



Laboratório de Corrosão
COPPE|UFRJ
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Environmentally Assisted Cracking and Energy Transition - Expected Impact on Materials and Equipment

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SUMMARY

- **BASIC DEFINITIONS – Energy transition and EAC**
- **CO₂ CORROSION - SCC - HYDROGEN EMBRITTLEMENT**
- **OUR BACKGROUND - LABCORR**
- **COMMENTS AND QUESTIONS**

BASIC DEFINITIONS – Energy transition and EAC

Energy transition

- From Watt energy transition – SCC as cause of steam boilers explosions – mitigated by new welding technologies (Between the years 1760-1820, the Industrial Revolution took place in Great Britain)
- Present - Alternative energy sources (renewable) – new application conditions required, much more aggressive or unknown (unexpected damage mechanisms)
 - Pure hydrogen at high pressure – Generation (green), transport and storage
 - H₂S build up and ageing facilities – pipeline grid worldwide – gas sources
 - CO₂ at high P and T – supercritical conditions, contaminants (greenhouse effect and oil and gas sector focus on better compliance)
 - Molten salts

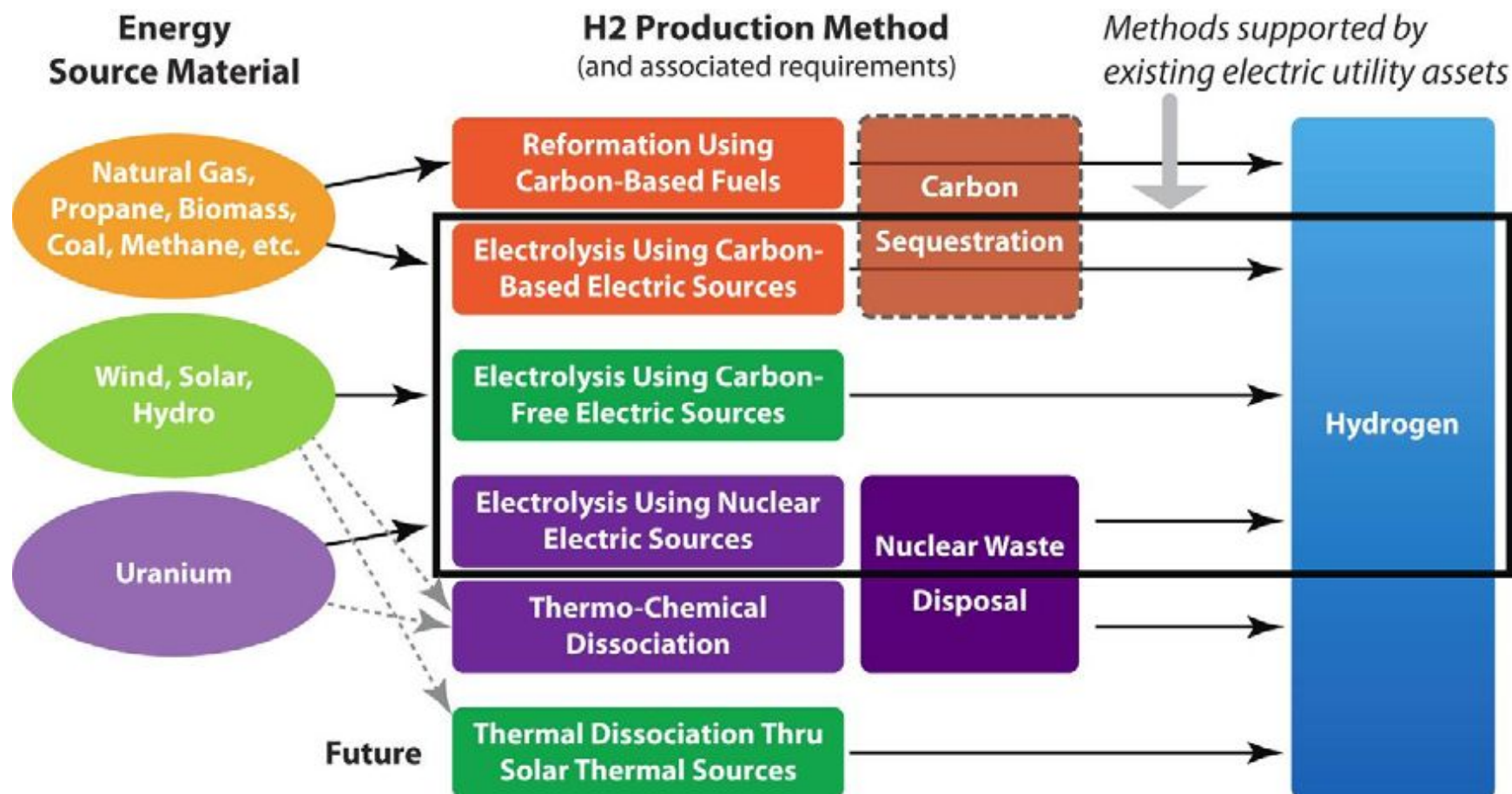
GLOBAL SCENARIO

- **EUROPE – ageing gas pipeline grid / H₂S build-up / CO₂ management**
- **BRASIL – CO₂ Presalt – reinjection /storage/transportation**
- **BRASIL – Green hydrogen – huge investment on eolic/electrolysis**
- **US – Wind to Power**

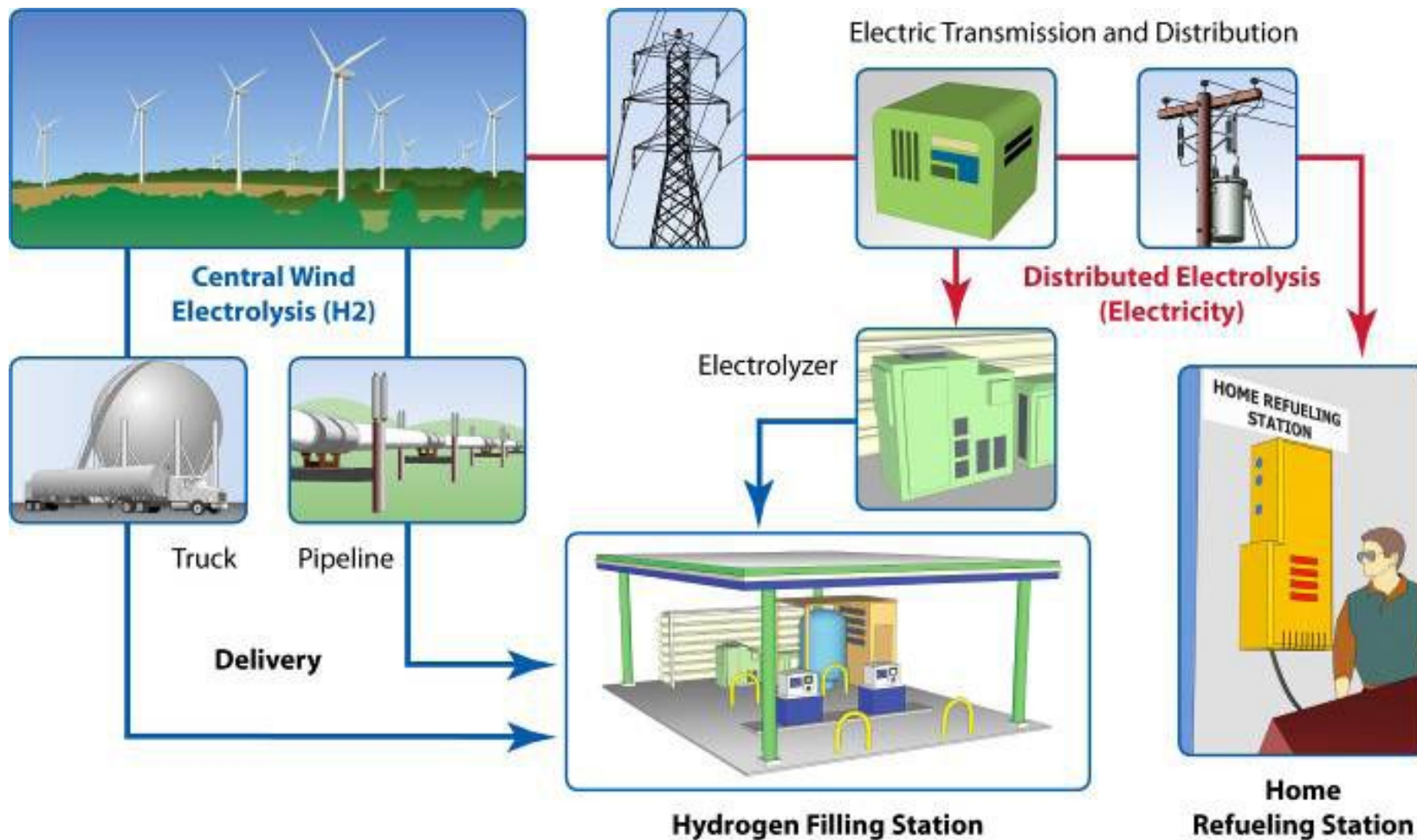
WIND TO POWER



Hydrogen production pathway



Examples of wind electrolysis being produced centrally or distributed at the point of use



CARBON CAPTURE

AND STORAGE

Carbon Capture and Storage (CCS) is a key available technology to mitigate emissions from large-scale fossil fuel use.

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Materials challenges with CO₂ transport and injection for carbon capture and storage

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CO₂ transport
Dense phase CO₂
Corrosion

ABSTRACT

Carbon Capture and Storage (CCS) is a key technology to mitigate emissions from large-scale fossil fuel use. CCS primarily involves capturing the CO₂ arising from energy-related and industrial sources, treating of the CO₂ to remove impurities, and injecting it in a storage site to ensure long-term isolation from the atmosphere. The specific difference in relation to experience with relatively pure CO₂ injection is caused by the impurity of the CCS CO₂ which will be dictated by the CO₂ source and the capture technology employed. The aim of this work is to identify an approach to materials selection and corrosion control that can address the specific requirements of a CCS project. Depending on the phase envelope and CO₂ composition, separate liquid phases may be formed. It has been identified that these phases can comprise of water (causing CO₂ corrosion) or reaction products including strong acids and elemental sulphur. The type of liquids formed and shifts in the phase envelope can significantly influence materials integrity due to corrosion, and impact the flexibility and degradation of polymers. For this reason, it is recommended to start each project with the identification of the CO₂ specification and operating scenarios, including aspects that might occur during the service life. Other concerns include the impact of low temperature scenarios, and the possible presence of O₂ and a high salinity brine on materials used in wells.

