Environment-Assisted Cracking of Pipeline Steel in Hydrogen-Prone Environment

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Abstract. Industries and researchers have identified Environment-assisted cracking (EAC) as one of the main causes of structural degradation and failure in hydrogen transport pipelines. With dwindling oil and gas reserves, interest in hydrogen as a green energy source has surged among industry, government, and stakeholders. Although repurposing existing natural gas (NG) pipeline systems for hydrogen transportation is viewed as the most economical solution, a lack of research findings and assessment criteria hinders its development and implementation. Therefore, this paper primarily presents recent research outcomes related to the effect of EAC on the structural integrity of pipeline steel in hydrogen-rich environments. This paper also proposes a conceptual framework to assess the structural integrity of NG pipelines for hydrogen transportation in the context of EAC. Additionally, an integrated experimental test procedure is proposed to evaluate the effect of EAC.

Keywords: Pipeline steel, Environment-assisted cracking, Hydrogen embrittlement, Structural integrity

1 Introduction

Corrosion is an irreversible and prominent damage phenomenon of metals due to a chemical or electrochemical reaction that converts a metal to its more thermodynamically stable compounds, such as oxides, hydroxides, sulfides, etc., in a corrosive environment[1-3]. The outcomes of corrosion damage can be much more exaggerated due to catastrophic accidents that have claimed lives and substantial economic losses[2, 4-7]. Previous studies show that the estimated global cost of corrosion was approximately 3.4% of the GDP in 2013[7-9]. There has been an increase in corrosion-related incidents reported in industries such as steel bridges, long-span suspension bridges, the oil and gas sector, offshore wind turbines, and others. Most current oil and gas fields being developed worldwide are highly corrosive. As a result, the associated costs are expected to rise due to the increased investment required to manage facilities in such environments [10]. The severity of corrosion and its far-reaching effects on the global socio-economic environment are evident through the statistics.

There are mainly two factors affecting the corrosion process. One is the nature of the metal, and the other is the nature of the environment. When considering the first factor, which is the nature of the metal, its position in the galvanic series, purity or the

composition of the metal, the nature of the surface film, and the nature of the corrosive product are critical. For the nature of the environment, factors such as temperature, Humidity of air, the composition of the environment(Air composition, sea water, etc), and the Effect of p^H play vital roles[1, 3]. Corrosion directly affects the integrity of structures. It reduces the stiffness of the structures due to the thickness reduction and pitting of the structural members. Also reduces the tensile strength, ductility, fracture toughness, fatigue strength, and the hardness of the structures[1, 3, 11]. There are various types of corrosion, such as uniform corrosion, galvanic corrosion, pitting corrosion, crevice corrosion, intergranular corrosion, erosion-corrosion, and EAC [1, 3, 12].

The EAC plays a crucial role in ensuring the safety and reliability of high-risk engineering systems, including nuclear power plants, fossil fuel power plants, oil and gas pipelines, offshore oil production platforms, aircraft, aerospace technologies, chemical plants, and similar facilities[2, 5, 6, 13-15]. When compared to the other corrosion types, there is another factor affecting the EAC other than the nature of the metal and the nature of the environment, which is the stress level of the material. This can be either externally applied stress, residual, or the stress due to temperature changes[5, 15]. Moreover, changes in the material due to EAC are mainly microstructural and sometimes not visible to the naked eye [5]. Therefore, the complexity of crack initiation and propagation has resulted in fewer studies on EAC. Consequently, many researchers have suggested that further investigation in this area is necessary [13]. Hence, this study mainly focuses on EAC. There are three major types of EAC: stress corrosion cracking (SCC), corrosion fatigue (CF), and hydrogen embrittlement (HE) [15, 16]. SCC occurs due to the continuously applied stress in a corrosive environment [17, 18]. CF is the failure of the elements due to applied cyclic stress in corrosive media. HE can be defined as the reduction of ductility and toughness of metals due to hydrogen infiltration in hydrogen-prone environments[1-3].

Considering the number of suspension bridges, plenty of offshore wind turbine projects, and structures of the oil and gas industry in Europe, there is a higher risk of deterioration and degradation by EAC. Further, with the rapid growth of the renewable energy sector, projects like offshore wind turbines and hydrogen-based infrastructure have become more prominent in the region, where EAC poses a significant safety concern [19, 20]. Most of the countries are now turning their economies to renewable energy production, specifically the hydrogen-based economy (see Figure 1). There are three main key stages in the clean hydrogen value chain, which are production, distribution (including storage), and end-use applications. Different production methods have been utilized for each type of hydrogen production, such as fossil-based hydrogen, renewable hydrogen, and fossil-based hydrogen with carbon capture. When developing a hydrogen economy, transport and storage infrastructures will play a vital role. Hydrogen can be transported and stored by three methods: as liquid (liquid hydrogen, ammonia, methanol & LOHCs), as solid (solid inorganic hydrogen carriers), or as a gaseous form (pure hydrogen gas) [14, 21, 22].



Fig 1. Average hydrogen demand projections in Europe [22]

The most cost-effective method to transport hydrogen is through pipelines up to a certain distance. Distribution by ship would be the optimum solution for the long-distance transportation of hydrogen. There are two main options for hydrogen transportation in the gaseous state via pipelines: (i) building new hydrogen-carrying pipelines (ii) repurposing existing natural gas pipelines for the transportation of pure hydrogen. Most of the current research focuses on improving pipeline safety and sustainability while preventing risks of leaks and addressing industrial problems of repurposing existing natural gas pipelines for transporting pure hydrogen[23]. The EU is aiming at enhancing the hydrogen economy through infrastructure development, such as the European Hydrogen Backbone project, aiming to facilitate hydrogen transport [20, 21, 24]. The hydrogen pipeline network in Europe in 2023 consisted of 17 pipelines with a total length of more than 1,500 kilometres. These pipelines are integral to transporting hydrogen between production sites, storage facilities, and industrial consumers, supporting Europe's shift toward a hydrogen-based energy system. The emerging context of the hydrogen infrastructure can be identified in Figure 2 [22].

However, the deterioration of steel pipelines and storage due to the effect of EAC has become a prominent problem within this industry. In particular, HE and other hydrogen-associated degradation processes have become leading degradation phenomena, as per most research findings. Significant degradation of the structural integrity of pipelines is observed due to the EAC, which further causes the failure of the pipeline systems. The mechanical properties, such as yield strength, tensile strength, ductility, fracture toughness, fatigue strength, and hardness, are affected by this phenomenon[25-27]. As a result, the capacity of the system is reduced, and performance is reduced. Hence, the risk of failure increases[28].



Fig. 2. Europe's hydrogen infrastructure projects interactive map (a) existing, (b) proposed plan[22].

However, aside from the published guidelines by ASME, EIGA/CGA, and IGEM, there is no comprehensive guideline specifically dedicated to pipeline design for hydrogen transportation. Therefore, further investigation into the behavior of steel in hydrogen transport pipelines and storage has become increasingly important for both academia and industry [29-31]. There are various experimental procedures have been developed to evaluate the effects of SCC, HE, and CF under different environmental and loading conditions. However, there is a lack of a comprehensive testing procedure specifically designed to assess EAC in hydrogen-rich environments. One significant reason for the scarcity of hydrogen-charged experiments is the limited availability of specialized testing machines equipped with gas chambers, coupled with the inherent risks associated with hydrogen's high flammability. Consequently, there is a pressing need for comprehensive investigations into electrochemical hydrogen charging methods. Such methods could serve as accurate alternatives to direct hydrogen gas charging, thereby facilitating a safer and more accessible approach for researchers. This shift would likely lead to an increase in experimental studies within this field.

