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Hydrogen Embrittlement in pipelines transporting sour hydrocarbons

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Abstract

Lamination-like defects in pipeline steels can be of both metallurgical and operational origin. In pipelines transporting hydrocarbon usually such defects are not a big challenge since they do not propagate under operating conditions. Nonetheless, in presence of a corrosion phenomenon and sour gas (H_2S), it is possible to observe blisters and cracks which may propagate in the steel. The observed damage mechanisms is Hydrogen Embrittlement and in spite of a huge amount of study and publications available, it is quite difficult for a pipeline owner to get practical data (crack propagation rate for instance) allowing a reliable estimate of the fitness for service of a pipeline. Taking advantage of a pipeline spool containing internal defects that was in service for more than 10 years and recently removed, a comprehensive study is underway to obtain a complete assessment of the pipeline future integrity. The program is comprehensive of study and comparison of ILI reports of the pipeline, to determine the optimum interval between inspections, assessment of inspection results via an accurate nondestructive (UT) and destructive examination of the removed section, to verify ILI results, lab tests program on specimens from the removed spool at operating conditions (75-80 bar and 30°-36° C) in presence of a small quantity of water, H_2S (5%) and CO_2 (7%), in order to assess defect propagation and to obtain an estimate of crack growth rate, and test in field of available methods to monitor the presence of Hydrogen and/or the growth of defects in in-service pipelines. This quite ambitious program is also expected to be able of offering a small contribution toward a better understanding of HE mechanisms and the engineering application of such complex, often mainly academic, studies.

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Keywords: Hydrogen Embrittlement; pipelines.

1. INTRODUCTION

Integrity Management is a process requiring continuous improvement and feedback with reference to pipeline design, materials specifications & procurement, construction, operation, inspection and maintenance, aimed at reducing failure risks as low as reasonably practicable (ALARP) and maximizing the efficiency of industrial components, Gabetta, et al. (2015).

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Knowledge of damage mechanisms is very important to achieve a good integrity management. A lot of work has been done in the past and is still underway towards a better understanding of Hydrogen Embrittlement (HE) and its consequences on load carrying steel.

It is very difficult to select between the huge amounts of published papers those that can be helpful in engineering applications. Engineers need a simple and effective approach in materials selection at design stage, in order to avoid damage and failures in structural materials during the operating lifespan and sometimes further on to increase operational life, Bruschi et al. (2017). Typically, engineers must know if a material is susceptible to cracking; moreover, early day choices or operational measures are often necessary during service life, to avoid or retard this type of damage. Not a simple task, Gabetta et al.(2018).

Following ASTM F2078, HE is "a permanent loss of ductility in a metal or alloy caused by hydrogen in combination with stress, either externally applied or internal residual stress". However, the interaction of Hydrogen with metals under stress is very complex and many different mechanisms are proposed, S.Lynch (2012). Diffused Hydrogen, for instance, can be associated to embrittlement but also to enhanced ductility.

In many cases, hydrogen can play a role in crack propagation, e.g Stress Corrosion Cracking (SCC) and Corrosion Fatigue (CF).

Three conditions are required to cause cracking - potentially developing to failure: presence of water solution, tensile stresses and material susceptibility, S.Brahimi (2014). The first two i.e. the nature of the flow wetting the pipe wall and the working factors of line pipe material when in service, commonly act as triggers for cracking, while the root cause remains the line pipe material susceptibility.

International guidelines, e.g. the standards issued by Nace International and EFC. Commonly, have shown a few weak points that already impacted the safety performance in recent projects, namely:

- In the definition of sour service, since more severe environments are nowadays common. The role of fluid composition needs to be better assessed and understood. Data on material susceptibility are more reliable in close-to-service environments, G.Gabetta et al. (2014).
- Mechanisms of crack initiation and crack propagation can be different. Hydrogen Embrittlement can play a different role in these two phases. Stress state and stress variations are very important in HE.

The relationship between corrosion resistance and crack susceptibility can affect the linear application of recommended practices. The presence of H2S and/or Sulphur in crude oil can be responsible for both general and localized corrosion. While a small amount of H2S is believed to cause a decrease of the general Corrosion Rate (CR) of carbon steel, J.I. Skar (2012), little information is available on the effect of high H2S partial pressure, also due to the difficulty of performing laboratory tests in such challenging conditions. The amount of data gathered from field experience is however increasing, offering a support for engineering choices, M.Bonis and R.MacDonald (2015).