1. Introduction and background to the CCS process

A substantial amount of the world's rising energy demand is forecast to still be met by fossil fuels over the next decade (IPCC, 2006). Carbon Capture and Storage (CCS) is a key available technology to mitigate emissions from large-scale fossil fuel use. Therefore, developing and commercialising this technology is essential to help reduce the impact on climate change (Barker et al., 2017; Bertin, 2015). CCS primarily involves capturing the CO₂ arising from energy-related and industrial sources, treating of the CO₂ to remove impurities, and compressing, transporting and injecting it in a storage site to ensure long-term isolation from the atmosphere (Dahl, 2010; Gassler et al., 2013).

In using fossil fuels to generate power, the purity of CO₂ emissions is not an important parameter and as a result the quality of CO₂ for CCS transport and injection will be predominantly dictated by the CO₂ capture technology employed at the plant with secondary consideration of the pipeline and storage limitations.

1.1. CO₂ source

Removing impurities down to very low concentrations may create a significant energy requirement and cost penalty (Barker et al., 2017). Consequently, CO₂ captured from power generation and industrial sources for CCS is likely to contain many impurities. For CCS projects the threats related to the purity of the CO₂ can be classified by the gas source as:

- **Relatively clean CO₂ gas.** There is a lot of experience with CO₂ gas injection used for EOR (Enhanced Oil Recovery). This is a relatively clean CO₂ source and experience has shown that there are few operational problems provided the fluid is kept relatively pure and the water content is controlled (Barker et al., 2017; Paul et al., 2012; Dugstad and Halseid, 2011; DRET 2009).
- **Impure CO₂ gas.** For CCS the source of CO₂ can originate from combustion or from a range of industrial sources. The impurities include those present in the gas source (e.g. H₂O, NO_x, SO_x, O₂) as

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BASIC DEFINITIONS – EAC

- Stress Corrosion Cracking
- Hydrogen embrittlement
- Corrosion fatigue

Minor players - Corrosion erosion/liquid metal embrittlement/fretting corrosion, etc....

All together sometimes

CO_2 CORROSION – SCC

CO₂ environments – Materials issues

Low temperature fracture that can lead to sudden and catastrophic failures. Joule Thompson effects – low ductility under cryogenic conditions. Besides, supercritical CO₂ can make CCS pipelines more susceptible to cracking

CO₂ corrosion - general aspects

Hydrogen embrittlement

CO₂ Stress Corrosion Cracking – ANP warning issued in Brasil 2017

CO₂ Corrosion

Starting from CO₂ corrosion basic knowledge (De Waard pioneer model)



Confinement conditions, saturation ratio and precipitation under very low V/S conditions



Loading conditions or loading history – Static/Dynamic/ Mixed

Surface condition as a key factor to be considered. Will depend on time, temperature, iron concentration and CO₂ fugacity – Precipitated iron carbonate film morphology, adhesion, chemical and electrochemical stability. Surface morphology of the metal surface underneath the FeCO₃ film. In order to preserve the wire texture, segments of full thickness wires are used as working electrodes on mechanical tests in corrosive environments.

CO₂ SCC

From literature review, specific “knowledge packages” could be identified

1) Old school people from Germany investigated the so called “fire extinguisher steel failure analysis”. Schmitt and others. At least one of the steels tested is comparable to the flexible wire steel (C about 0,3%)

2) Near neutral SCC (NNSCC) – origin in Canada from buried pipeline failures. Investigated for several decades. Based on concepts introduced by Parkins (Newcastle Upon Tyne). Search of similarities between FSICC and cracking produced at the interface coated steel/soil.

3) Side approach considering the contribution of carbon monoxide (CO) to cracking. Not considered into the frame of FSICC investigation. Papers from 1976 to 2023

4) New approach, after 2017, ANP technical note. Conducted by flexibles manufacturers, operators and R&D institutions, going from test of materials to full scale tests.

EAC – FLEXIBLE PIPELINES

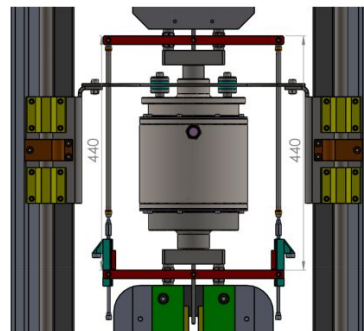
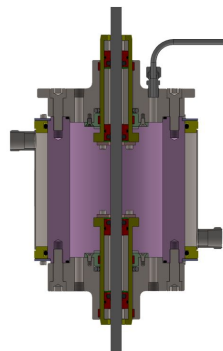
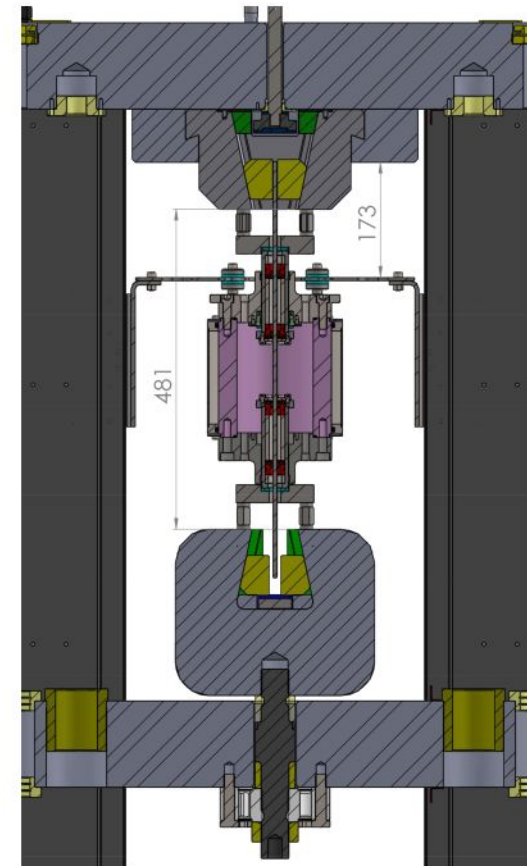
Safe conditions limits are pulling down

HE embrittlement – expected concentration – diffusion models and others

SCC CO₂ – expected concentration – diffusion models and others

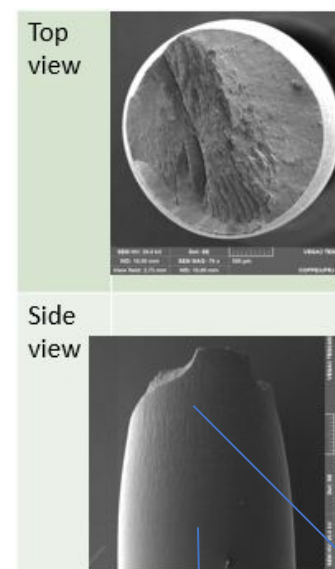
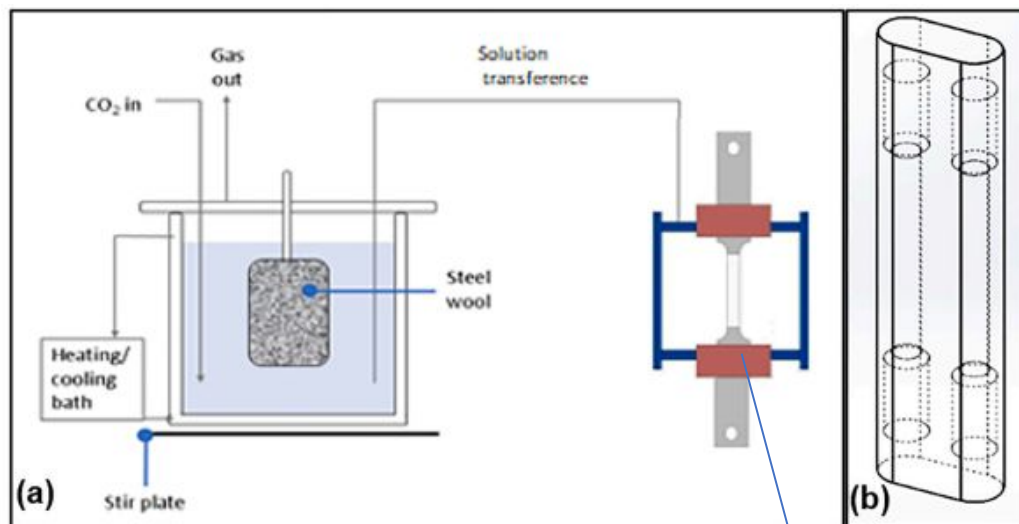
OUR BACKGROUND - LABCORR

HPHT (SSRT)

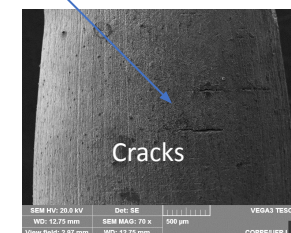
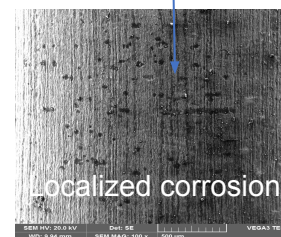
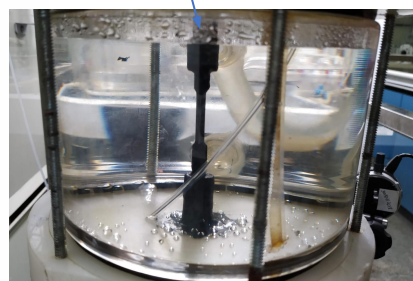
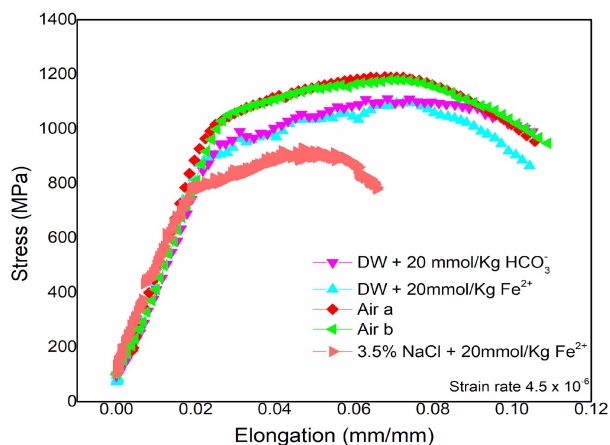
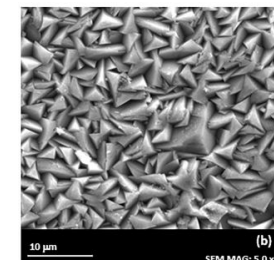


