially given the fact that a very large number of parameters are taken into account. To demonstrate the previous statement, a concentration of H_2S in amine solution will be taken as an example: as previously mentioned, the chemical compound H_2S can be used as a corrosion prevention means where H_2S forms the protective sulfuric layer in the acidic environment (in this case H_2S has a function of a barrier); this barrier is active for relatively lower flow rates and when there is no increased concentration of HSAS; when conditions are met for one of these two parameters to change, the protective sulfuric layer is then removed which creates the condition for corrosion development, or even for accelerated corrosion development if a material is chosen in such a way that it is counted for the presence of protective sulfuric layer.

The consideration of the conditions when the identified passive damage mechanisms should be considered, the mechanism *Carbonate SCC* should be taken into account when carbonate presence in the stream is confirmed; the mechanism *Wet H_2S damage* is covered with mechanisms *Sour water corrosion* and *Sulphide stress cracking*; mechanisms *Erosion/erosion corrosion* and *Erosion – droplets* are possible in regard to the fact that flow can be limited due to the constraints in the amine service thus creating conditions for phase change; the mechanism *Brittle fracture* is identified as a potential damage mechanism due to temperature constrains for thick-walled components and low temperatures.

CONCLUSION

A number of damage mechanisms discussed in this paper is significantly higher than what API 571 /3/ suggests for given combinations of operating conditions, working fluid and used material, due to the fact that during analysis the following aspects were also taken into account:

• combined damage mechanisms (e.g. amine corrosion) as well as singular damage mechanisms (e.g. H_2S, CO_2 induced corrosions),
• conditions that do not correspond to operating conditions (various upset conditions).

The described approach is adopted due to the fact that a comprehensive inspection plan can subsequently show indications of damage resulting from the actions of non-dominant damage mechanisms.

As a result of an RBI analysis or any other independent optimisation process for component/equipment/unit, it is possible to introduce measures (barriers) that restrict one specific damage mechanism, by action or by time, or completely eliminate it. In a traditional, well established approach for conducting an RBI analysis, such component should be categorized without any active damage mechanisms due to

the presence of the applied barrier. With the above-mentioned approach, by identifying and documenting passive/potential damage mechanisms, it is achieved that other damage mechanisms are not overlooked, because given the right set of conditions, they can become active or even amplified as a consequence of introduced barriers for the reduction of primary damage mechanisms. The selected operating material can be specified as another example of applied barrier for identified damage mechanisms from the analysed system if the selected operating material is suitable for work in a corrosive environment. If applied correctly this barrier can reduce impact of following active damage mechanisms: sour water corrosion (presence of water and H_2S); CO_2 corrosion (presence of CO_2 in the stream); amine corrosion, but enhance passive damage mechanisms carbonate stress corrosion cracking (SCC). Finally, based on identified damage mechanisms it is possible to form a table, as shown in Table 3, which would summarize location and/or the characterization of damage and barriers.

Table 3. Summarized location/characterization of damage and identified barriers for the analysed unit.

Location/characterization of damage	Potential barriers
General corrosion Local corrosion Fluid side	Material of construction Corrosion allowance Temperature controls Pressure controls Flow control Fluid composition control Lining/cladding/refactoring Inhibitor/chemistry Equipment tracing/phase control

The approach that is based on full documentation of all active and passive damage mechanisms, as well as the documentation of applied and/or present barriers and their efficiency, insures safe application of an RBI method, eases a process of inspection planning, enables more consistent approach to an RBI analysis where components that are exposed to similar operating conditions are easily identified. To conclude, this approach also represents basis for the development of an IoW (Integrity Operating Window) for specified component, system or unit.

REFERENCES

1. ASME PCC-3 - 2017, Inspection Planning Using Risk-Based Methods, December 2017, The American Society of Mechanical Engineers
2. API Recommended Practice 580, Risk-based Inspection, Third edition, February 2016, American Petroleum Institute
3. API Recommended Practice 581, Risk-based Inspection Methodology, Third edition, April 2016, American Petroleum Institute
4. API Recommended Practice 571, Damage Mechanisms Affecting Fixed Equipment in the Refining Industry, Second edition, April 2011, American Petroleum Institute
5. API Recommended Practice 970, Corrosion Control Documents, First edition, December 2017, American Petroleum Institute
6. Rajković, M.P., *Nafta i prirodni naftni gas: istorija, geneza, tržište, hemija, prerada, derivati, primena, tribologija, petrohemija, ekologija*, Prometej, Novi Sad, 2009. (in Serbian: *Petroleum and natural petroleum gas: history, genesis, market, chemistry, processing, derivates, applications, tribology, petrochemistry, ecology*, Prometej, Novi Sad, Serbia, 2009)
7. API Recommended Practice 584, Integrity Operating Windows, First edition, May 2014, American Petroleum Institute