Hence, this study will focus on addressing the effect of EAC in hydrogen environments, specifically in the context of repurposing existing oil and gas pipelines for hydrogen transportation. During this study, a comprehensive review was conducted covering the materials used, factors influencing structural integrity, types of EAC, and their respective effects on mechanical performance, as well as the experimental methods available to quantify the severity of these effects. Further, a conceptual framework has been developed to assess the susceptibility of pipeline steel to EAC in hydrogen environments.

2 Pipeline material

2.1 Material for oil and gas transmission pipelines

Steel has been widely utilized as the primary material for pipelines in the oil and gas industry across the globe for several decades. Although steel is susceptible to various forms of degradation, its durability, high strength, and resistance to extreme pressures and temperatures make it the preferred choice for transporting crude oil, natural gas, and refined petroleum products over other materials [32, 33]. The American Petroleum Institute's (API) API 5L standard is widely adopted by steel manufacturers worldwide and serves as the primary specification for the majority of pipeline applications [34, 35]. Most of the pipeline steel grades used in the industries around the globe are API 5L X52 to X80[10, 26, 33-39]. API 5L specifies two Product Specification Levels (PSL): PSL1 and PSL2. PSL1 represents the standard quality level, while PSL2 includes more stringent requirements for chemical composition, mechanical properties, and testing protocols. In recent years, the use of X60 to X70 grades for offshore pipelines and X70/X80 grades for onshore pipelines has increased significantly. As shown in Figure 3, the use of high-strength low-alloy steels such as X60, X65, and X70 has increased in recent years for onshore pipelines. Grade X65 is one of the most established pipeline materials in sour fluid service. Also, the X70 pipeline has been installed and operated successfully around the world [33]. Years: 1970 - 2022



Fig. 3. Total length per grade of material [40].

This trend is driven by the need for higher-strength materials that enhance pipeline performance, improve cost efficiency, and withstand demanding environmental conditions[19, 35, 36, 41-43]. Moreover, pipeline steel has been evolved up to higher strengths steel such as X100/X120, Austenitic (300 series) stainless steels, and duplex stainless steel even though their adoption is not yet widespread mainly due to susceptibility to HE, complex welding requirements, availability, and high cost [33, 34, 44-46]. For normal environmental conditions, carbon steel, low-alloy martensitic, austenitic, line pipe, and duplex ss are being used, while Carbon, duplex stainless steel, lined pipe, and nickel alloy-clad pipe can be used for sour services. High strength grades of steel are more expensive. However, the increase in the grade may reduce the wall thickness and result in an overall cost reduction. However, lower-grade pipes are more cost-efficient [35].

2.2 Material for hydrogen transportation pipelines

Many metallic materials have been proposed for the hydrogen transmission, including carbon steels, low-alloy carbon steels, stainless steels, and nickel alloys. Still, they are susceptible to embrittlement in hydrogen gas environments. When selecting a material grade, it is essential to consider factors such as cost, mechanical properties, and corrosion resistance. Corrosion resistance is influenced by environmental conditions, including temperature, pressure, water quality, and the presence of gases like CO₂, H₂, and H₂S[35]. Hence, carbon steel piping grades, such as API 5L X52 and ASTM A106 Grade B, have been extensively used in hydrogen gas service with minimal reported issues[28, 47]. This reliable performance is largely due to the relatively low strength of these alloys, which enhances their resistance to HE and other brittle fracture mechanisms[47, 48]. While the effects of chemical composition, microstructure, and environmental factors on HE are not well-documented, few engineering organizations have provided guidelines to assist in material selection for hydrogen transportation. Notable among these are the American Society of Mechanical Engineers (ASME), the European Industrial Gases Association (EIGA), and the Institution of Gas Engineers and Managers (IGEM). Susceptibility to HE increases with material strength. Specifically, the threshold stress intensity factor (Kth) for hydrogen-assisted fracture decreases as yield strength rises. Therefore, to manage HE effectively, specifications for hydrogen gas service should define not only minimum yield strength but also maximum yield strength limits[48]. The maximum hardness and carbon equivalent specified for hydrogen transport is 250 (Hardness Brinell) and 0.43[47, 49]. However, the maximum tensile strength (690 MPa by IGEM and 800 MPa by EIGA) and maximum steel grade (X52 by ASME, EIGA, and X70 by IGEM) are specified differently across various guidelines. The legal and regulatory framework for the transportation of hydrogen is not yet fully established, and the framework for re-qualifying existing natural gas pipelines is still under development. Therefore, it is crucial to conduct thorough investigations to provide more accurate recommendations in this field.[50].

3 EAC of hydrogen transport pipelines

EAC occurs when three key factors coexist: tensile stress, a susceptible material, and an aggressive environment (see Figure 4). Tensile stress, whether residual from manufacturing or externally applied during service, and cyclic stresses can make materials more vulnerable to cracking. Certain metals, due to their inherent properties, are more prone to EAC. Additionally, exposure to specific corrosive environments can initiate and propagate cracking. The simultaneous presence of these factors can lead to the initiation and propagation of EAC in susceptible materials[16, 32, 38, 51]. EAC has been identified as one of the main degradation processes affecting hydrogen transport pipelines[32, 38]. EAC may cause the degradation of mechanical properties of the pipeline steel, such as tensile strength, ductility, hardness, fracture toughness, and fatigue strength, which will affect the structural integrity of the pipeline system and may lead to pipeline failure[15, 33]. Consequently, EAC has emerged as a crucial safety and economic factor in the repurposing of existing oil and gas pipelines for hydrogen transportation.

3.1 Factors affecting EAC and prevention

Three different factors affect EAC in pipeline steels. (i) Environmental factors, (ii) Structural factors, (iii) Metallurgical factors [15, 38]. All these factors affect the EAC in different ways. The effect of each factor on the EAC across different applications is discussed below, focusing on pipeline material.



Fig. 4. Necessary Factors for EAC initiation.