Simulation of annular space of flexible pipes and 4-point bend tests

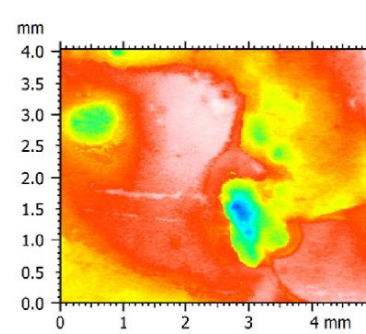
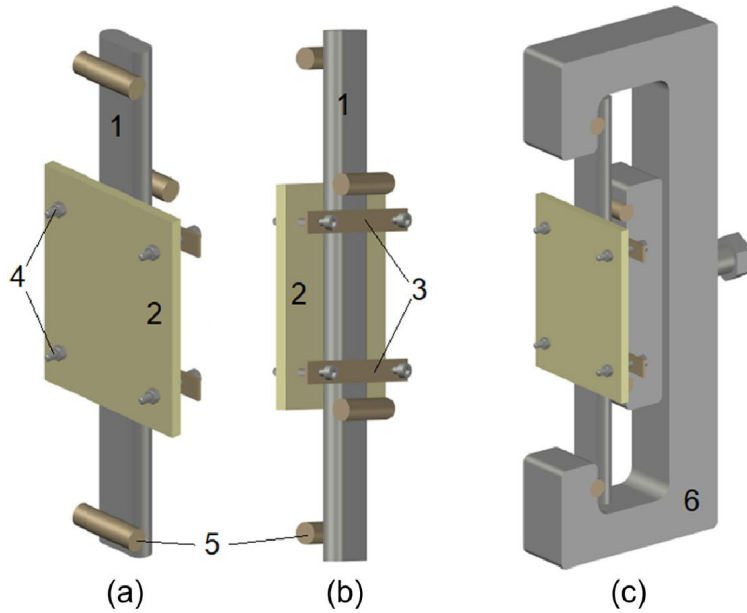
SSRT of machined tensile armor wires in simulated annulus conditions



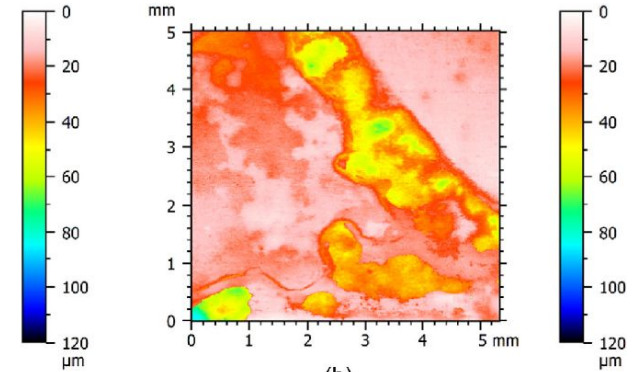
Influence of the filmed surface



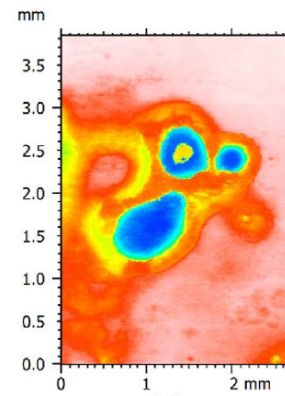
CREVICE CORROSION – 4 POINT



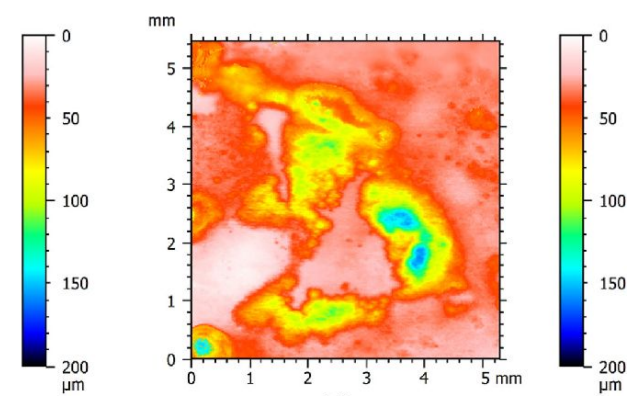
(a)



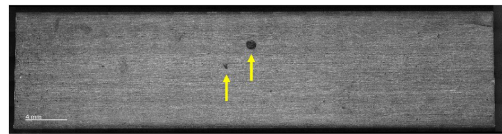
(b)



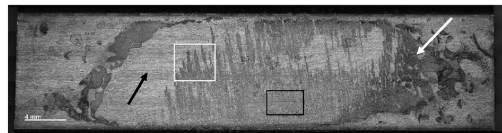
(c)



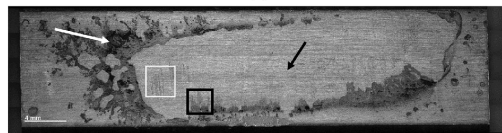
(d)



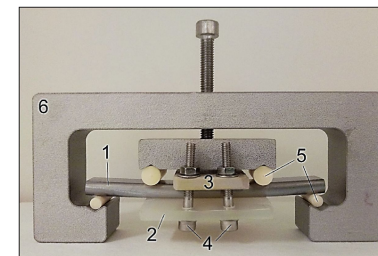
(a)



(b)



(c)

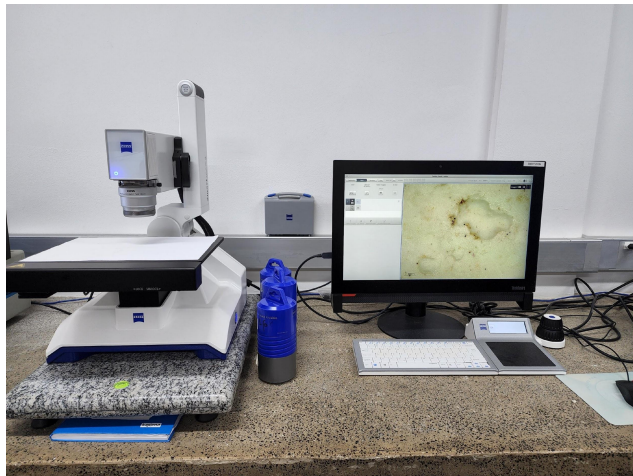


HYDROGEN PERMEATION



SURFACE ANALYSIS

OPTICAL MICROSCOPY



CONFOCAL MICROSCOPY



SEM/EDS



ADDITIONAL TECHNIQUES

A) Tomography

B) Digitalization

C) Electric potential drop

D) Fretting corrosion tests – Zeta wire

E) Phased array US

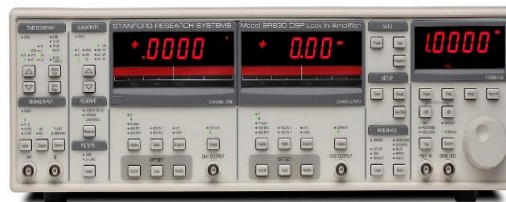
POTENTIAL DROP - (PD)

Bipolar operational power

(a)



Amplifier
Lock-in



(b)

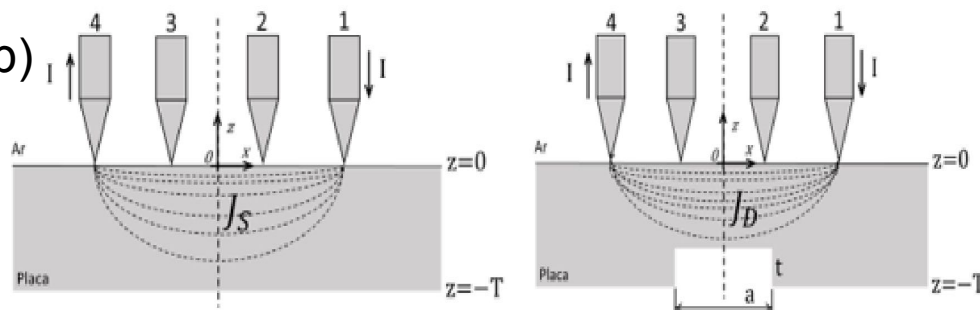


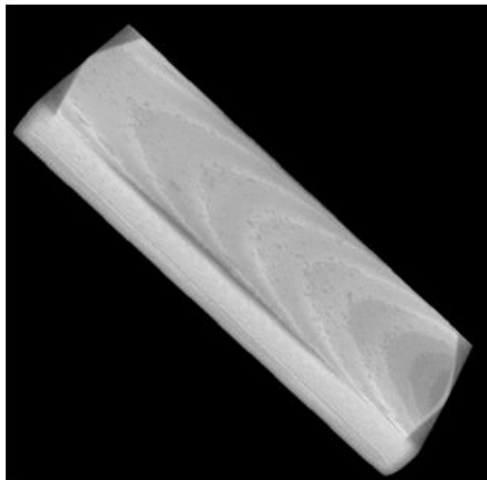
Fig 3 (a) Equipments used for potential drop method. (b) Schematic representation of PD technique.

PD inspection methods:

- ACPD (Alternating current potential drop): Detection of internal and superficial defects. (e.g. localized corrosion and SCC-CO₂).
- DCPD (Direct current potential drop): Detection of internal defects. (e.g. HIC cracks)

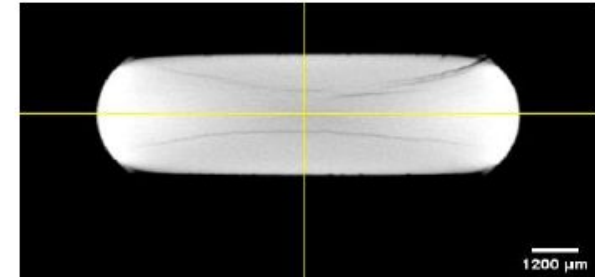
TOMOGRAPHY

- Results

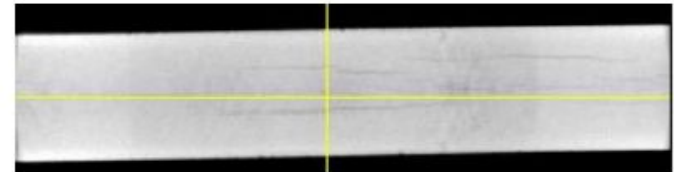


3D tomography image from a tensile wire after being exposed to an H_2S solution.