Eni Head Quarters has a long term experience on pipeline integrity assessment. Operative activity was implemented in a dedicate project on Pipeline Integrity Management, still underway, Latronico and La Grotta (2013). Moreover, research projects were activated to study damage mechanisms, Bolzon et al. (2014) and Zwirko, et al. (2016), and to model internal corrosion in pipelines with reference to ILI results, De Masi, et al. (2016).

The present paper deals with the prediction of damage evolution in sour service pipelines, where HE can be foreseen. A case history will be the support to define inspection intervals with reference to available models, test results and literature data.

Engineers are mainly interested in procedures to avoid and/or manage the damage. In the case of internal corrosion and /or cracking in pipelines transporting sour hydrocarbons, international standards rely on steel metallurgy (composition, microstructure) and hardness, with the aim at selecting not susceptible materials. Field observations at the opposite show that, due to the large variation of fluid compositions and process variables, the concept itself of Stress Corrosion Susceptibility is probably too simple. A better understanding and a quantitative approach to different aspects of Hydrogen Embrittlement are required to assess damage evolution.

2. CASE STUDY

The present paper refers to pipelines transporting multiphase crude oil from production wells to treatment plant. The trunk lines operate at pressures between 75 Barg and 80 Barg, and temperatures between 30°C and 36°C. Essential design data is as follows:

- Size: 14"Diameter x 11.1mm wall thickness x 3.98 km in length
- Material: API 5L X60 seamless pipe to ISO 15156 for sour service
- Design Pressure: 97 Bar

The well fluid is crude oil with the following constituents in the gas phase:

- H_2S approximately 4.6 mole%
- CO_2 approx. 7.2 mole%

The fluid is considered non-corrosive provided that the water content is low enough to be entrained to form a stable emulsion. In fact, water content is kept low (max.2 wt%), since if any of the wells are found to be producing with excessive water content, the well is closed down.

The pipelines are in operations since 2003. The first inspection was performed in 2013. After 10 years of operating life the ILI report states: "no immediate remedial action is required as neither features with a calculated ERF≥1 (according to ANSI/ASME B31G) nor features with a calculated wall loss≥80% have been detected". However, the decision was made to repeat the ILI with a different tool (HiRes Ultrasonic Wall). In this case, a number of lamination type defects was detected. A few of them was closed to welds and/or sloping. A repair program was started and new ILI were planned at short intervals.

Laminations are a plane of non-fusion in the interior of a steel plate that results from the steel manufacturing process. They are planar defects that exist on one or more planes in the equipment, but cause no bulging of the metal surface, have no cracking in the through thickness direction, and are not linked. Following the Standard API 579- 1/ASME FFS-1 Fitness-For-Service (2016), laminations are a significant threat to the integrity of the pipeline if subjected to: high external loads, cyclic loading and sour environment (in weld and in pipeline steel not specified for sour service)

In the examined case, the steel is specified for sour service. However, since the ultrasonic ILI surveys reported several laminar features, due to the presence of H_2S in the fluid, preliminary studies recommended replacing the lines at a suitable time; in the meantime, a short to medium term integrity management strategy was designed, comprising repair of the priority features, and testing to investigate the possible evolution of the damage.

The Fitness for Service approach is schematically shown in Figure 1.

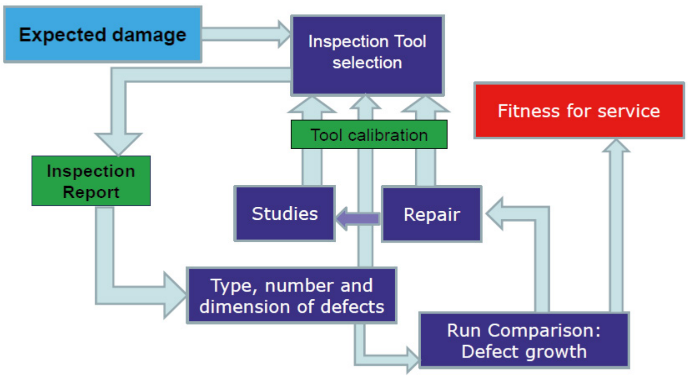

Fig.1: Schematics of the Fitness for service study approach

Milling defects in pipeline steel mid-thickness (lamination-like defects) usually do not propagate under working conditions in pipeline transporting hydrocarbons. In presence of wet H_2S in the fluid, however, it is possible to observe blisters. From blisters, cracks may propagate in the steel. An estimate of crack growth rate for these defects can be useful to assess the integrity of pipelines and to establish appropriate ILI intervals. However, only a few papers in literature deal specifically with this aspect of the problem. A model, based on laboratory tests, to calculate Crack Growth Rate in sour environment in pipeline steel was proposed more than 20 years ago, J.L. Gonzalez et al. (1997).