Metallurgical factors: EAC of steel is influenced by several metallurgical factors, including material composition, microstructure, steel grade, and can be influenced by the manufacturing processes such as forming, shaping, and heat treatment. The presence of alloying elements can enhance susceptibility by weakening grain boundaries. As an example, Hydrogen-assisted crack propagation of alloy classes is higher with lower nickel content[52, 53]. High-strength steels are particularly vulnerable to EAC due to their increased hardness and tensile residual stresses, which facilitate crack initiation and propagation[54]. Also, higher yield strength reduces the fracture toughness at the onset of subcritical crack growth in H_2 environments[53]. Microstructural features like phases, inclusions, precipitates, and grain size also play a critical role; for example, coarse grains and brittle phases (e.g., H diffusion coefficient inside austenite is typically more than three orders of magnitude lower than that in ferrite at room temperature[53]) can accelerate crack growth[39]. Further, alloys with the presence of non-metallic inclusions absorb more hydrogen, which increases the HE degradation [23]. Proper material selection, heat treatment optimization, and surface treatments can help mitigate these effects and improve the resistance of steel to EAC. Using alloys with a homogeneous fine-grained microstructure enhances toughness and resistance to HE. Avoiding excessively hard or high-strength alloys is crucial, as they are more susceptible to cracking in hydrogen environments. Steels with enhanced cleanliness, minimizing non-metallic inclusions, improve toughness, and reduce vulnerability to HE. Additionally, ensuring components are free from significant surface and internal defects helps prevent crack initiation and propagation, thereby improving the pipeline's durability and safety in hydrogen service[47]. The material's resistance to crack formation can be improved by modifying its microstructure, including its grain size and phase distribution. Surface coating and heat treatment increase the material's resistance to corrosion and reduce the risk of HE [51].

Environmental Factors: Hydrogen-assisted degradation in hydrogen transport pipelines is influenced by several environmental factors: concentration and purity of hydrogen are important because impurities can speed up material degradation and embrittlement; temperature and pressure also affect hydrogen uptake and diffusion, with extreme temperatures and high pressures potentially exacerbating embrittlement[47, 51, 55, 56]. Tests on two pipeline steels (X42 and X70) reveal that fracture toughness is lower in the presence of H_2 and CH_4 mixed gas than it is in the presence of pure H_2 , but that the addition of certain gases, like CO or CO₂, to the testing environment appears to remove the H degradation effect and raise fracture toughness as shown in the Figure 5[53]. Further, an environment's p^H value affects the corrosion reactions of metals, where acidic conditions can speed up hydrogen generation and absorption[38]; and finally, the type of environment, like water chemistry in the field, including oxygen and ionic concentrations in the groundwater close to the pipeline steel surface, air quality, or hydrogen-containing aqueous solutions, affects the severity of degradation, requiring careful material selection and protective measures [33, 47]. The pipelines are usually protected with a corrosion coating and cathodic protection [38] as a remedial measure. Cathodic protection (CP) systems are provided for the subsea pipelines to provide adequate protection from any defects occurring during the coating application, installation, and operation. DNV-ST-F101 recommends an electrochemical potential range between -0.80 to -1.15 V relative to Ag/AgCl/ seawater for subsea or submerged pipeline systems. More negative potentials than -1.15 V relative to Ag/AgCl/ seawater can be detrimental due to hydrogen stress cracking and HE.

Structural Factors: Structural factors influencing the process of EAC in hydrogen pipeline steel are cathodic current, loss of coating, externally applied stresses and residual stresses on the pipelines, and other structural details such as joints and welds[39, 47]. Pipelines gain hydrogen mainly from two sources: internal pressurized hydrogen and hydrogen generated by cathodic current. According to the experiment performed

by Rong Wang in 2009, during continuous hydrogen charging of X70 pipeline at 1.67x10⁻⁶ s⁻¹ strain rate, the measurement of fracture toughness values reduced drastically, and when cathodic current density increases, the rate of reduction decreases [57]. Long-term stress fluctuations, such as internal gas pressure fluctuations, gas medium stratifications, and externally applied stresses outside of the pipe, can cause corrosion fatigue damage[26]. When the peak stress of the given stress range increases, the effect of corrosion fatigue decreases because under the high stresses, the effect of corrosive environment is reduced, while the impact of mechanical stress governs the fatigue damage[58]. Furthermore, heat treatment and welding processes can introduce residual stresses and microstructural inhomogeneities, further increasing the risk of EAC[38, 43]. Experimental results of X52 pipeline steel showed that the fusion zone (area of the welded joint) has absorbed the most hydrogen compared to the other locations of the pipeline[23]. The risk of EAC can be mitigated by lowering the stress levels. Therefore, material selection, fabrication processes, and material thicknesses should be selected to lower residual stresses. Typical methods of lowering stresses once the operating temperature and pressure have been decided are to reduce the spacing of pipe supports, increase the wall thicknesses, and use thermal relieving to reduce residual welding stresses[47, 55]. Further, controlling the grain boundary inside the material and designing and machining parts to avoid stress concentration are effective methods to reduce the EAC susceptibility of pipeline steel. [51]



Fig. 5. Effect of gas composition on fracture toughness of pipeline steel X42 and X70[53]

3.2 Types of EAC and their effects on pipeline steel

Hydrogen transport pipelines are primarily affected by two types of corrosion: internal corrosion, which happens inside the pipe, and external corrosion, which occurs outside the pipeline. Hydrogen gas is the primary cause of internal corrosion or degradation, while the many causes mentioned in the previous section can cause external corrosion [13, 47].

Internal Corrosion. The internal degradation of the pipeline material can be defined as Hydrogen-assisted cracking (HAC), which is the same phenomenon as environment-assisted cracking, but in hydrogen environments such as hydrogen gas exposure or electrochemical hydrogen exposure. HAC can be divided into three processes: Hydrogen stress cracking (HSC), Hydrogen environment embrittlement (HEE), and Hydrogen-assisted fatigue (HAF), which are discussed below[47].

Hydrogen stress cracking (HSC): HSC is the same phenomenon as SCC but occurs in hydrogen-prone environments. In the presence of hydrogen, material becomes brittle and, with the pertinent stress on the material, eventually tends to fail by cracking. In HSC, a decrease in fracture toughness and tensile characteristics is noted. The reduction of yield strength of X80 pipeline steel after electrochemical charging was observed by Zhang, T., et al., during their experiments. Further, increased reduction of yield strength is visible with increased cathodic current densities[59]. Pre-cracked fracture toughness testing can be used to determine the critical stress intensity factor K_H, below which hydrogen-induced crack propagation does not occur (i.e., threshold stress). The steel grade and the hydrogen environment conditions determine the threshold stress. Most often, a fracture occurs at sustained loads below the yield strength of the material. The cracking mechanism may be accelerated by local flaws, including joints, dents, and uneven surfaces, by increasing the local stress concentration [47, 51, 60].

Hydrogen environment embrittlement (HEE): HEE is the process that causes the reduction of the material's ductility and eventually leads to brittle fracture in hydrogen environments [25, 28, 61, 62]. HEE can be evaluated through slow-strain-rate tensile tests conducted in air and hydrogen environments[47]. The resultant stress-strain curve shown in Figure 6 for X65 pipeline material tested under nitrogen environment(N) and hydrogen environment(H) exhibits a significant reduction in elongation due to HE[63]. Hydrogen typically localizes the fracture process, causing especially vulnerable materials to crack at an apparent engineering stress lower than the material's tensile strength[52]. Steels with high hardness and high strength are more vulnerable to HE [35, 36]. However, the effect of HEE can be different with the specific environmental systems as described in section 3.1.