(a)



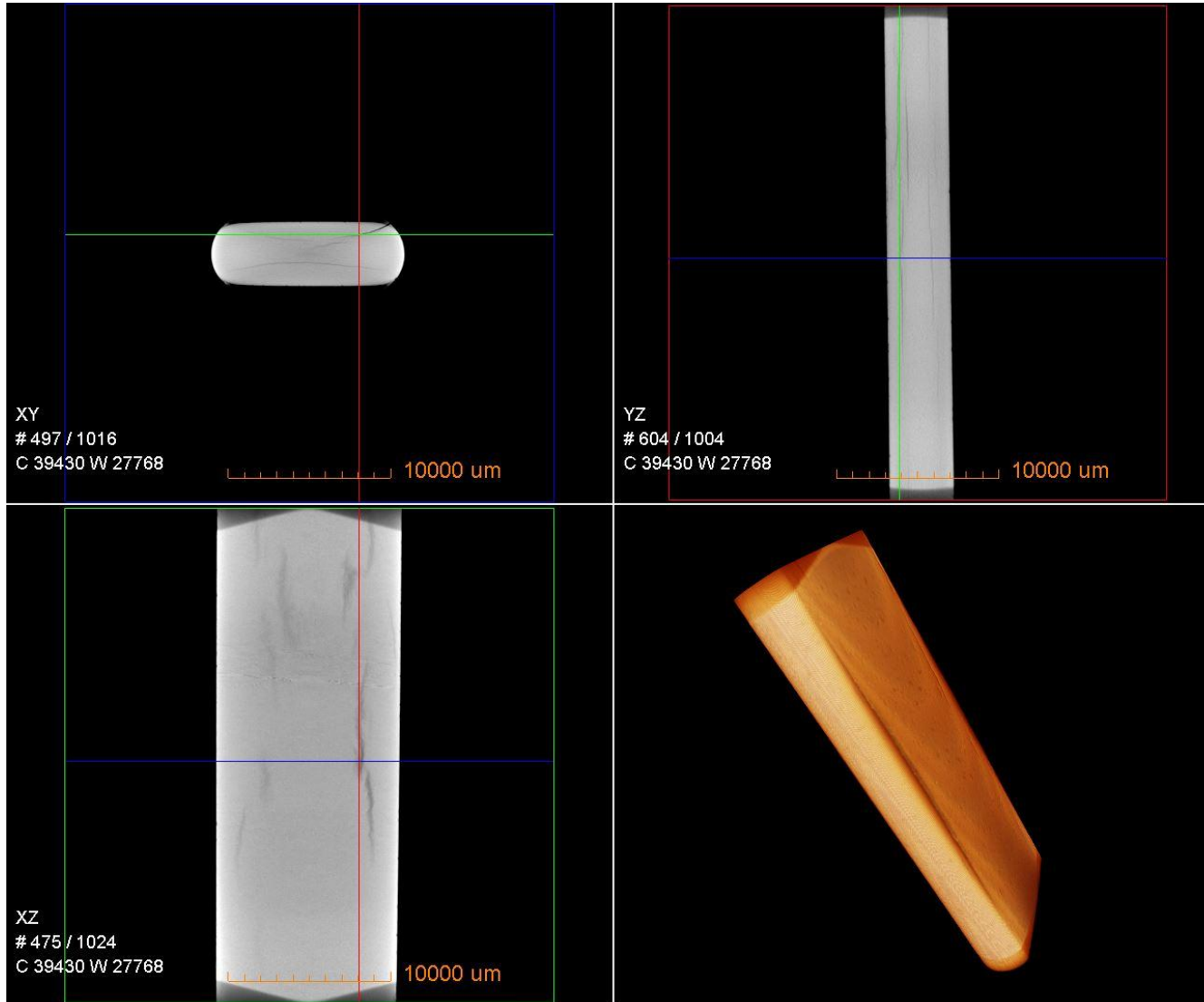
(b)



Tomography images (a) Cross-section. (b) Coronal plane.

- Conclusions → it is possible to use tomography to detect, locate and dimension internal cracks in armor wires that have been exposed to a corrosive environment.

TOMOGRAPHY



HPHT tests (Static and RCage/RCE)



H₂S test system



Erosion-Corrosion System

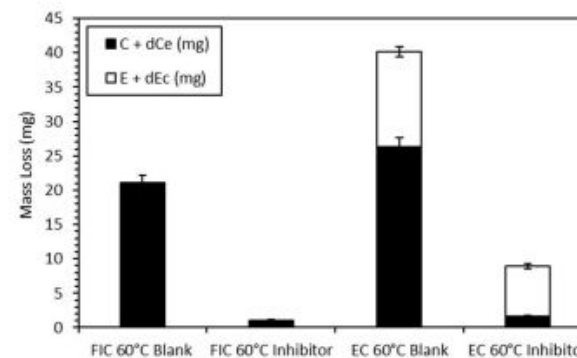
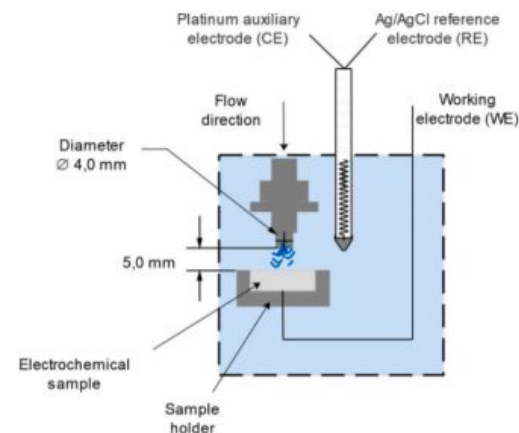
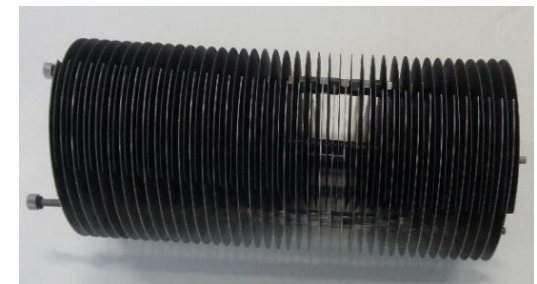
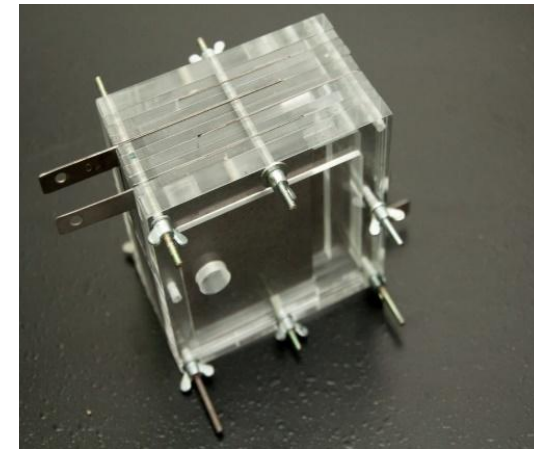


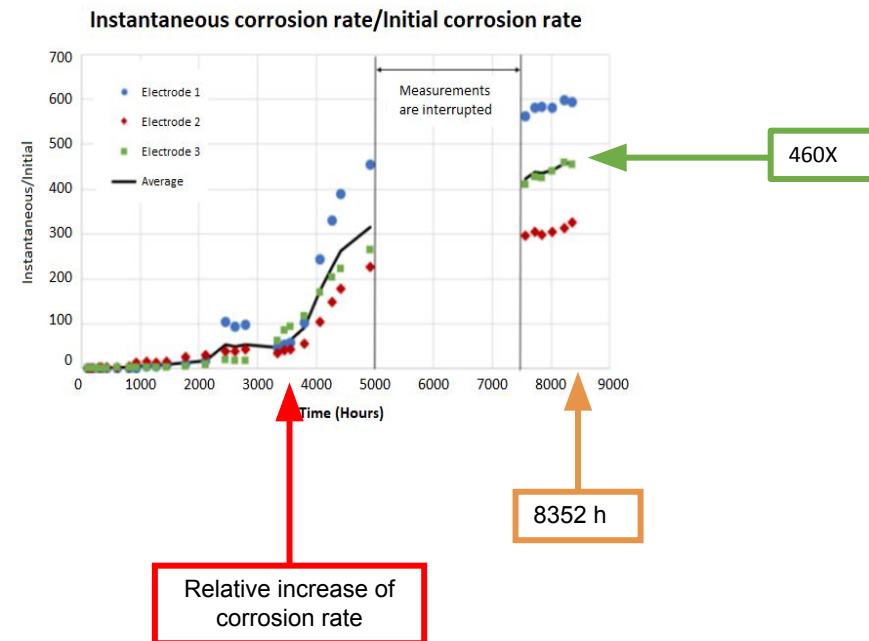
Fig. 5. Contribution of erosion and corrosion components of degradation, drawing attention to the influence of the sand particles on inhibitor performance at 100 ppm.

Contribution of erosion and corrosion components of degradation drawing attention to the influence of the sand particles on inhibitor performance at 100 ppm.

Electrochemical treatment of wastewater

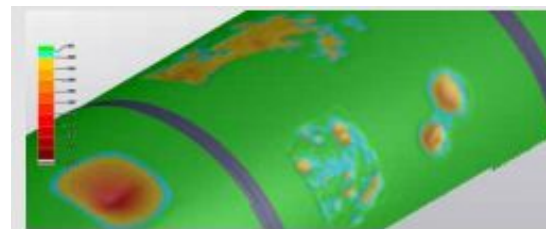
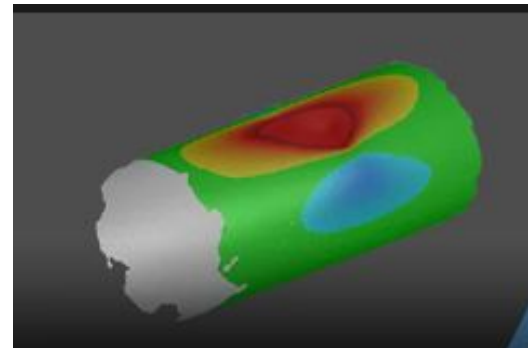