The model is based on diffusion reactions compared with measures on carbon steel plate specimens. Tests were performed in Nace Solution. The so-called "NACE solutions (A and B)" are water-based solutions simulating production fluids (with low pH and presence of Chlorides) in equilibrium with one bar H2S gas. Obtained crack growth rates are comparable with Stress Corrosion Crack Growth literature data, but tests do not reproduce the service situation of a pipeline, were moreover laminations are not in contact with aqueous environment.

H_2S is a weak acid. It causes a small decrease in the pH of a water solution and may corrode steels and alloys in neutral solutions, with a generally low uniform corrosion rate. It may play an important role in the stability of corrosion products film, increasing or decreasing their strength as a function of the interaction with other components such as CO_2. Iron Sulphide (FeS) based films can form if H_2S is prevalent, and iron carbonate ($FeCO_3$) will form if CO_2 is predominant. For hydrocarbon systems where methane and water are present, the stability of Sulphide scales is very difficult to predict, due to the complexity of Sulphides that can form depending on pH and temperature. Film stability is also a function of flow regime and fluid velocity. Iron Sulphide scales stability appears to be strongly dependent on the presence of chlorides, elemental Sulphur and/or dissolved Oxygen. Sulphides are more sensitive than iron carbonate to breakdown under turbulent conditions.

What discussed above refers to internal corrosion in the pipeline. The presence of H_2S in the conveyed fluid could have an influence on blister formation, due to enhanced hydrogen diffusion in the steel, since H_2S is a chemical poison for cathodic hydrogen recombination. Cathodic Hydrogen, however, is expected to be present only if corrosion (due to water hold up) is active.

To obtain more information toward assessing pipeline integrity, taking into account that more than 10 years elapsed without problems, and that a couple of years are necessary to design and build the new pipeline, a comprehensive activity started on a spool cut from the pipeline after more than 10 years of service. Preliminary examination of the ILI results allowed to establish a plan for the laboratory tests.

2.1 Flow Dynamics

A flow-dynamics simulation of the geometric shape of a 14" pipeline was made. The examined pipeline is supposed to carry a fluid with water cut equal to 1.4%. In this situation, the flux is dispersed and no water hold up is evidenced. To obtain a sensitivity analysis, the run was repeated with the following values for Water Cut (WC): 5%, 10%, 15%, 20%, 50%. Results show that water hold-up can be expected - only for WC larger than =15% - in the pipeline sections evidenced in red in Figure 2.