Hydrogen-assisted fatigue (HAF): When hydrogen interacts with pipeline steel, fatigue life is reduced, and stress concentration rises. Fatigue fracture is a key component of pipeline safety design and lifetime assessment since it is one of the primary failure modes of gas pipelines during operation[26]. The main degradation related to hydrogen-assisted fatigue is the acceleration of fatigue crack growth rate (FCGR) and degradation in fatigue endurance limits[47]. The effect can be evaluated by tests of susceptible materials via pre-cracked and smooth specimens in dry hydrogen gas environments or electrochemical charging environments[26, 33, 58, 64, 65]. Even at slightly lower pressures in hydrogen gas, carbon and low-alloy steels exhibit this kind of deterioration. At room temperature, the rapid fatigue crack propagation is more noticeable; at higher temperatures, it becomes less noticeable. Additionally, the threshold cyclic stress intensity factor (ΔK_{th}) is decreased when hydrogen is present. The decrease in crack tip

ductility in the presence of hydrogen has been identified as one of the causes responsible for the deterioration of fatigue characteristics[47]. Fatigue cracking is not an issue if the pipeline operates under nearly constant pressure. However, fatigue deterioration may occur due to variations in gas pressure, with the impact varying according to alloy strength, heat treatment, and temperature, as detailed in 3.1. For example, the low-cycle fatigue (LCF) lifetime of X80 pipeline steel decreases exponentially with the increase of hydrogen pressure[26]. Moreover, according to the experiment performed by P. Fassina et al., the FCGR of X65 pipeline steel has increased due to the effect of hydrogen and lower loading frequencies have shown increased FCGR values than higher loading frequencies[66].



Fig. 6. Behaviour of nominal stress-strain of X65 steel in nitrogen and hydrogen environments[63].

External Corrosion: External corrosion of pipelines is typically influenced by environmental factors and is generally not affected by the hydrogen gas being transported. Pipelines are always in contact with the environment externally, such as soil, seawater, or the atmosphere. Hence, the interplay between the metal surface and the environment causes corrosion as explained earlier. It is a time-dependent mechanism that depends on the age of the pipe, protective methods, and harsh environmental conditions. Generally, external corrosion initiates after damage to the protective coatings or the oxide layer of the pipeline. The exterior surface of the pipelines can undergo various types of corrosion such as uniform corrosion, crevice corrosion, pitting corrosion, and galvanic corrosion [13]. Due to the combined actions of applied hydrogen pressure from inside and the other externally applied stresses with metal and environment, EAC is also prominent on the external surface of pipelines. As the hydrogen concentration is lower compared to the internal levels SCC is prominent externally [47]. Considering the stress cracking of the low alloy steel pipes mechanisms such as anodic stress corrosion and hydrogen stress cracking have been reported. Further, hard-spots due to welding, phase defects due to various processes, coating defects, microbiological activities, and

improper cathodic protection can accelerate this process[47]. However, the severity of EAC due to SCC increases with hydrogen evolution. Stress-driven hydrogen diffusion leads to its accumulation at the fracture process zone, causing HE. Hence, externally absorbed hydrogen-assisted-cracking mechanisms such as hydrogen-induced cracking, hydrogen blistering, and sulfide stress cracking also can cause degradation as per the specific environmental conditions[47].

Mitigating external corrosion in oil and gas pipelines involves several key strategies. Applying protective coatings, such as galvanizing, powder coatings, epoxy, polyurethane, and polyethylene, creates a barrier that shields the metal from corrosive environments. Cathodic protection is also often used as another method to control corrosion. Regular maintenance and monitoring, including routine inspections and timely repairs, are crucial to addressing any corrosion-related issues promptly [13, 67].

Other types of corrosion in a hydrogen environment but not pertinent to H₂ transport pipelines: There are a few other hydrogen-associated degradation mechanisms that are not pertinent to hydrogen transport pipelines but can occur in other structures and operating conditions, such as elevated temperatures, contaminated environments, etc. Hydrogen attack (Decarburization) is one such mechanism where carbon reacts with hydrogen to form methane in carbon or low alloy steel types, which results in cracking[55]. Hydrogen attack typically becomes significant at temperatures above $200 \,^{\circ}$ C, where methane gas forms and becomes trapped at grain boundaries and around internal carbide precipitates. This leads to crack initiation and a reduction in the mechanical properties of the steel [60, 68]. Hydrogen blistering is another form of hydrogen-induced degradation that becomes prominent in the presence of significant amounts of acidic electrolytes. In this mechanism, steels exposed to acidic electrolytes absorb substantial amounts of hydrogen at localized cathodic sites, eventually forming fissures and blisters. A degrading process known as "sulfide stress cracking" takes place in situations with certain hydrogen sulfide concentrations, which are frequently present in oil and gas structures or sour service conditions. Atomic hydrogen created during corrosion can become trapped in microscopic spaces surrounding non-metallic inclusions, most frequently manganese sulfide, causing a type of hydrogen damage known as hydrogen-induced cracking (HIC). High internal gas pressures caused by the trapped hydrogen may cause localized stresses that facilitate crack initiation. Another mechanism related to hydrogen is degradation caused by the precipitation of metal hydrides, which is frequently seen in metals like vanadium, magnesium, and niobium alloys. In this process, the metal and hydrogen combine to produce brittle hydride phases, which can drastically lower the material's toughness and ductility and cause embrittlement or cracking under stress[47, 60].

4 Experimental methods

EAC degrades the structural integrity of metals, with its severity influenced by factors such as metal type, stress levels, and environmental conditions[27, 52, 69]. The impact is more pronounced with higher hydrogen concentrations in the environment, affecting

crack initiation and propagation mechanisms differently. Although various experimental test procedures exist to assess processes like SCC, HE, and CF, discrepancies remain among the proposed mechanisms due to conflicting interpretations. The primary reason for this is the lack of conclusive experimental evidence. As a result, comprehensive testing and material qualification are essential before repurposing existing pipeline infrastructure for hydrogen transport[25]. Both electrochemical hydrogen charging and high-pressure gaseous hydrogen charging have been explored in previous studies to evaluate the effects[53]. A review of previous electrochemical and gaseous hydrogen charging experimental studies is given in Tables 1 and 2. However, the limited availability of test facilities for gaseous hydrogen charging and mechanical testing, along with the risks associated with hydrogen gas, remain significant challenges in meeting the growing demand for research in this area[25, 27]. Therefore, this paper focuses on electrochemical hydrogen-charged experimental procedures to assess the structural integrity of metals.

SCC, HE, and CF often occur simultaneously in hydrogen environments, collectively contributing to EAC. Assessing the impact of EAC necessitates accountability for the effects of all three mechanisms. This task is particularly challenging due to the complex interactions among these processes and the practical difficulties associated with laboratory experiments. Pipelines' structural integrity may be impacted by the deterioration of steel's mechanical properties, which can be evaluated using a variety of test methods and standards. The following important mechanical properties are usually assessed: fatigue endurance limit, fatigue crack growth rate, ductility, hardness, fracture toughness, tensile strength, and yield strength. However, it is crucial to carefully select a suitable test method considering the specific type of EAC and the corresponding environmental and structural conditions, particularly in the presence of hydrogen charging.