Under deposit Corrosion System

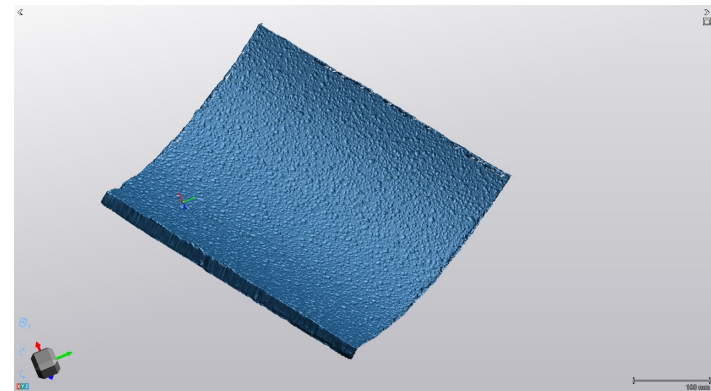
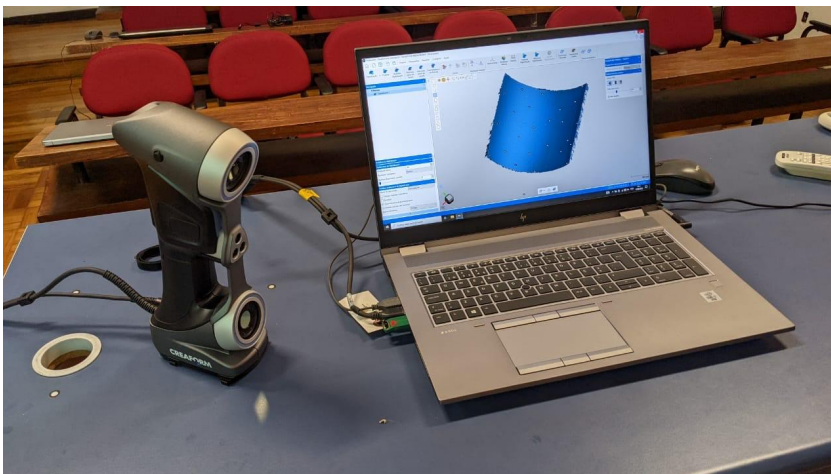
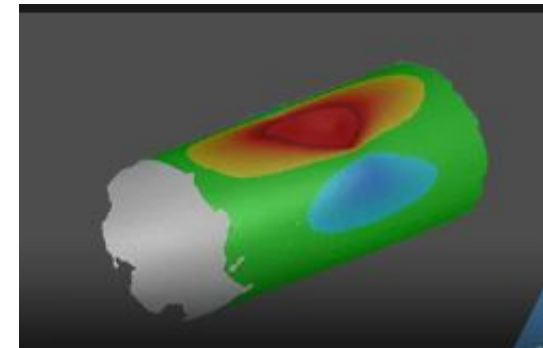
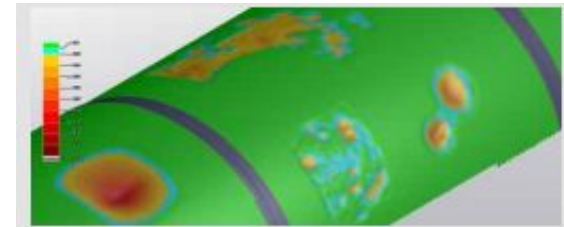
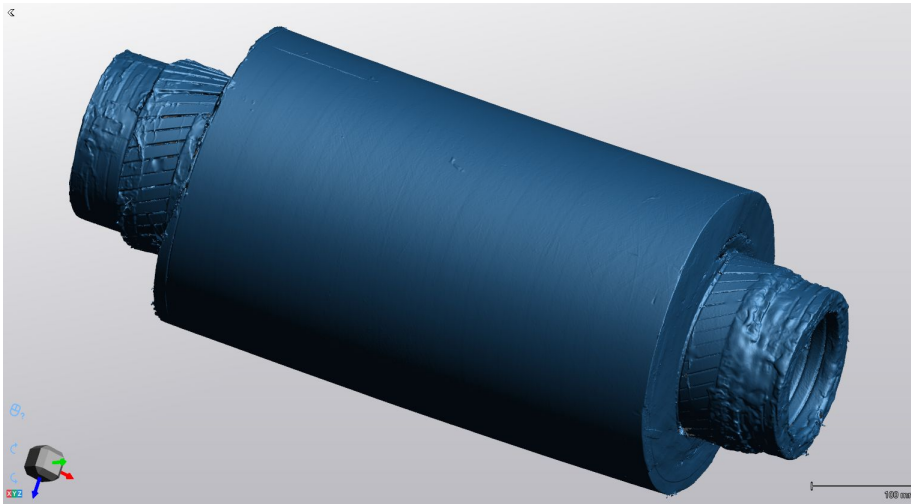


HandyScan – Scanner 3D Pypecheck and PolyWorks Software

In the acquisition process

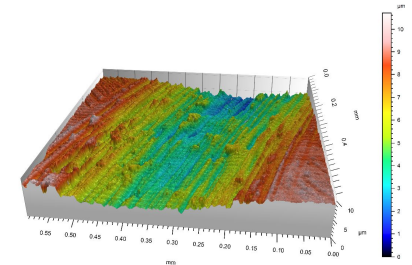
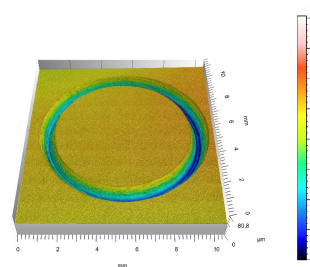
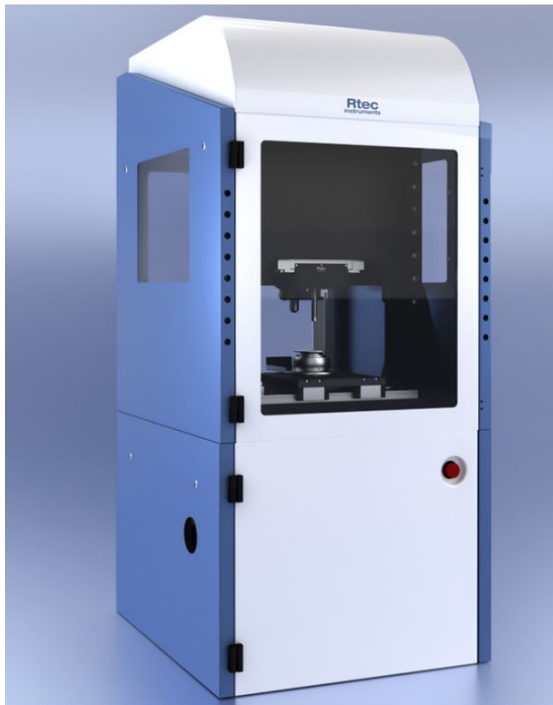


FIELD ACTIVITIES - SCANNER 3D



TRIBOCORROSION

The analysis includes tribocorrosion assessments performed in tribometer and characterization of surfaces under wear and corrosion conditions, in relative motion and loading. In this field our main evaluations are in flexible pipes and in the biomedical area such as dental and orthopedic implants.



APPLIED ELECTROCHEMISTRY - INTEGRITY MANAGEMENT

Phase 1 - Development of Electrochemical treatment process of refinery sour water with co-product generation

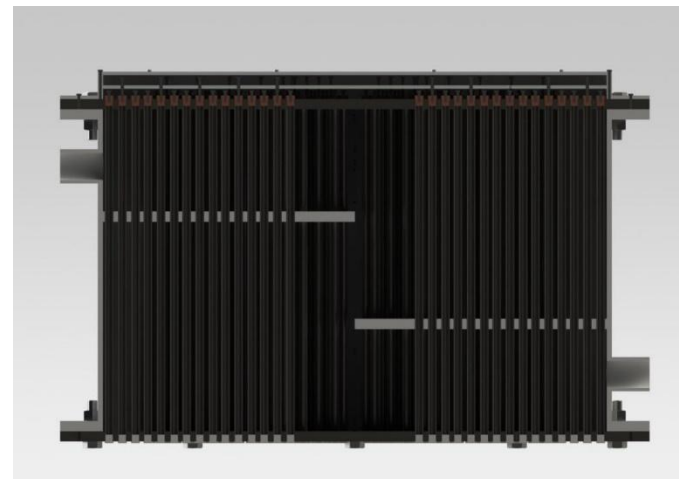


Electrochemical conversion cell for H₂S removal

Tested materials:

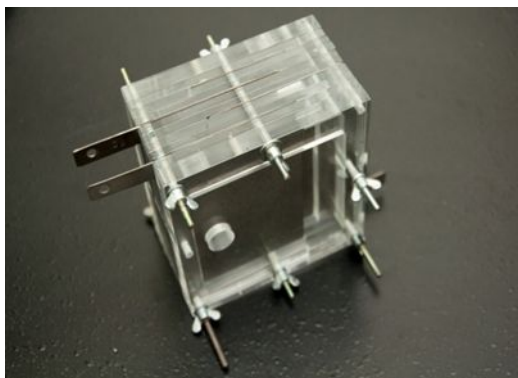
- Carbon steel
- Nickel** → high anodic and cathodic current densities
- Titanium
- Graphite
- Platinum

Results: H₂S removal and H₂ generation



APPLIED ELECTROCHEMISTRY - INTEGRITY MANAGEMENT

Phase 2 : Improvement of alternative electrochemical technology for the treatment of sour water generated in refineries



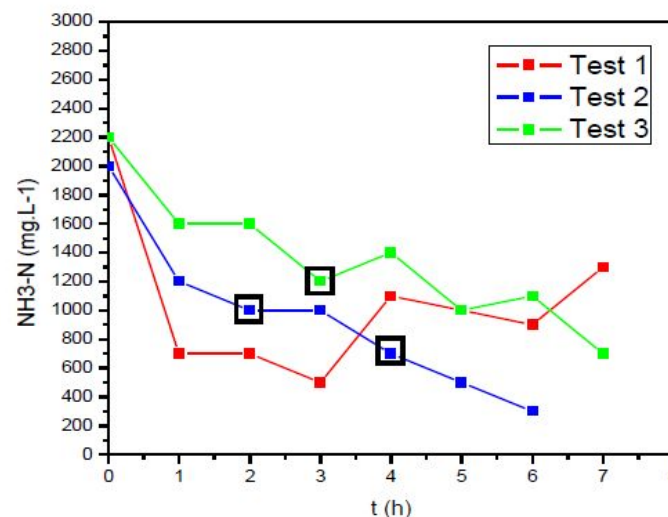
Parallel plate electrochemical reactor – bench scale

Tested materials for N-NH₃ oxidation:

- Platinum – high electro-activity
- DSA®** - high electro-activity and higher affinity for ammonia
- Nickel – corrosion
- Anodized Al – no satisfactory corrosion resistance or electrochemical activity
- Graphite – undefined parallel reactions

Tests	Initial COD concentration mg.L ⁻¹	Final COD concentration mg.L ⁻¹	Removal %
1	6040	380	93.7
2	2170	550	74.6
3	7790	1150	85.2

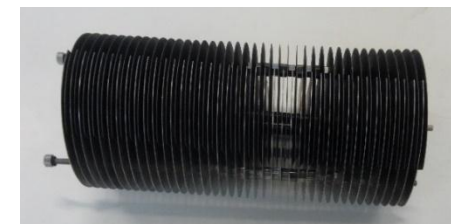
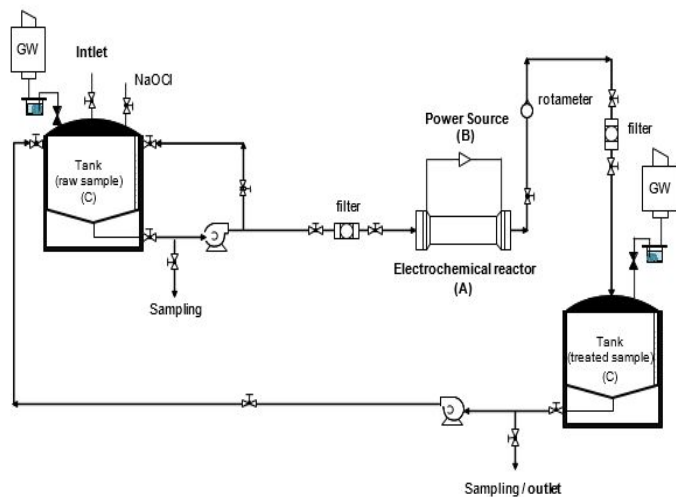
COD removal from the electrochemical treatment.



