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Engineering thoughts on Hydrogen Embrittlement

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Abstract

Hydrogen Embrittlement (HE) is a topical issue for pipelines transporting sour products. Engineers need a simple and effective approach in materials selection at design stage. In other words, they must know if a material is susceptible to cracking, to be able of:

- selecting the right material
- and apply correct operational measures during the service life.

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”. In many cases, hydrogen can play a role in crack propagation, as for instance in Stress Corrosion Cracking (SCC) and Corrosion Fatigue (CF). Three parameters are required to cause failure: presence of hydrogen, tensile stress, and material susceptibility. The two previous ones are triggering the failure, while the root cause is usually material susceptibility. This is why material selection is the important step to safely manage engineering structural materials.

As an example, material selection for sour service pipeline is the object of well-known standards, e.g. by Nace International and EFC: they pose some limits in the sour service of steels, with reference to surface hardness. These standards have shown some weak points, namely:

- In the definition of sour service;
- In defining the role of crack initiation and propagation, considering that in Hydrogen embrittlement, stress state and stress variations are very important.

As for the second point, in hydrogen generation anodic processes shall be taken into account too. For instance, there is a relationship between corrosion resistance and crack susceptibility. In carbon and low alloy steels, cracking will not normally occur when there is a significant corrosion rate. If a brittle layer (or a brittle spot) is present on the metal surface, this one can initiate a crack.

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Keywords: Hydrogen Embrittlement; Environmentally Assisted Cracking; Stress Corrosion Cracking; Sour Service; Pipeline Steel

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Nomenclature

CF	Corrosion Fatigue
CR	Corrosion Rate
EAC	Environmentally Assisted Cracking
HE	Hydrogen Embrittlement
MIC	Microbiologically Induced Corrosion
SCC	Stress Corrosion Cracking
SSC	Sulphide Stress Cracking
SOHIC	Stress Oriented Hydrogen Induced Cracking

1. Introduction

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. In Oil&Gas Industry, however, this is a topical issue for components working in burdensome environments, such as for instance pipelines transporting sour products, Bruschi et al. (2017). 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. 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.

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 by different authors, as summarized for instance by Lynch (2012). Diffused Hydrogen 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 hydrogen, tensile stresses and material susceptibility, 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.

Material selection for sour service pipeline is the subject of international guidelines, e.g. the standards issued by Nace International and EFC. Commonly, standards pose limitations to carbon steel line pipe for sour service, which regard lower bound for 'cleanness' and surface hardness as well, further a satisfactory performance in specific test conditions. Unfortunately, these standards 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, 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.

Damage mechanisms due to Hydrogen and their effects on different class of materials are nowadays of increasing importance for Oil companies, since the exploitation of fields with high H_2S and/or CO_2 content became more diffused worldwide. In pipelines, Hydrogen is generated by corrosion of the internal surface, where electrochemical reactions (anodic and cathodic processes) take place. There is a relationship between corrosion resistance and crack susceptibility. In carbon and low alloy steels for instance, cracking will not normally occur when there is a significant general corrosion rate, but hydrogen generated by corrosion can cause embrittlement of the material. If a brittle layer (or a brittle spot), due to fabrication processes, is present on the metal surface, a crack can initiate at the brittle zone

interface. The transition between crack nucleation and crack propagation and the influence of surface hardness in components cracking can be modeled using fracture mechanics, Gabetta and Torri (1992).
The presence of H_2S and/or Sulphur in crude oil can be responsible for both general and localized corrosion. While a small amount of H_2S is believed to cause a decrease of the general Corrosion Rate (CR) of carbon steel, Skar, J.I., (2012), little information is available on the effect of high H_2S 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, Bonis, M. and MacDonald, R. (2015).

2. EAC in buried pipelines

Environmentally Assisted Cracking (EAC) is defined as a damage form where acute defects (cracks) nucleate and grow due to the combined action of aggressive environment, applied load and metallurgy of the material. EAC can be the result of different damage mechanisms, as for instance hydrogen diffusion in the metal and/or anodic dissolution coupled with stress at the crack tip. However, when corrosion occurs, anodic and cathodic processes are present at the same time and it is often difficult to distinguish between different damage mechanisms.