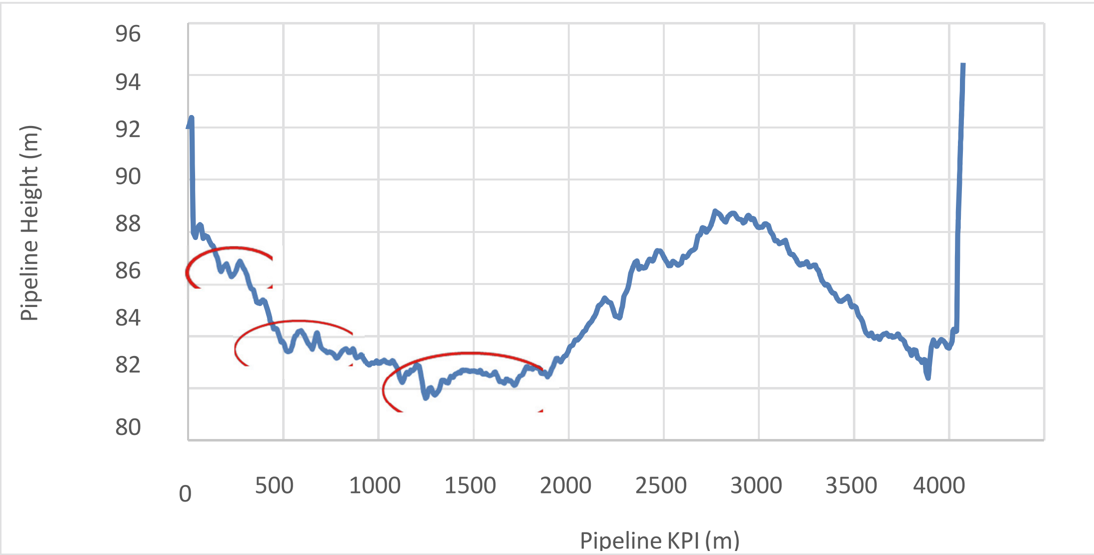

Fig. 2: Water Hold-up location estimate in a pipeline

The position of corroded areas observed by the MFL pig run in 2013 (see the pink marks in Figure 3 below) is roughly corresponding to the hold up positions predicted by the flow assurance study. The information about internal corrosion is missing in the second ILI report, obtained by UT tool. This tool is not effective in detecting internal loss of thickness due to corrosion; it is much more effective in evidencing milling defects such as lamination.

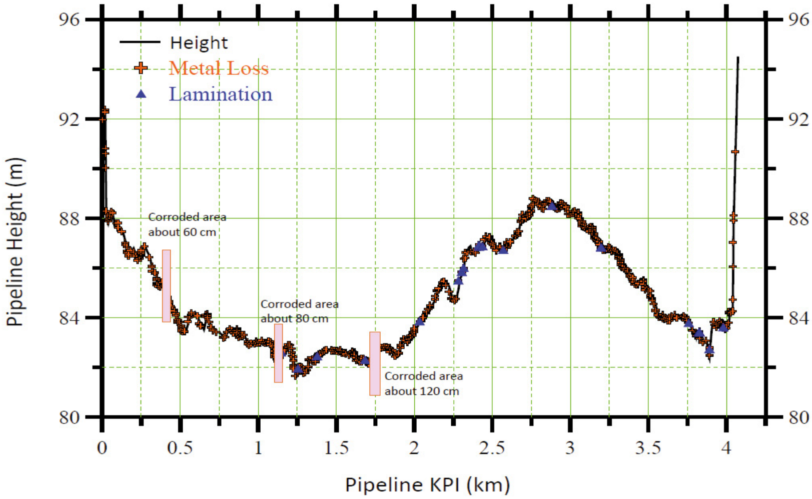

Figure 3: Position of corroded areas and defects inside a pipeline (MFL and UT pig).

After removing a section of a pipe where a large lamination was detected, manual UT does confirm the presence of a large defect of triangular shape, as shown in the picture in Figure 4. Dimensions of the defects measured by the ILI tool are compared with manual UT, performed in field and at the testing laboratory. The length of the defects, compared using different methods and tools, is in good agreement; differences are larger for width, as shown in Table 1. For comparison, dimension of the lamination detected with the MFL tool at a close KPI are shown in the same Table.

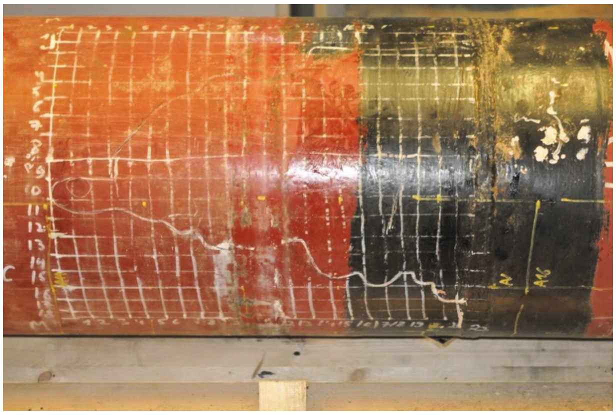

Fig. 4: Examined spool with indication of UT results (courtesy of EniProgetti).

At a closer examination of the removed spool, the detected feature appears as a cluster of small inclusions, evident in section already at the naked eye. See an example in Fig.5. No blisters were found during the preliminary characterization activity (still underway). At a first glance, it seems that MFL tool can reveal laminations only in a few cases; however, UT tool, much more sensitive towards laminations, does not seem to discriminate between lamination and blisters. Differences in sizing do confirm that defect growth is not easy to detect and to quantify.