Variations in NH₃-N content according to the NaOCl injection system. Test 1: NaOCl added at the beginning of the process; Test 2: NaOCl added at the beginning and at two additional occasions during the process; Test 3: NaOCl added at the beginning and once more during the process. Intermediary NaOCl injections are indicated by the squares.

APPLIED ELECTROCHEMISTRY - INTEGRITY MANAGEMENT

Phase 3 : Improvement of alternative electrochemical technology for the treatment of sour water generated in refineries – Optimization of the Electrochemical Reactor



B)

Main results:

- The electro oxidation of $\text{NH}_3\text{-N}$ species was found to be reversible, indicating the formation of co-products
- H_2 sensor improvement enabling field use



Stress corrosion cracking susceptibility of armour layers in CO₂ annulus environments – SSRT experimental simulation

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ARTICLE INFO

Keywords:
CO₂ Stress Corrosion Cracking
Annular space
Flexible pipes
FeCO₃ precipitation

ABSTRACT

Flexible wires present wet occluded spaces where corrosion induces supersaturation of ferrous ions and precipitation of FeCO₃. Localized corrosion is possible due to discontinuities of the precipitated FeCO₃. This work aims to investigate the Stress Corrosion Cracking susceptibility of armour layer in FeCO₃ supersaturated seawater, addressing the influence of CO₂ partial pressure and strain rate, at 25 °C and at 40 °C, using the Slow Strain Rate Test. The results were expressed by ASTM G129 standard parameters. The material showed loss of ductility under all experimental conditions. The most aggressive conditions were at 25 °C, 10 bar, under 10⁻⁷ s⁻¹ and 10⁻⁶ s⁻¹ strain rates, respectively. The results showed that fracture mechanism is related to hydrogen embrittlement, suggested by the presence of internal secondary cracks on the fracture surface. These secondary cracks suggest the interference of delamination. From the results it was possible to rank the severity of experimental conditions imposed.

1. Introduction

The flexible pipes have been used by the oil and gas industry for many decades to ensure characteristics that are considered essential to the project, such as easy configuration adjustment, transport and storage conditions [1,2,3].

Corrosion in confined environments of the annulus of flexible pipes, which have a restricted volume of electrolyte in relation to the steel surface, may cause different corrosion morphologies, such as crevices, pits and environment assisted cracks. Different corrosion morphologies are likely to occur, such as crevices, pits and environment assisted cracks. It is estimated that the ratio between the volume of solution and the surface area (V/S) of the metallic wires of carbon steel or high-strength low-alloy steel (HSLA), is lower than 0.1 mL/cm² [4,5]. Along with other parameters, such as the composition of the electrolyte (condensed water or sea water, as well as the dissolved gases present), temperature and pressure, it was experimentally evidenced that the V/S ratio is the main factor affecting the corrosion process of armour layers [5].

The confined environment of annulus of flexible pipes can assume different and complex characteristics which can affect the properties of many layers comprised between the inner and outer sheath. These variations of the environment formed in the annulus can occur due to a wide range of events during service, leading to degradation of the internal components, and can jeopardize the integrity of the equipment, with failure of premature replacement.

Damages to the outer sheath of the flexible pipes also frequently occur, allowing seawater to ingress into the annulus, in presence of

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2022 - Experimental investigation of CO₂ SCC using SSRT as a screening tool to spot the influence of key parameters – pCO₂, T and strain rate.

SCIENCE SECTION

Effect of Flow Rate on the Corrosion Behavior of API 5L X80 Steel in Water-Saturated Supercritical CO₂ Environments

Jonas da Silva de Sá,^{1,***} Wenlong Ma,^{****} Joshua Owen,^{**} Yong Hua,^{**} Anne Neville,^{**} José A.C. Ponciano Gomes,¹ and Richard Barker^{**}

The effect of the water-saturated supercritical carbon dioxide (scCO₂) flow rate on the corrosion behavior of API 5L X80 steel at a temperature of 35°C and pressure of 80 bar was investigated. Tests were performed with the samples attached to a rotating shaft inside an autoclave. Results indicate that increasing the scCO₂ flow rate had no significant influence on the general/localized corrosion rate under the various dynamic conditions considered. The average general corrosion rate was 0.064 mm/y, while the average measured pitting penetration rates were one order of magnitude higher. The size of the corrosion features on the surface of the samples, which were believed to provide an indication as to the size of the condensed water droplets, was much smaller than the calculated critical droplet size needed to be displaced by the flow, supporting the theory as to why flow rate had little effect on the corrosion response.

KEY WORDS: carbon dioxide, flow effects, steel, supercritical environment

INTRODUCTION

Global warming has become a wide public concern, with CO₂ emission into the atmosphere representing one of the biggest contributors to the rise in the Earth's temperature. Carbon capture and storage (CCS) technology is currently a feasible and economic method for reducing greenhouse gases emissions. It consists of capturing CO₂ from large source points, compressing it into a liquid or supercritical state, and transporting it to a storage site for sequestration or for the purposes of enhanced oil recovery (EOR).¹ Hence, the implementation of CCS technologies has the potential to reduce CO₂ emissions into the atmosphere, while also facilitating the recovery of hydrocarbons through the application.² The handling of CO₂ during CCS needs to be conducted in a safe manner; therefore, it is essential to evaluate the corrosion risk in CO₂ transport and injection pipelines.³⁻⁴

Although dry CO₂ is not corrosive to steels, the presence of free water has been regarded as a particular cause for concern for supercritical CO₂ applications. If water is present, it quickly becomes saturated with CO₂, producing carbonic acid, thus creating a local corrosive environment that may affect the pipeline integrity.⁵ Therefore, most applications focus on sufficiently drying the CO₂ before using it. However, in water-alternating-gas (WAG) EOR applications, the well is flooded alternately with CO₂ and water, and in such applications residual water cannot be avoided and the injection lines would be periodically exposed to CO₂ fluids with different water contents.¹

The effect of water content, impurities, temperature, and pressure on the corrosion of the steel in static supercritical CO₂ has been extensively studied in recent years.^{3,6} However, the effect of flow rate on the supercritical CO₂ corrosion behavior of the steel has rarely been reported. It has been shown that in the specific aqueous phase environments, the corrosion rate of the steel can increase substantially due to the mass-transfer generated by the flow. The increase in local turbulence in aqueous environments can also hinder the formation or damage the protective corrosion products film on the surface.⁶⁻⁷

However, in the supercritical CO₂ phase, the corrosion mechanism is substantially different from that encountered in a single-phase flow aqueous environment, and more akin to corrosion in condensate/wet-gas systems. In this scenario, the water can locally exceed the solubility limit and condense via a dropwise or film-wise mechanism onto the steel surface, leading to corrosion of the area in direct contact with the aqueous phase.⁸ The corrosion in such systems is expected to be controlled by the electrochemical reaction occurring at the interface between the steel sample and the free water. Consequently, the corrosion rate measured would be influenced by the extent of the wetted area.^{1,8-9} Therefore, understanding this initial stage of the condensation process is very important for the prediction of the extent of corrosion in CO₂ injection wells. However, the condensation of water droplets in the supercritical CO₂ phase is still not fully understood. Some authors believe the water droplets condense directly on the steel surface similarly to atmospheric corrosion,¹⁰ while others believe that a variation of temperature or pressure is required for the

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2022 – CO₂ corrosion under supercritical conditions. Peculiar corrosion mechanisms in different Supercritical CO₂ phases (aqueous and gas)

Corrosion of tensile wires covered with PA11 layers in simulated annulus environments at low CO₂ pressure

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Abstract

High-strength carbon steel wires covered with polymer layers were exposed to different test environments simulating the conditions in the annulus of flexible pipes at low CO₂ pressure and flooded with seawater. The polymer layers mimicked the antiwear tapes which are placed in between the steel layers of the tensile armor of the pipes. Specimens without the polymer layer were exposed to the same test environments for comparison and allowed identifying how the presence of the polymer layer influenced the corrosion mechanism. In some of the experiments, oxygen was introduced into the gas mixture to simulate fresh seawater entering the annulus after a breach in the outer sheath. Surface analysis of the corroded specimens after removal of corrosion scales was carried out by scanning electron microscopy, optical profilometry, and confocal microscopy. The polymer layers were observed to have a considerable effect on the corrosion morphology.

KEYWORDS

antiwear tape, carbon steel, CO₂ corrosion, crevice, flexible pipe, oxygen, tensile wire

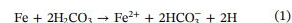
1 | INTRODUCTION

In flexible pipes used in offshore production systems, the tensile armor consists of high-strength steel wires, which correspond to the outermost metallic layers in the cross-section of the pipe (Figure 1). The antiwear layers are placed between overlaying tensile wires to avoid contact and prevent wear. Polyamide 11 (PA11) is commonly used for this purpose.^[1]

If the annulus is filled with water (either condensed water or seawater), an environment that is potentially corrosive to the steel wires is generated. However, because of the annulus configuration, where the ratio of water volume to steel surface area (V/S) is very small, typically below 0.1 ml cm⁻², the accumulation of corrosion products is fast, and saturation is quickly achieved. This leads to the formation of corrosion scales on the steel surface, which can give a varying degree of

corrosion protection to the steel depending on factors such as temperature, water chemistry, and the steel microstructure.

In the flexibles used in gas injection lines, carbon dioxide (CO₂) diffuses from the bore to the annulus through the inner pressure sheath. In the water-filled annulus, carbonic acid (H₂CO₃) is formed as CO₂ dissolves into water. In the absence of oxygen, the steel wires corrode according to Equation (1), producing ferrous ions (Fe²⁺) and an equivalent amount of bicarbonate (HCO₃⁻). Some of the bicarbonate ions dissociate (Equation 2) until equilibrium is reached, and when the concentration of dissolved Fe²⁺ and CO₃²⁻ is high enough, iron carbonate (siderite, FeCO₃) precipitates on the steel surface (Equation 3).