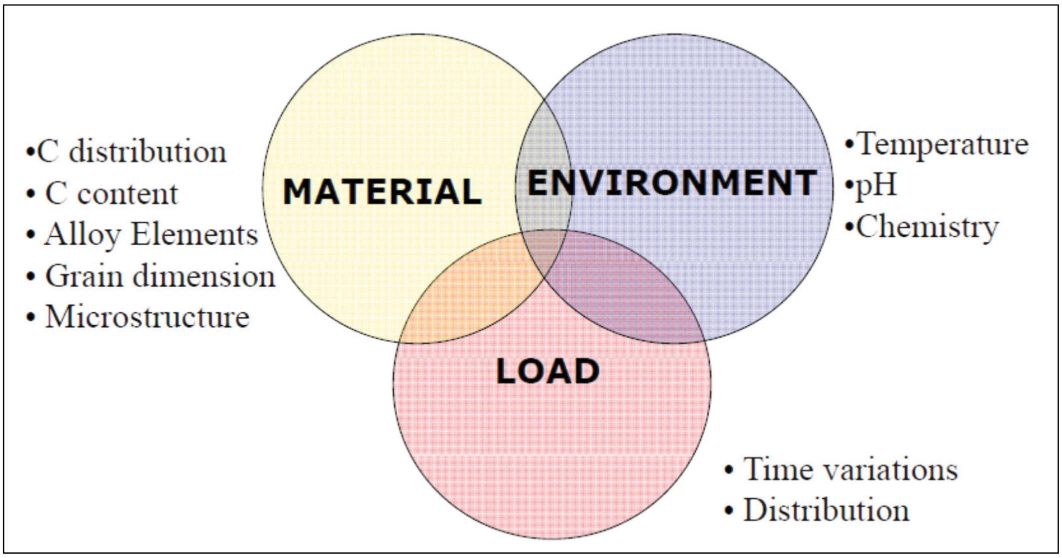

Fig. 1. Main parameters involved in EAC.

In Figure1, main parameters involved in EAC are graphically represented. To observe EAC, the applied load can be both static or dynamic, so that the damage form can be called either Corrosion Fatigue, Stress Corrosion Cracking, Sulfide Stress Cracking, and so on. Each one of the damage forms listed above can be triggered and/or supported by one or more damage mechanisms (which can act simultaneously).
Mechanisms of SCC were schematically described in the early sixties by prof. Parkins at Newcastle University as shown in Fig. 2, Parkins, R. (1963). Parkins summarized a few well known (at the time) forms of SCC damage as a continuum spectrum, evidencing the predominant cracking mechanism. This approach suggested that in metal and environment systems where the conditions are between those for general dissolution and complete inactivity, localized corrosion and stress might act conjointly to promote crack extension. Cracking is triggered by either:

- selective attack upon compositional or structural features pre-existing in the metal
- stress, exposing relatively small areas of bare, reactive metal
- adsorption of appropriate species at sites where the energy for fracture is thereby lowered.

Corrosion Dominant			→				**Load situation dominant**
Intergranular Fracture	C Steel in NO$_3$	Al-Zn-Mg Alloy in Cl$^-$	Mg-Al Alloy in CrO$_4$-Cl$^-$	Cu-Zn Alloy in NH$_4$	Ti Alloy in metanol	HR Steel in Cl$^-$	BRITTLE FRACTURE
Intergranular fracture following active paths			Transgranular fracture following stress generated path			Fracture due to absorption, decohesion, rupture of brittle phases	
Buried pipeline (external Corrosion)							
Carbonate-Bicarbonate SCC (high pH)							Transgranular SCC

Fig.2. Stress Corrosion Spectrum (Parkins, ’63).

A change in composition or structure of the alloy, or in the characteristics of the environment, may result in a change in the mechanism of cracking and indeed, in some cases, that crack extension may be the result of more than one mechanism operating, Parkins, R. (1972). A case well described by Parkins approach, summarized in Figure 2, was confirmed by observations of external cracking in buried pipelines, Sutcliffe, J.M. et al. (1972). Intergranular cracks initiate and propagate at grain boundaries and usually form at high pH (8.5-10.5). Such cracking initiates at the outer surface of pipe and results from the generation of a carbonate-bicarbonate solution. Corrosion along active anodic paths is dominant. On the other hand, Transgranular cracking has been found associated with dilute solutions of lower pH in regions where coatings are disbonded, in presence of slowly changing load, with the predominant action (dominated by stress variation) of HE mechanisms, Gabetta, G. (1997). Landslide are often triggering external SCC, Gabetta, G., et al. (2000). Based on Parkins observations, the management of external SCC of pipelines became a well-known recommended practice. The same simple approach, however, seems to be not fit to model other forms of hydrogen damage. Depending mainly on steel metallurgy, in literature different fracture surfaces are associated with HE.