4.1 Electrochemical hydrogen charging

An electrochemical hydrogen charging process was adopted to simulate the hydrogen exposure to the metals by researchers and recommended by relevant governing bodies[26, 51, 70-73]. Specifically, electrochemical hydrogen charging is proven to be used to simulate hydrogen gas exposure in hydrogen transport pipelines, and researchers have successfully used this method[25, 26, 74-76]. The electrochemical hydrogen charging of metals is accomplished by providing an external cathodic potential to the sample, which causes water molecules to dissociate. This potential must be sufficient to overcome the binding strength of water molecules and separate hydrogen ions, which are then adsorbed by the metal surface [25]. These electrochemical reactions are governed by the applied potential, charging time, metal surface, used electrolyte solution, p^{H} value of the solution, presence of oxygen, type of counter electrodes, etc [36, 73]. Adding chemicals such as sodium sulphate (Na₂S), sodium arsenite (NaAsO₂), or Thiourea (CH₄N₂S) to the electrolyte promotes hydrogen atom absorption into the metal by inhibiting the hydrogen recombination to its molecular form [25-27]. Hydrogen damage occurs both on the external surface and internally within the metal. Internal damage arises from infiltrated hydrogen atoms, whereas external hydrogen damage originates

from the metal surface [14]. Effective testing setups should include both internal and external hydrogen charging methods. Electrochemical charging includes immersing specimens in aqueous solutions (e.g., NaCl, Na₂SO₄, etc.) for a particular duration, enabling hydrogen to permeate into the material via electrochemical processes[73, 77]. The most commonly employed electrolyte solutions for previous experiments can be found in Tables 1 and 3. Most research findings and guidelines propose electrochemical pre-charging for internal hydrogen charging, which entails charging samples for the necessary period with operational cathodic current before testing in machines. This will guarantee that the amount of trapped hydrogen within the metal is sufficient to begin the HE under operating circumstances. For external hydrogen charging, the same approach will be employed during mechanical testing to ensure hydrogen saturation of the external metal surface[14]. Many investigations have utilized a three-electrode electrochemical cell with a steel specimen as the working electrode and a platinum electrode as the counter electrode, with a saturated calomel electrode or a silver/silver chloride electrode serving as the reference electrode[25, 26, 51, 58, 74, 78, 79].

Ref	Steel	Electrolyte	Current	Test details	Outcomes of the study
		solution	density		
			(mAcm ⁻²)		
[25]	X65	3.5 wt.%	Potential -	The test setup has been devel-	Obtained the equivalent hydrogen
		NaCl + 2	1050, -1125	oped to investigate the equiva-	gas charging conditions using the
		g/L CH4N2S	mV	lent electrochemical charging	stated solution, providing im-
			(Ag/AgCl)	conditions for hydrogen gas	portant information about hydro-
				pressure	gen uptake and diffusion
[74]	X65	3.5 wt.%	Potential -	An electrochemical charging test	Electrochemical charging condi-
		NaCl+ 2 g/L	10501275	was used to calculate the equiva-	tion successfully simulated equiv-
		CH_4N_2S	mV	lent hydrogen pressure by ana-	alent hydrogen pressure of 12.3
			(Ag/AgCl)	lytical method	bar at room temperature.
[77]	Armco	NaCl,	1,10	An electrochemical charging	Using acidic solutions and in-
	iron,	H_2SO_4 ,		with different solutions and ca-	creasing current density has more
	L80	CH ₄ N ₂ S,		thodic currents was tested to ob-	influence on the hydrogen uptake
		H_2S		serve the hydrogen uptake	in both metals
[27]	Pres-	0.5 M	2.5 - 50	Disk-shaped thin specimens	Information on the effect of elec-
	sure	$H_2SO_4 + 1 \\$		were tested in an electrochemical	trochemical charging on hydrogen
	vessel	g/l CH4N2S		charging setup to investigate hy-	cracking and flaking
	alloy			drogen flaking	
[54]	3.5NiC	0.1 M	Potential -	Hydrogen concentration inside	Hydrogen concentration increased
	rMoV	NaOH/ 0.1	1090	the steel was measured after	with potential and gas pressure
	steel	M Na ₂ SO ₄	2228mV	electrochemical and gaseous	due to increased fugacity
			(Hg/Hg ₂ SO ₄)	charging	
[80]	X70	0.5 M	50	Electrochemical charging was	Cracking was found to be highly
		H_2SO_4 /		used to investigate the formation	dependent on microstructure, and
		250mg/L		of hydrogen-induced cracks and	crack initiation sites were mostly
		NaAsO ₂		blisters	

Table 1. Previous experimental studies of electrochemical charging.

					terfaces
[76]	X70	5 wt.% NaCl	0.5 - 2	modified Devanathan-Stachur-	The hydrogen permeation rate
		/ 0.5wt.%		ski cell was used to perform hy-	was affected by both H2S partial
		CH ₃ COOH		drogen permeation test to inves-	pressure and pH of the test solu-
				tigate effect of H2S partial pres-	tion
				sure, pH and current density on	
				HIC	
[81]	X70,	0.5 M	0 - 70	Electrochemical oxidation	Observed that the hydrogen con-
	16Mn	H_2SO_4		method test was used to deter-	centration increased approxi-
	steel			mine the absorbed hydrogen un-	mately linearly with the logarithm
				der cathodic charging	of pre-charging time
[82]	Carbon	H_2SO_4+	100, 500	Electrochemical charging setup	Hydrogen concentration profile in
	steel	H_2SeO_3		was used to study the hydrogen	steel was established
				absorption and distribution in	
				steel	
[83]	Iron,	5 wt.%	50	Electrochemical hydrogen charg-	Apparatus developed to measure
	HT-80	$H_2SO_4 / 5$		ing was used to determine the	the diffusible hydrogen in steel
	steel	mgl-1 As2O3		diffusible hydrogen in iron and	
				steel	

Table 2. Previous experimental investigations of EAC with gaseous hydrogen charging

Ref	Steel	Type of test	Strain/disp. rate / Frequency	Gas pres- sure (MPa)	Outcomes of the study
[52]	Type 304, 316	Tensile	10 ⁻⁵ s ⁻¹	1, 40	Ductility reduction by hydrogen charg- ing is higher for the steels with lower nickel content and external hydrogen than internal hydrogen
[64]	X65	Fatigue crack growth	1 Hz	10	Test done as per ASTM E647. The fa- tigue crack growth rate was more than ten times higher after hydrogen charging than in uncharged samples.
[77]	Armco iron, L80	Charging only	-	20, 100	A significant hydrogen absorption has not been observed
[84]	Spring steels	Fatigue	20kHz	10	Information about the effect of hydrogen on granular-bright-facet (GBF) size has provided
[85]	Туре 304, 316	Fatigue	0.0015, 1.5 Hz	63	Basic mechanism for HE was identified as hydrogen-induced slip deformation due to hydrogen concentration near crack tips
[61]	X65, X70	Fracture toughness	0.14-0.57 MPa√m/h	130, 150	A master curve for fracture toughness design for pipelines has been proposed. ASTM E1820, E1681 was used for frac- ture toughness testing.
[61]	X65, X70	Fatigue	1 Hz	60, 100,200	Test done as per ISO 12108. Fatigue en- durance properties have reduced signifi- cantly by hydrogen gas.

inclusions and ferrite-pearlite in-

 [86] X70
 Fatigue
 0.1, 1 Hz
 34
 Test done as per ASTM E647. For values of ΔK between 7 and 15MPa√m, the FCGR has increased by two orders of magnitude in hydrogen exposure.