2022 - Interaction of polymeric materials and steel leading to localized corrosion and possible evolution to cracking

SCIENCE SECTION

Corrosion of High-Strength Carbon Steels in Siderite Supersaturated Water at Near Neutral pH

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and José A. Ponciano Gomes^{*}

When carbon steel corrodes in anaerobic carbonated water, and the steel surface area to liquid volume is high, the concentration of ferrous and bicarbonate ions increases rapidly even though the corrosion rate is low. Such solutions with high bicarbonate concentration and a near neutral pH are believed to induce stress corrosion cracking of high-strength carbon steels. This work was conducted to investigate the solid precipitation in siderite supersaturated solutions. It was also an objective to measure the corrosion rate of high-strength carbon steel in solutions with high bicarbonate concentration at pH close to neutral. Preloading the solutions with ferrous ions and bicarbonate made it possible to measure desupersaturation and corrosion rate as function of time. The initial siderite supersaturation was more than 1,000 in the desupersaturation experiments. Despite this, the nucleation and growth of siderite was so slow that the solutions remained supersaturated for 100 h to 500 h at 10°C to 25°C. The ferrous ion concentration decreased from 1,200 mg/kg to 100 mg/kg in less than 24 h at 40°C, but did not reach equilibrium within 250 h. The precipitate was siderite at 5°C to 25°C. At 40°C, the solid was a mixture of siderite and chukanovite in low salinity water and siderite with dissolved Ca²⁺ in artificial seawater. The corrosion rate of carbon steel at pH 6.7 to 7.2 at 25°C decreased to less than 0.01 mm/y in 5 h. Siderite precipitated and grew to a thin protective layer at the steel surface. Even though the solutions were highly supersaturated with respect to siderite throughout the experiments, the carbonate layer at the steel surface did not grow to more than 5 μm thickness during 250 h to 400 h. The investigated steels were armor wires for flexible pipes. They have an oxide layer at the surface which is an inherent result of the manufacturing process. The presence of these oxides did not impede the formation of protective siderite layer.

KEY WORDS: annulus, CO₂ corrosion, flexible pipe, near neutral pH, siderite, stress corrosion cracking

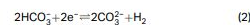
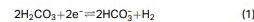
INTRODUCTION

Various industries use coatings and insulation to minimize corrosion. However, corrosion is seldom eliminated as corrodents may enter manufacturing defects and delamination voids. Corrosion in such occluded spaces is characterized by a limited supply of water and a fast buildup of corrosion products.¹⁻²

Flexible pipes are extensively used as risers and flowlines in offshore oil and gas production systems. They have armor wires of high-strength carbon steel in a confined annular space between an inner and outer polymer sheath. During operation, water from the bore may diffuse through the inner sheath while damage to the outer sheath or improper sealing will result in seawater ingress.³⁻⁶ Diffusion of CO₂ and H₂S from the bore through the inner polymer sheath increases the corrosivity of the water in the annulus.

When CO₂ diffuses through the inner sheath it maintains a low, but significant, concentration of CO₂ and carbonic acid in the water phase in the annulus. Although at lower concentration than in the bore, it may cause significant corrosion of the carbon steel wires. The corrosion reactions are probably the same as encountered at higher CO₂ concentrations, but their

relative contribution to the corrosion rate can be different. The cathodic and anodic reactions considered are given in Equations (1) through (5).⁵⁻⁹



The cathodic reactions either consume acid or produce alkali. If the alkaline corrosion products accumulate, the pH of the water in the annulus will increase and reach neutral pH (6.5 to 8.5).¹⁰⁻¹⁶ The V/S ratio (i.e., the relation between the free volume in the annulus [V] and the surface area of the carbon steel wires [S]) is commonly less than 0.1 mL/cm². So, even a low corrosion rate will result in a fast increase of Fe²⁺ and HCO₃⁻

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2021 Physicochemical conditions leading to Near Neutral SCC susceptibility in confined conditions of CO₂ corrosion – assumed to be one basic requirement for SCC CO₂

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Hydrogen embrittlement of API 5L X65 pipeline steel in CO₂ containing low H₂S concentration environment

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ABSTRACT

The basic corrosion mechanisms in CO₂ environments are widely investigated and reported by scientific community. However, cracking failure mechanisms in CO₂ environment or in environments where CO₂ coexist with other gases need a better understanding. Cracking susceptibility of API 5L X65 in pure CO₂ was recently reported and the basic mechanism was attributed to hydrogen embrittlement. The influence of hydrogen permeation and the detrimental effect of cathodic polarisation support the assumption of hydrogen embrittlement as the determining factor for the loss of plasticity and strength. The loss of strength of an API 5L X65 steel when CO₂ and H₂S coexist in the same environment is the focus of the present work. Hydrogen embrittlement (HE) and hydrogen induced cracking (HIC) of pipeline steels are failure modes expected to occur in CO₂ with traces of H₂S environments. The present work aims to approach the performance in laboratory of an API 5L X65 steel in CO₂ with traces of H₂S environment (slightly sour), using as baseline the performance of the material in pure CO₂ environment (sweet), already reported. Hydrogen permeation and Slow Strain Rate Tests (SSRT) were carried out in CO₂ environment containing low concentration of H₂S. It was observed that traces of H₂S in CO₂ environment promote much more intense hydrogen permeation, much higher than in purely CO₂ environment. Loss of ductility was also much more severe than in CO₂ environment, with and without the influence of cathodic polarisation. Hydrogen generation enhancement promoted by traces of H₂S in solution, corresponding to an average content of 21 ppm in solution, had a heavy effect on hydrogen embrittlement of the steel, confirmed by the lower ratio of reduction in area (RRA) and time to fracture in comparison with sweet service conditions.

1. Introduction

Carbon pipeline steels are exposed to severe operational conditions and the hydrogen embrittlement susceptibility is a primary concern for the material selection in oil and gas production and transport [1]. The growing demand of oil and gas industry support the search of low-cost and safe transport systems. The development of high-strength carbon steel pipelines is necessary in order to significantly reduce the total cost of long-distance oil and gas pipelines. However, there is a strong concern about the environments in which these pipelines are employed, owing to the presence of aggressive ions, such as Cl⁻, and gases as CO₂ and H₂S [2]. CO₂ corrosion (sweet corrosion) and H₂S corrosion (sour corrosion) in aqueous solution are among the most severe problems for oil and gas industry. CO₂ gas present in oil production or transport is used to enhance the oil recovery. Nevertheless, this gas reacts with the brine

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2021 - EAC results in mixed H₂S/CO₂ environments, showing different hydrogen embrittlement mechanisms. Potential control within immunity corrosion domain



Assessment of hydrogen embrittlement severity of an API 5LX80 steel in H₂S environments by integrated methodologies



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ABSTRACT

High strength steel, as API 5L grade X80 and above, have been applied in pipelines for sour service in oil and gas industry. Hence, comes the concern about the risks comprising hydrogen diffusion and embrittlement due to combined effect of operational conditions and corrosive environment containing hydrogen sulphide (H₂S). Many efforts have been made to predict and understand the mechanisms involving hydrogen embrittlement under applied strain, nonetheless they are still not entirely understood. Furthermore, the growth of iron sulphide scales can influence on the diffusion process. This study investigates the behaviour of the API X80 steel concerning hydrogen absorption in solutions with different concentrations of H₂S, by integrating different test methodologies at static and tensile conditions. It aims to evaluate hydrogen embrittlement susceptibility of the steel by means of hydrogen permeation and slow strain rate tests and a new complementary image processing methodology. Particularly, the embrittlement phenomenon is studied alongside with iron sulphide film influence as a protective barrier to hydrogen entry in sodium thiosulphate brines containing up to 10 ppm of H₂S. Investigations by means of electrochemical impedance spectroscopy and surface analysis indicated that exists a relationship between different concentrations of H₂S, scale precipitation and its barrier protectiveness to hydrogen uptake. It was observed a diminution of hydrogen permeation through the steel due to formation of mackinawite, however under tensile stress the film breakage may allow not only hydrogen diffusion into the steel, but also the occurrence of hydrogen embrittlement.

1. Introduction

H₂S present in oil and gas sour fields can affect the metallurgical properties of structural steels, such as its ductility, which results in loss of mechanical properties. Hydrogen embrittlement is a relevant process that can lead to catastrophic pipeline failures. Operational conditions of the pipelines, such as high temperature, high pressure and flow conditions, together with the presence of hydrogen, results in the scenario required for the occurrence hydrogen embrittlement (HE) and hydrogen induced cracking (HIC). Each year, tens of millions of dollars are expended to replace or repair pipelines and vessels that suffer excessive localized corrosion, stress corrosion cracking (SCC) or hydrogen embrittlement (HE) degradation processes [1].

During the past decades much effort has been made in order to achieve a better understanding of the embrittlement phenomena, and how to prevent it [2,3]. Still, up to now these mechanisms are not fully understood due to the high number of driving variables

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2020 – Several integrated techniques to assess hydrogen embrittlement susceptibility – mechanical tests in corrosive environments, hydrogen diffusion, including image processing tools.

2020 – Similar experimental approach in pure CO₂ environment carried out under cathodic polarization using mechanical tests, hydrogen diffusion to confirm the influence of hydrogen



Cracking mechanism in API 5L X65 steel in a CO₂-saturated environment – Part II: A study under cathodic polarisation



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ABSTRACT

The aim of this work is to achieve a better understanding of hydrogen effect in CO₂ environments, isolating its contribution by imposing cathodic polarisation on Hydrogen Permeation (HP) and Slow Strain Rate Tests (SSRTs). The influence of Fe₃C and FeCO₃ layers on hydrogen embrittlement (HE) susceptibility was a specific focus of this study. The results indicate that CO₂ environment generates hydrogen, which permeates through steel, although in lower amount compared to H₂S environments. Moreover, in Fe₃C-rich surface, the HP current achieves values higher than in wet-ground surface. Furthermore, in FeCO₃-filmed surface HP current is higher at the beginning of the test but decreases over time. The results of SSRT show the loss of ductility of the steel under cathodic polarisation that was driven by hydrogen and the embrittlement effect magnitude depends on the surface condition, indicating that a pre-corroded steel surface can raise the HE susceptibility in a CO₂ environment.

1. Introduction

Carbon steel pipelines are widely used due to their high yield strength while maintaining enough ductility as required by structural materials [1]. Pipeline steels must have high strength and fracture toughness as well as provide an economical and safe option to transport oil and natural gas along far distances [2–4]. However, carbon steels are susceptible to uniform corrosion in aqueous environments [1] being CO₂ corrosion one of the major integrity issues for the oil and gas industry. Also known as “sweet corrosion”, this particular degradation mechanism has been reported to cause 25% of safety incidents. It has been associated with damage by both general and localised corrosion. Furthermore, the presence of corrosion products/films has been shown to have a significant effect on the corrosion mechanism [5,6]. Transgranular Stress Corrosion Cracking (TGSCC) has been studied and related to environments with CO₂ as a main contaminant [5]. Among the determining factors of TGSCC is hydrogen embrittlement. It is known that the application of a cathodic potential below the thermodynamic equilibrium potential H/H^+ ensures the hydrogen generation in metallic interface. Based on this, Asher [7] examined the effect of hydrogen on mechanical properties of pipeline steels by using slow strain rate tests. Initial tests were conducted in the standard TGSCC environment with the application of cathodic polarisation to ensure that hydrogen would be generated at the steel surface and then would permeate into the steel test specimens. Increased hydrogen generation on the steel surface by cathodic polarisation resulted in a reduction of deformation to failure, thereby indicating loss of ductility. As previously mentioned, further important aspect to be understood in CO₂ corrosion is the influence of corrosion products formed on the carbon steel surface. In CO₂-saturated aqueous environment, the formation and precipitation of iron carbonate (FeCO₃) and iron carbide (Fe₃C) enrichment can occur [8] and these layers can be protective or harmful for the pipeline steel.