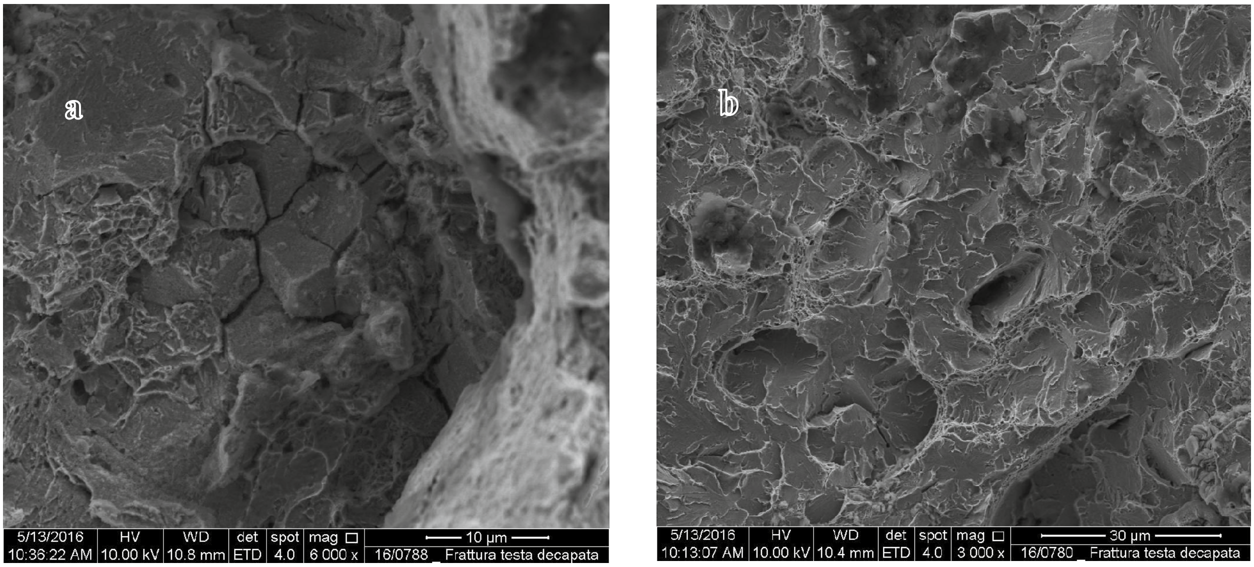

Fig.3. Examples of fracture surface in high strength steel (a) Intergranular, (b) Cleavage.

In Figure 3 aspects of fracture surface in a high resistance bolt, Gabetta, G. et al., (2016) show Interganular zones closed to regions ductile deformed, Fig.3a. In different zones of the same fracture, cleavage is also observed (Fig.3b). Fracture surface features could be important to better understand HE in metals. With reference to the superposition model, Cullen, W.H. et al., (1988), it is possible to assume that corrosion is superimposed to a growing crack, as observed for both SCC and CF, Gabetta, G. (1987). In the case of a corrosion fatigue crack in a RPV steel (a ferritic-pearlitic quite similar to pipeline steel), an accurate examination of fracture surface features allowed to compare fatigue striation spacing with local crack propagation rates, as shown in Fig.4, Rinaldi, C. (1988).

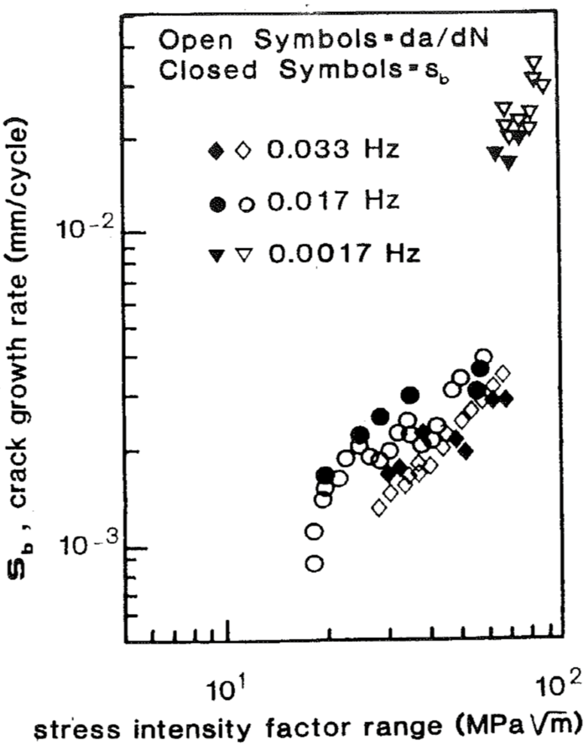

Fig. 4. Comparison of crack growth rate and striation spacing.