4.2 Slow strain rate testing (SSRT) with hydrogen charging

Loading rate is highly important to ensure sufficient time for the EAC mechanism to initiate and propagate during the test. Hence, slow strain rates are generally recommended by the guidelines and also by the researchers, as given in Tables 3 and 4. The test measurements of mechanical and material properties shall be taken in charged samples and uncharged samples to compare and evaluate the effect[70, 87]. The uncharged measurements shall be taken in neutral environments such as inert gas conditions, etc.[68, 88]. The gauge length and diameter are selected as per the steel element to be evaluated, and small dimensions are preferred as they take less time to saturate with hydrogen charging. From the measurement of applied force and strain, tensile mechanical properties such as yield strength, tensile strength, elongation, fracture strength, and reduction in area can be measured[70]. Further EAC resistance of the metal can be evaluated by measuring time to failure, plastic elongation ratio, and calculating the threshold stress intensity factor[87]. Equation (1) defines the susceptibility index (Embirtlement index), which is used in most studies to assess a metal's susceptibility to SCC and HE [16, 79, 89, 90].

$$T(\%) = \frac{x_n - x_H}{x_n} \ge 100$$
 (1)

 X_n is the measured parameters during the SSRT test, such as time to failure, yield strength, ultimate strength, elongation (total/plastic), or reduction of area in a neutral environment. X_H is the measured value of the same parameters in a hydrogen environment.

Ref	Steel	Type of test	Strain/dis p. rate / Frequency	Electrolyte so- lution	Current density (mA cm ⁻²)	Outcomes of the study
[51]	X80	Tensile	Constant load	3.5 wt% NaCl	Open cir- cuit	Crack initiation and growth details were obtained with changing loads
[88]	9Cr fer- ritic/mar tensitic steel	SSRT	10 ⁻⁵ s ⁻¹	0.2 N NaOH + 0.3g/L NH ₄ SCN	10	Resistance to HE increased initially and decreased with the increased Si content, reaching its highest at 0.7% Si content.
[91]	13Cr stainless steel	Tensile	Constant load	3.5 wt.% NaCl	Open cir- cuit	Susceptibility to pitting cor- rosion increases and passive film's performance degrades with increasing applied stress.
[92]	AISI 420	Tensile	Constant load	0.3 M NaCl	Immersion only	Proposed mixed SCC and HE mechanism as the cause of EAC

Table 3. Mechanical testing of EAC with electrochemical charging

[79]	718 al- loy	SSRT	$2 \times 10^{-5} \text{ s}^{-1}$	2:1 mixture of glycerol +	15	Information about the effects of cathodic charging
[93]	dual- phase steel	SSRT	5 mm/min	0.5 M H ₂ SO ₄ + 1 g/l CH ₄ N ₂ S	0.8	Increased loss of ductility maximum 50% was observed with increased pre-charging time
[75]	X100	SSRT	0.02 mm/s.	0.05 M, 0.5 M H ₂ SO ₄ +As ₂ O ₃	20, 200	Hydrogen charging has in- creased the susceptibility to HIC and cracks were initiated from inclusions in the steel
[89]	X70	SSRT	1.36×10^{-6} s ⁻¹	0.1,0.05, 0.01, 0.005 M Na- HCO ₃ +100 ppm As ₂ O ₃	0.1	SCC mechanism governed by film rupture and anodic dis- solution in the as-received and water-sprayed condi- tions, and by HE for quenched, quenched tem- pered ones
[94]	SA508 Cl.3	SSRT	10 ⁻⁵ -10 ⁻³ s ⁻¹	1 M H ₂ SO ₄ / 0.25gl ⁻¹ As ₂ O ₃	10, 100	Significant decrease in duc- tility at the low strain rate was observed, with quasi- cleavage or cleavage features appearing near the inclusions
[95]	Vana- dium steel	Tensile	Constant load	3 wt% NaCl / 3 g/l NH ₄ NCS	0.02 / 1.0	Trapped and diffusible-hy- drogen content increased with charging time and be- came steady at about 100 h for 5mm diameter specimens
[59]	X80	SSRT	5.7×10 ⁻⁶ s ⁻	$\begin{array}{l} 0.5 \; M \; H_2 SO_4 / \\ 0.25 g l^{-1} \; As_2 O_3 \end{array}$	2-20	Additional tensile stress pro- vided by hydrogen, which advances linearly with in- creasing hydrogen content, was observed to act together with the external stress to in- duce plastic deformation.
[96]	A508.3	Tensile	Not speci- fied	HC1	5	A model was developed for hydrogen-induced mi- crocracking and the for- mation of fisheve cracks
[97]	AISI- 1045	SSRT	0.51 mm/min	1N HaBO3, 0.05 M KCI + 0.5 CH ₄ N ₂ S,1 M H ₂ SO ₄ +10 mgl ⁻¹ As ₂ O ₂	4.5	Found that hydrogen reduces the extent of deformation and raises the slope of the stress- strain curve.

Table 4. Experimental test standards of EAC investigation

Ref	Designation	Material	Type of EAC	Type of test	SSRT	Electrolyte	Cathodic cur- rent / Potential
[70]	BS ISO 16573-2:2022	HSS	HE	SSRT	10 ⁻⁵ s ⁻¹	NaCl 30g/l + NH4SCN 3g/l	0 - 20 Am ⁻² for 48 h
[98]	ASTM G47 – 22	Aluminium Alloy	SCC	Tensile	-	3.5 % NaCl alternate im- mersion	Immersion only
[87]	ASTM G129 – 21	Metals	SCC, HE, SSC	SSRT	$10^{-4} s^{-1}$ - $10^{-7} s^{-1}$	Not speci- fied	Not specified

[99]	ASTM G44 – 21	Metals and Alloys	SCC	Not specified	-	3.5 % NaCl, alternate im- mersion	Immersion only
[100]	ISO 7539-9	Metals and Alloys	SCC	Tensile	Not specified	Not speci- fied	Not specified
[71]	ASTM F1624 – 12	Steel	HE	SSRT, Fracture	Step loading	3.5 % NaCl	0.0 to -1.2 V vs. SCE
[101]	ISO 7539-6	Metals and Alloys	SCC	Tensile	Not specified	Not speci- fied	Not specified
[72]	ANSI/NACE TM0177-2016	NA	SCC, SSC	Tensile	Not specified	NaCl, CH3COOH, CH3COONa	Not specified
[102]	ISO 7539-11	Metals and Allovs	HE, HAC	SSRT	start with 10 ⁻⁶ s ⁻¹	Not speci- fied	Not specified
[103]	ISO 7539-7	Metals and Alloys	SCC, HIC	SSRT	start with 10 ⁻⁶ s ⁻¹	Not speci- fied	Not specified
[104]	ASTM E 1681 – 03	Metals	EAC	Tensile	Not specified	3.5 % NaCl alternate im- mersion	Not specified

4.3 Hardness testing of pre-charged specimens

Hardness can be defined as the resistance to localized plastic deformation of materials such as scratching, cutting, indentation, or wear. Simply, steel can withstand being permanently dented or scratched. There are three recognized hardness testing methods: Brinell, Rockwell, and Vickers. Hardness of the steel influences HE; therefore, existing guidelines for hydrogen services have established certain limiting values for the steel. Increasing hardness values increases the risk of embrittlement. As per IGEM/TD/1 and EIGA DOC/121/14, the maximum value of hardness for hydrogen services is stated as 250 HV, and it is 235 HV as per ASME B31.12. However, it is crucial to perform more investigations to further evaluate the effect of hardness on HE [23, 61].