Table 1. Lamination dimension

Measure and year	Location (KPI, m)	Location Joint	Length (mm)	Width (mm)
ILI tool MFL - 2013	8507	7920	445	64
ILI HiRes UT - 2017	8406	7900	427	240
Manual UT in Field	Removed spool		430	310
Manual UT at Testing lab	Removed spool		420	320

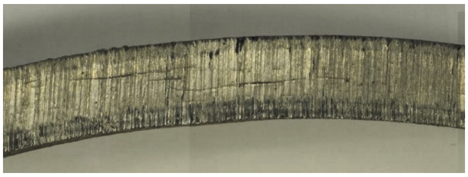

Fig. 5: Section of the spool in a zone where defects are evident at the naked eye (courtesy of EniProgetti).

In the removed spool, defects are mainly string of inclusions. The distribution in volume of the inclusions can be mapped with X-ray tomography (Figure 6), which can help to select specimens position. Closer examination with Scanning Electron Microscope equipped with X-Ray diffraction tool, allows a better understanding of inclusion composition. As shown in fig. 7, inclusions are mainly Aluminum oxide (blu particles) or Spinel (double oxide, green particles) in the ferritic-pearlitic strutture of the steel (red). The presence of such compounds in a killed steel is not surprising; however, further study is necessary to understand the effect of these inclusions on HE susceptibility, Elboujdaini and Revie (2000) and the threshold conditions for blisters formation. The activity is underway and will be completed with laboratory tests in environment simulating service conditions.

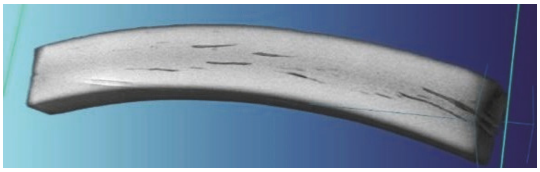

Fig. 6: Example of X-ray mapping (courtesy of Eni LAIP).

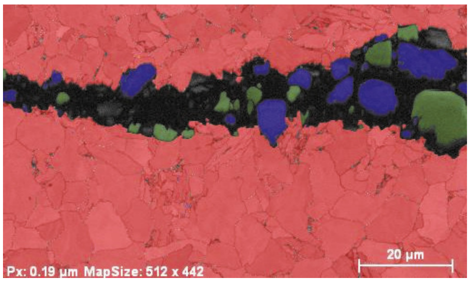

Fig. 7: Example of inclusion shape and composition courtesy of EniProgetti Venezia).

3. TEST PLAN

Tests are underway on a spool cut from the pipeline after more than 10 years of service. Planned activities are:

1. UT measurement in the full spool to select the defective zone and compare with ILI results (completed).
2. Through defects examination with metallographic and microscopy techniques (underway)
3. Mapping of defect distribution in specimens with X-ray tomography (completed)
4. Material properties assessment in the defective part and comparison with the section without defects
5. Defect propagation tests (HIC/SCC) performed in environment simulating the actual transported fluid (with

different contents of water to understand threshold values for the onset of HE)

Objective of the activity is to assess the fitness for service of sour service pipelines, and to suggest appropriate nondestructive control /inspection plan.

4. CONCLUSIONS

The presence of lamination as milling defects in the pipelines is confirmed by ILI; however, after more than 13 years of service, no evidence of blisters has been confirmed to date in the removed spool. Lamination-like defects are shown by UT pig, but the capability of this tool to size defects and to discriminate between laminations and blisters needs to be confirmed; information about corrosion, better evidenced by MFL pig, are also important. The knowledge of pipe sections potentially prone to corrosion could be useful for instance to select locations for Hydrogen monitoring. Problems can be foreseen when a water hold up zone is located near a defective zone in the pipeline. As a consequence, fluid dynamics studies are also suggested.

Towards a safe management of HE in field components, a better understanding and a quantitative approach to different aspects of Hydrogen Embrittlement are required. To implement knowledge in this field the following approach can be useful:

- To test candidate materials in environments simulating as close as possible the real field conditions, taking into account pipeline process parameters
- To explore different forms of Hydrogen Embrittlement with the aim at obtaining quantitative estimates of Crack Growth rate, Corrosion rate and other parameters useful for damage evolution prediction
- To check "susceptibility" concept for pipeline materials of different grades/microstructure

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