HE is a complex phenomenon, comprehensive of interaction with defects, increased pressure in cavities, and influence on metal properties. In literature, blisters and cracks are recognized as due to Hydrogen present in the metal, but data reporting detailed observations of crack morphology are often missing.

3. Internal EAC in pipelines transporting sour fluids

With reference to pipelines transporting sour fluids, different types of localized damage and/or cracking can be observed (Sulphide Stress Cracking-SSC, Stress Oriented Hydrogen Induced Cracking-SOHIC…), often associated to different mechanisms of damage, due to the high number of involved variables:

- Fluid variables: flow dynamics, fluid composition, scale formation, pressure and temperature…
- Metallurgy of the steel
- Different possible corrosion forms: general corrosion, localized corrosion (pitting, mesa, flow assisted corrosion…)
- Different possible corrosion mechanisms: CO_2 corrosion, H_2S corrosion, Microbiologically Induced Corrosion (MIC), corrosion-erosion…

- Formation and/or damage of different types of scales
- Load variations due to operational changes

For hydrocarbon systems characterized by xCO_2/xH_2S ratio lower than 20-50 (H_2S dominated systems) formation of a metastable sulfide scale prevails on iron carbonate scale. Corrosion rates are usually lower than in sweet systems, were CO_2 and its corrosion products control corrosion rate. Cracking can be observed when nucleation due to the breakdown of iron sulfide protective layer takes place.

Engineering approach for material selection in sour service requires that the selected pipeline steel is not susceptible to stress corrosion cracking. Internationally recognized guidelines are available for the Oil and Gas Industry, namely:

- International Standard Nace MR0175/ISO15156: based on pH and H_2S partial pressure, classifies the susceptibility to SCC in four regions. Region 0 is where no precautions are required; in region 1,2,and 3 metallurgical requirements and tests are specified
- EFC 16 Guideline: with reference to the same four regions for sourness of the environment, this guideline requires maximum hardness value. The lower the sourness, the higher the allowed hardness values.

Hardness and metallurgical conditions are in summary the material characteristics determining susceptibility to stress corrosion cracking in sour environment. The concept itself of “susceptible” or “not susceptible” material seems under certain respects a too simple approach. While damage can be described by many different mechanisms and forms, susceptibility is based on hardness alone. The so-called susceptibility is measured in test solutions having a standard composition, which is far from field situation. Engineers are aware that cracking is often observed in the so-defined “non susceptible materials”, Azevedo, C. (2007).

As suggested above, one shall consider separately crack nucleation and propagation. Material susceptibility may be different in the two phases and a fracture mechanics approach can be of help. Corrosion in the steel surface, for instance, will decrease the fatigue life of specimens and components, since corrosion features act as small cracks on the surface. This behavior was observed on specimens tested in laboratory, i.e. at the external surface of cylinders in rotating bending, Gabetta, G. et al.(1990). Not only corrosion features may act as crack initiation sites; if a brittle layer or a brittle spot is present on a ductile metal surface, a crack can nucleate. Further studies are required to better quantify responsible parameters of different cracking aspects and mechanisms.

The influence of thin hard coatings on fatigue properties was studied for instance in turbine shafts, Baragetti, S. (2007). Results show that the presence of a thin hard coating creates residual stresses on the surface, and the presence of these stresses can increase the fatigue resistance of the component. Cracks in this case do nucleate at the interface between coating and bulk material, where nucleation sites correspond to inclusions or defects present in the substrate materials. In the quoted work, purely mechanical resistance is considered. In presence of an aggressive environment, corrosion shall be taken into account to understand if under the effect of environment, hard spots can be considered as nucleation sites for stress corrosion and/or corrosion fatigue. Nucleation sites and mechanisms shall be studied in field failures.

A further aspect is crack dimension, Turnbull et al., (2013). Drawing a distinction between small and short cracks is important. A short crack propagating in a fracture mechanics specimen “samples” hundreds of grains along the crack front and the crack growth rate then represents an average over a large number of grains. In contrast, a small crack samples only a small number of grains in the early stage of development and will be affected also by near-surface gradients in microstructure, hardness and residual stress.

4. Conclusions

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.

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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