4.4 Fracture toughness testing with hydrogen charging

Fracture toughness is a quantitative measure of a material's resistance to fracture and/or resistance to brittle fracture when a crack is present, and evaluated by the parameter called critical stress intensity factor (K_{IC}), J-Integral (J_{IC}), or crack tip opening displacement (CTOD) [25, 71, 104-106]. The K_{IH} , the threshold stress intensity factor for hydrogen stress cracking, can be determined by a fracture mechanics test. A pre-cracked specimen is loaded in tension, and a gaseous hydrogen atmosphere or an electrochemical hydrogen charging environment is used during the test[23]. The minimal applied stress intensity factor capable of causing crack propagation (K_{IH}) can be used to assess resistance to hydrogen-assisted cracking[47]. There are several test standards available that can be used in this regard (see Table 5).

As per the IGEM [49] it is recommended to use QSRT (Quasi-strain rate testing) or SSRT (Slow strain rate testing) for the determination of fracture toughness, but in the absence of the above two methods, Charpy impact test values have been proposed to evaluate fracture toughness. The maximum value should be the lowest of 50% of the measured impact test value or 27J. The maximum recommended K_{IH} by ASME B31.12 is 55 MPa· \sqrt{m} . IGEM has proposed two fracture control options: Option A- Perspective design method and Option B-Performance based design method. The procedure

recommended in option B also aligns with the requirements in ASME B31.12 based on ASTM E 1681. This test determines the EAC threshold stress intensity factor from constant force or constant displacement tests using pre-cracked beam or compact fracture specimens. However, consideration should be given to the electrochemical charging process and the time duration of the test, as it normally takes longer testing times. A more accelerated test is given in ASTM E 1624 to evaluate the HE threshold by the incremental step loading technique[71]. Further, BS-EN-ISO 7539 part 6 and part 9 also provide test procedures to evaluate stress corrosion intensity from constant loading and increasing loading conditions[49]. Researchers have also followed general fracture test methods with locally developed hydrogen charging test arrangements. ASTM E399, ASTM 1820, BS 7448, and BS 8571 are some of the test methods that the researchers have utilized as per the specific requirements and modifications. Generally, one test is performed under a neutral environment (or in air), while other tests are conducted under hydrogen charging to compare the percentage reduction. A significant degradation of fracture toughness has been observed in pipeline steel due to the effect of environmental hydrogen [23, 80, 107].

Ref	Steel	Used stand- ard	Strain/dis p. rate / Frequency	Electrolyte so- lution	Current density (mA cm ⁻²)	Outcomes of the study
[73]	X65, 2.5Cr1 Mo steel	ASTM E1820	Not speci- fied	0.2M CH ₃ COOH/ 0.2M CH ₃ COONa/ 1.5g/L Na ₂ S·9H ₂ O	0.6	Significant fracture tough- ness reduction was observed in both steels at all testing temperatures
[78]	AISI 4340	ASTM E1820	4 x 10 ⁻⁴ mm/s	3.5 wt.% NaCl	Potential - 950, 1050, - 1250 mV (Ag/AgCl)	More negative potentials led to decreased tensile fracture loads regardless of the bolt coating.
[90]	Cr- Mo-V- Ni steel	ASTM E1820	8.33 x 10 ⁻⁶ s ⁻¹	$\frac{1N}{4} \frac{H_2SO_4}{S_2O_3} + \frac{1}{2} \frac{H_2SO_4}{S_2O_4} + \frac{H_2SO_4}{S_2O_4$	20	Tensile strength and fracture toughness values have re- duced by over 50%
[65]	AISI 4130	ASTM E1820	Not speci- fied	CH ₃ COOH/CH 3COONa/sul- phides	0.5	Fracture toughness has de- creased to a quarter due to the hydrogen charging
[57]	X70	ASTM E399	1.67 x 10 ⁻⁴ mms ⁻¹	0.5 M H ₂ SO ₄	1, 10, 100, 1000	Critical hydrogen concentra- tion was obtained, and the re- lationship between hydrogen and fracture toughness was determined
[108]	X65	ASTM E399	2×10^{-4} mm/s	3.5 wt.% NaCl	potential– 1050 mV (Ag/AgCl)	A comparison was made be- tween increasing SSRT, step- wise increasing, and constant loading systems for fracture toughness
[23]	X52	BS 8571	0.05 mm/min	0.01M H ₂ SO ₄ + 2.00 g/L CSN ₂ H ₄	10	The fusion (weld) zone has absorbed most hydrogen in all charging times

Table 5. Previous experimental details of fracture toughness testing

[25]	X65	BS 8571	2×10^{-4}	3.5 wt.% NaCl	Potential -	Investigated the feasibility of
			mm/s	+ 2 g/L	1050, -	electrochemical hydrogen
				CH_4N_2S	1125 mV	charging for equivalent gas
					(Ag/AgCl)	charging

4.5 Fatigue testing with hydrogen charging

Two distinct measures of fatigue performance can be found in the literature: fatigue crack growth rate and fatigue endurance limit. Due to the effects of hydrogen, the fatigue crack growth rate increases while the fatigue endurance strength decreases compared to the corresponding neutral environment values, which threatens the structural integrity of pipelines[26, 65, 109]. For some materials, the fatigue endurance limit was not observed, indicating that even at very low stress levels, below the fatigue limit in air, fatigue failure may occur in hydrogen environments[58]. Previously followed experimental procedures are detailed in Table 2 and Table 6. Moreover, several experimental standards were followed for the corrosion fatigue testing. Among them, ASTM E647 has been utilized widely with modified hydrogen charging arrangements [65, 66]. ISO 12108 was also followed by some researchers for the fatigue crack growth rate test, and it recommends six types of specimens, such as compact tension, center cracked tension, single edge notch tension, three-point single edge notch bend, four-point single edge notch bend, and eight-point single edge notch bend [110]. Further, ASTM E466 was also used to assess the effect of corrosion fatigue, but only for force-controlled constant amplitude axial fatigue loading [109]. Although limited literature is available, mentioning other relevant test procedures such as ASTM E606 and ISO 11782 Parts 1 and 2 is still valuable. It is worth noting that most of the corrosion fatigue experiments were carried out in electrochemical charging conditions due to economic and safety constraints, and due to their ability to replicate the effect of gaseous hydrogen [25, 65, 84]. Further proper consideration must be given to select the loading frequency, as it is evident that crack growth rates are higher in lower loading frequencies[65].