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Analysis of the use of environmentally friendly corrosion inhibitors for mild steel in a carbon dioxide saturated chloride solution via experimental design

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In the oil and gas industry, carbon dioxide (CO₂) gas dissolved in produced fluids can cause both general and localized corrosion of carbon steel pipelines due to the speciation of carbonic acid. To mitigate corrosion, the injection of inhibitors into the production fluid is one of the most commonly used methods. However, recent changes in regulations has resulted in a requirement for the development of new corrosion inhibitors that conform to European regulations. This paper presents a full two-level factorial experimental design approach to study individual effects of environmentally friendly classed inhibitor components (phosphate ester, imidazoline, and quaternary amine derivatives) as combined inhibitors and their interactive effects on carbon steel corrosion processes in CO₂-saturated 3.5 wt.% NaCl brine. Through the application of in situ electrochemical monitoring, post-test interferometry, and scanning electron microscopy (SEM) it was possible to determine the influence of each component within the blends and their effect on both general and localized corrosion. Based on 24 h experiments, the phosphate ester derivative reduced general corrosion rate in all blends; imidazoline derivatives reduced the uniform corrosion rate only when it was at the high level in the blend; and the quaternary amine derivative promoted pitting on the surface.

KEYWORDS

carbon dioxide corrosion, corrosion inhibitors, environmentally friendly chemicals, imidazoline, mild steel, phosphate ester, quaternary ammonium salt

1 | INTRODUCTION

Internal carbon dioxide (CO₂) corrosion of carbon steel pipelines is a serious and costly problem in the oil and gas industry.^[1] Carbon steels are extensively used in this industry, despite being highly susceptible to corrosion under these conditions.^[2] This is a result of their low cost and high level of availability. CO₂, generally present in the fluid produced in the form of dissolved gas, is an influential component in oil field production fluids and its presence permits the formation

of carbonic acid, a weak acid which can result in significant levels of corrosion, unless appropriately mitigated.^[3–5]

Among the different forms of corrosion control, the application of inhibitors is one of the most common methods, being widely used in oil and gas production systems in order to control internal corrosion of carbon steel structures.^[6–7] Such chemicals can be administered through continuous injection, batch treatment, or squeeze treatment. Traditional inhibitors tend to consist predominantly of nitrogen-containing compounds (imidazolines, amines,

2019 – Corrosion inhibitor (green) as mitigation technology in CO₂ environments.



Cracking mechanism in API 5L X65 steel in a CO₂-saturated environment



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Pipe-line failures

ABSTRACT

Hydrogen charging in low alloy steels poses a significant problem in the oil and gas industry. Detrimental hydrogen effects are not commonly expected in CO₂ aqueous environments. However, the acid nature of these environments and the high corrosion rates expected justify the assessment of cracking susceptibility of carbon steel in a CO₂-saturated environment as presented in this work. The focus of this investigation is to understand how different surface films/corrosion products influence the hydrogen permeation and cracking mechanism of an API 5L X65 carbon steel in a saturated CO₂ environment. The experiments were carried out to assess hydrogen permeation at open circuit potential on steel samples which were either wet-ground, or pre-filmed with iron carbide (Fe₃C) rich or iron carbonate (FeCO₃) layers. Tafel measurements were also performed to determine the effect of the surface composition on the cathodic reactions. Slow strain rate tests (SSRT) were conducted in order to evaluate the effects of hydrogen on the cracking mechanisms of the steel in this sweet environment. Results indicated that at open circuit conditions, Fe₃C was able to increase the steady state hydrogen permeation current due to accentuation of the cathodic hydrogen-evolution reaction. Although FeCO₃ suppressed the cathodic reaction at the steel surface, the development of the protective and densely packed crystalline layer increased hydrogen uptake marginally from that of the ground steel reduced. SSRT indicated a very moderate loss of ductility in wet-ground and FeCO₃ steel surface conditions. However, a more significant reduction in area was observed in the tests carried out on Fe₃C rich samples. These results imply that a corroded API 5L X65 steel surface in a CO₂ rich environment can enhance the hydrogen embrittlement (HE) susceptibility and as such, hydrogen permeation susceptibility needs to be considered in material selection.

1. Introduction

Carbon steel pipelines play an extremely important role throughout the world as a transporting system of oil and gas over long distances from their sources to ultimate consumers. Under specific operating conditions, the risk of hydrogen embrittlement of steels can be one of the primary concerns. CO₂ is known for its strong impact on corrosion. Besides its impact on global electrochemical kinetics, CO₂ might also have a direct contribution to the hydrogen charging mechanism [1], seeing that is well-known that in

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2019 - Cracking in pure CO₂ environments is possible even with low carbon steels (API X65) and hydrogen is part of the cracking mechanism behind.

APPLIED ELECTROCHEMISTRY - INTEGRITY MANAGEMENT

760 Jambo, Freitas and Ponciano

Materials and Corrosion 52, 760–765 (2001)

Assessment of hydrogen permeation on steels by a simplified device using two electrode configuration based on passive interfaces

Beurteilung der Wasserstoffpermeation an Stahl mit Hilfe einer vereinfachten Zwei-Elektroden-Anordnung mit passiven Grenzflächen

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and J. A. C. Ponciano

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Electrochemical Treatment of Oil Refinery Wastewater for NH₃-N And COD Removal

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Scanning photoelectrochemical analysis of hydrogen permeation on ASTM A516 grade60 steel welded joints in a H₂S containing solution

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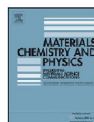


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Evaluation of anode materials for the electro-oxidation of ammonia and ammonium ions

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Preparação e uso de polímeros sólidos como eletrólito em sensores de hidrogênio

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APPLIED ELECTROCHEMISTRY - INTEGRITY MANAGEMENT



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United States Patent [19]
Jambo et al.

[11] **Patent Number:** 5,858,204
 [45] **Date of Patent:** Jan. 12, 1999

- [54] **ELECTROCHEMICAL SENSOR AND PROCESS FOR ASSESSING HYDROGEN PERMEATION**
- [75] Inventors: **Hermano Cezar Medaber Jambo, José Antônio da Cunha Ponciano Gomes**, both of Rio de Janeiro, Brazil
- [73] Assignee: **Petroleo Brasileiro S.A.:Petrobras**, Rio de Janeiro, Brazil
- [21] Appl. No.: **615,885**
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|---------------|------|--------|--------------|
- [51] **Int. Cl.⁶** **G01N 27/26**
- [52] **U.S. CL** **205/775, 204/400, 205/790.5**
- [58] **Field of Search** **204/400, 404, 205/775, 775.5, 776, 776.5, 777, 790.5**

WO8303007 9/1983 WIPO .

OTHER PUBLICATIONS

Corrosion 84, Paper No. 237, "Corrosion Monitoring with Hydrogen Probes in the Oil Field" by William H. Thomason, 13 pages.

Corrosion 91, Paper No. 444, "Electrochemical Noise for Detection of Susceptibility to Stress Corrosion Cracking" by E.A. Eden, et al., 13 pages.

Primary Examiner—T. Tung
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[57] **ABSTRACT**

An electrochemical sensor designed to be employed in equipment of petrochemical plants made of an electrochemical cell without polarization which includes an outer tube or first electrode and an internal rod or second electrode. Both first and second electrodes being provided with wires for external electrical contact. The first and second electrodes being separated by a standard electrolytic solution for the oxidation of the nascent hydrogen which is generated by the corrosion reactions caused by sulfur compounds in contact with the hydrogen-permeable metal which constitutes the equipment of petrochemical plants. The sensor is coupled to a zero resistance ammeter which assesses the electrical current generated by the oxidation of the nascent hydrogen and provides a plot of electrochemical noise.

14 Claims, 3 Drawing Sheets



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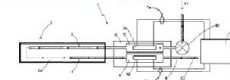
(54) **Título:** SISTEMA PARA DETECÇÃO E MEDIÇÃO DE FLUXO DIFUSIVO DE HIDROGÊNIO PERMEADO E DISPOSITIVO DETECTOR DE HIDROGÊNIO PERMEADO

(51) **Int. Cl.:** G01N 17/02; G01N 27/00

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(57) **Resumo:** SISTEMA PARA DETECÇÃO E MEDIÇÃO DE FLUXO DIFUSIVO DE HIDROGÊNIO PERMEADO E DISPOSITIVO DETECTOR DE HIDROGÊNIO PERMEADO, mais precisamente, trata-se de um sistema (1) que permite monitorar a deterioração de equipamentos (E1) através da detecção da difusão do hidrogênio oriundo das reações de corrosão do aço. O sistema (1) é formado num circuito fechado composto por uma sonda (2), a ser montada na parte interna ou na superfície externa do equipamento (E1); a sonda (2) mantém uma entrada de ar (A1) atmosférico, proveniente de bomba de ar (B1) e uma saída de mistura de ar com arraste de hidrogênio (A2); tubos capilares (3) e (4) associados à entrada de ar (A1) e saída de mistura de ar/hidrogênio (A2) são interligados a correspondentes termorresistores (3a) e (4a), cada qual disposto em uma cavidade independente (5) prevista em um bloco de posicionamento (6); a mistura de ar/hidrogênio (A2) é conduzida a um termorresistor especialmente montado com conexões elétricas formando um circuito eletrônico em ponte de Wheatstone; o sistema (1) possui uma unidade eletrônica (U1) capaz de efetuar o processamento do sinal dos termorresistores, a c(...)



IMPACTS

- Materials in ageing systems – compliance with new demands - asset integrity, EAC stability.
- Impact of materials on ongoing projects – asset integrity, EAC stability and safe conditions. New materials (qualification, NDT tools, repair)
- Alternative electrochemical process – including the use of depolarizers and alternative energy sources.
- Alternative (tailored) materials for hydrogen production, separation and storage.
- Follow-up the Green Energy Era – just in case

KNOWLEDGE INTEGRATION

- **ELECTROCHEMISTRY**
- **MATERIALS SCIENCE**
- **NUMERICAL MODELLING**
- **NDT**
- **SIGNAL PROCESSING - DIGITALIZATION**
- **ARTIFICIAL INTELIGENCE – DATA AND TEXT MINING**
- **OTHERS**

Thanks for your time and
attention!!