Ref	Steel	Fre- quency	Electrolyte solution	Current den- sity (mA cm ⁻²)	Outcomes of the study
[26]	X80	1	0.5M H ₂ SO ₄ / Na ₂ S	5	Fatigue life decreased with increased hydrogen content under different strain amplitudes.
[58]	Q420B	1-10	3.5 wt% NaCl	Open circuit	Provide useful information about corrosion fatigue damage and mech- anism, also found that fatigue degra- dation is higher when the peak stress is lower
[111]	X12CrNi- MoV12-3	10, 120	0.1 M NaCl + 0.044 M Na ₂ SO ₄	Free potential	Crack initiation is due to (i) the local de-passivation of the passive film and (ii) the corrosion pitting.
[109]	AA6061- T6 alloy	5	3.5 wt.% NaCl	Immersion only	Hydrogen promotes crack tip embrit- tlement and accelerates crack growth rate in mixed intergranular and trans granular cracking

Table 6. Previous experimental details of fatigue testing

[65]	AISI 4130	0.1, 1, 10	0.4M,0.2M CH ₃ COONa/ Sul- phides	0.5	Hydrogen charging has increased fa- tigue crack growth rate by two or three orders of magnitude. Test done as per ASTM E647.
[66]	X65, F22	10,20	0.4M,0.2M CH ³ COONa / Sul- phide	0.5	Hydrogen charging has increased the crack growth rates in both materials. Test done as per ASTM E647.
[112]	X12CrNi- MoV12-3	10, 120	0.1M NaCl/ 0.044M Na ₂ SO ₄	Free potential	Provide details about effect of load- ing frequency on the corrosion fa- tigue crack initiation mechanism
[84]	Spring steels	20x10 ³	3 wt% NaCl / 3g/L NH4SCN	0.6, 1, 2	The size granular-bright-facet (GBF) is greatly affected by the hydrogen content inside the steel
[113]	S355	0.2, 0.3, 0.5	Sea water	Immersion only	Tests performed as per ASTM E647 and BS 7910. Provides experimental results of the effect of waveform and frequency on CF.

5 Conceptual framework for structural integrity assessment of repurposing existing NG pipelines for H2 transportation

A conceptual framework for the experimental evaluation of the structural integrity of existing natural gas (NG) pipelines, intended for repurposing to hydrogen transportation, is proposed in this section. This framework is designed to support future experimental studies aimed at assessing the integrated effects of EAC in hydrogen transport pipelines, and it is shown in Figure 7.

The proposed framework consists of four phases. During the first phase, factors affecting the EAC of pipeline steel shall be identified. All the mentioned parameters such as steel grade, chemical compositions and heat treatments of the existing pipe, pressure and temperature that the hydrogen gas intended to be transported and cathodic current to be used, condition of the existing coating, stresses and pressure to be used and the welding details need to be identified at the first phase. Relevant details are discussed in section 3.1. Types of EAC and effects shall be identified during the second phase. Here, all the types (i.e., HSC, HEE, HAF, and External SCC) need to be taken into account for the experimental evaluation. The nature of the external corrosion type can vary with the type of external environment (i.e., buried, subsea, or onshore). Further, separate assessments may be performed to assess the effect of other possible corrosion types, such as uniform corrosion, pitting, crevice corrosion, and galvanic corrosion, which are not mentioned in this study. Refer to section 3.2 for further details. A series of experiments shall be carried out as the third phase of the framework to investigate each mechanical property of the steel pipeline, such as tensile strength, ductility, fracture toughness, hardness, pre-cracked fatigue crack growth rate, and fatigue endurance limit. Further details can be found in Chapter 4. Finally, phase four includes the assessment of the structural integrity of the pipe using the obtained results from the experiments and performing local and global analyses to check the feasibility. If the structural integrity of the pipeline is satisfied, recommendations can be proposed for hydrogen transportation. where it is not satisfied, restrengthening of the existing pipeline or replacing the pipeline can be proposed after a comprehensive study, which is not covered in this work.



Fig. 7. Conceptual framework to assess the structural integrity for repurposing existing NG pipelines for hydrogen transportation.

6 Conclusions

This paper investigates the effect of EAC in evaluating the structural integrity of pipelines designated for hydrogen service. This study critically reviewed the various types of EAC, namely hydrogen stress cracking, hydrogen environment embrittlement, hydrogen-assisted fatigue, and external stress corrosion cracking, and their degradation

effects on the structural integrity of the pipeline, highlighting the importance of an efficient and accurate experimental evaluation.

As the first step of the comprehensive process, a conceptual framework has been proposed to assess the structural integrity for repurposing existing NG pipelines for hydrogen transportation. This framework has a few distinguishing features compared to previous experimental procedures. The impact of EAC is highly dependent on the specific environmental conditions and loading scenarios relevant to the particular steel structural system. In this specific scenario, it is hydrogen transport pipelines. Therefore, it is essential to identify the dominant degradation mechanism, understand its influence on mechanical properties, consider all critical contributing factors, and most suitable test methods shall be selected to accurately assess the structural integrity of the system. Currently, there is no general guideline that addresses this requirement. Hence, this framework is proposed to systematically identify the most suitable test methodology, tailored to the specific environmental and mechanical loading conditions, to ensure reliable integrity assessment. Further, this framework recommends considering the integrated effect of all types of EAC with continuous hydrogen charging until failure of the specimen to achieve the most similar environment to the operational conditions of the system.

This framework consists of key stages, identifying material, environmental, and structural parameters, determining relevant EAC mechanisms, executing relevant experiments, and evaluating structural integrity for service. A proper material selection through a comprehensive testing and qualification process is imperative before repurposing the existing pipeline system for hydrogen transportation. Comparing the previous experimental studies, it is clear that the majority of the tests have been performed in electrochemical environments. Perhaps the existing difficulties with gaseous hydrogen charging were responsible for it. The primary causes have been found to be a lack of test facilities with high-pressure gas chambers, the accompanying economic issues of gaseous hydrogen charging, and the considerable risk involved with pressurized hydrogen gas. However, recent research findings and experimental investigations provide acceptable evidence to support the substitution of electrochemical environments for hydrogen gas environments.

Evaluating the effect of EAC is a difficult process due to the simultaneous existence of each phenomenon (SCC, HE, and CF) in the environment. Therefore, careful consideration must be given to the selection of electrolyte solution, strain or loading rate, specimen type, charging duration, and current density, depending on the specific type of EAC being studied and the mechanical properties of the steel being evaluated. In most studies, a three-electrode electrochemical cell was employed, consisting of a platinum counter electrode, a Saturated Calomel Electrode (SCE) or Silver/Silver Chloride (Ag/AgCl) as the reference electrode, and the steel specimen as the working electrode. Sodium chloride (NaCl) has been widely and successfully used as the electrolyte in both research and standardized testing procedures. Also, hydrogen recombination inhibitors, such as thiourea (CH4N₂S), have proven effective in enhancing hydrogen diffusion into the steel, achieving the required internal hydrogen pressure and simulating the hydrogen gas environment more accurately. Strain rate is also a critical factor when performing an SSRT test because strain rate should be slow enough for the EAC mechanism to initiate and propagate, but fast enough to induce failure or cracking to perform evaluation. The fatigue testing exhibits the same pattern since lower frequencies showcase increased fatigue crack growth rates due to hydrogen-assisted fatigue.

Ensuring safe and reliable hydrogen transport through repurposed pipelines requires a multidisciplinary approach that integrates material science, corrosion science and structural engineering. The framework and review outcomes of this paper provide a strategic guide/framework for future investigations and contribute to the development of more resilient hydrogen infrastructure.

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