



Corrosion of Carbon Steel in Presence of Mixed Deposits Under Stagnant Seawater Conditions on Block 2/05

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The present study assesses the performance of Channeling the corrosion of steel pipelines used for offshore water injection pipelines can be severe. Microbiological corrosion and sub-deposit corrosion are suspected. Samples of semi-tube steel with mixed deposits of magnetite, calcium carbonate and marine sand exposed to almost deoxygenated seawater, with a more severe corrosion of pot under the deposits than anywhere else. The addition of nitrates, used in practice to control bacterial production of H₂S in oil reservoirs, resulted in more aggressive localized corrosion under the deposits. This has implications for the management of the water injection pipeline.

1. Introduction

The exploration and research activity of hydrocarbons began in Angola in 1910. That year, the Company was granted Canha & Formigal, an area of 114,000 km² in the Offshore in the Congo Basin and the Kwanza Basin, being the first well drilled in 1915.

The Pema (Mining Research Company of Angola) and the Sinclair (U.S.A.) were also involved, from an early age, in the prospecting and research activity in Angola. After a brief stoppage, in 1952 the activity was restarted, with the concession to Purfina of the same area added to its extension on the Continental Shelf in 1955.

Also in 1955, occurred the first commercial discovery of oil, made by Petrofina in the Kwanza valley. In partnership with the colonial government, Petrofina created Fina Petroleum de Angola (Petrangol) and built the Luanda Refinery for crude oil processing.

In 1962, Cabinda Gulf Oil Company (CABGOC) carried out the first seismic survey of the Cabinda Offshore and in September of that year the first discovery was made. In 1973, oil became the main export. In 1974, production reached 172,000 bpd, the maximum of the colonial period. In 1976, total production was around 100,000 bbl/d and came from three areas: Cabinda Offshore, Kwanza Onshore and Congo's Onshore.

During the period of 1952–1976, 30,500 km of seismic surveys were carried out, 368 exploration and research wells were drilled and 302 development wells. In this phase, a total of 23 fields were discovered, three of which were in the Atlantic range.

The Offshore Block 2/05 located in the Province of Zaire, Soyo region located in the north of the country, on the border with the Congo Republic, according to the projections of the National Institute of [Statistics](#), has a territorial area of 5 572 km². It is the only Angolan municipality that is more populous than the capital municipality of its province, surpassing [Mbanza Congo](#).

Starting production in 1981 has 18 oil fields with reserves combined of more than 500 million barrels. The production-estimated potential is too much of 40,000 bpd. Of the 18 fields, 17 are developed and one continues to develop. The oil is there, the wells were perforated and are capable, but platforms have some integrity issues.



Figure 1. General Angola Map (Internet: [https://pt.m.wikipedia.org/wiki/Zaire_\(prov%C3%ADncia\)](https://pt.m.wikipedia.org/wiki/Zaire_(prov%C3%ADncia)) Deepwater exploration began in 1991 with the award of Block 16, followed by Blocks 14, 15, 17, 18 and 20.

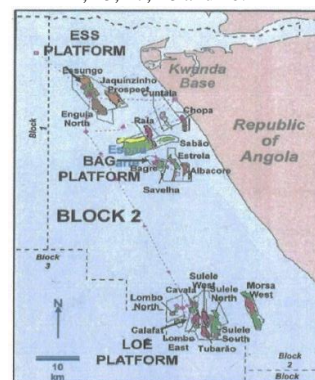


Figure 2. Block 2/05 - Map Oil and Gas (POLIEDRO, Shareholder company in Block 2)

Pipelines are widely used in the oil and gas industry as it is the most economical and viable choice for the transportation of materials such as oil and gas, hydrocarbons, seawater, produced water and other materials associated with the process of exploration, transportation, refining and storage in the oil and gas industry (Shahriar et al., 2012). A major threat to the management of pipeline safety in oil and gas production is corrosion that represents about 20% - 40% of the recorded pipeline failure incidents

(Palmer and King, 2004), more specifically, 81% of corrosion failures are caused by internal corrosion. Internal corrosion can cause a severe reduction in thickness and reduce the mechanical capacity of pipelines (Chen et al., 2014). In addition, opposition corrosion is considered one of the most dangerous forms of corrosion in offshore structures. The development of opposition corrosion could also result in pipeline drilling and, consequently, cause considerable human, environmental and economic losses if the materials are toxic and flammable (Bhandari et al., 2015).

Water injection is an important process in the offshore oil industry to inject seawater (and other waters) into oil reservoirs to promote secondary oil recovery. Water injection pipelines (WIPs) are typically carbon steel. The internal pressure is usually in the range of 200–250 bar, water flow speed in the range of 1–5 m/s and temperature in the range of 10–60°C.

Internal corrosion is a potentially serious problem and for pipelines it is often associated with microbiologically influenced corrosion (MIC). To try to control corrosion, water is usually deoxygenated, before injection, about 20 ppb of oxygen. It is also filtered and treated with biocides.

Pipelines are usually tramped, regularly or irregularly, in an attempt to remove internal rust from the surface and a proportion of any microbiological deposits. However, field experience shows that these techniques do not completely eliminate corrosion. It's concern some pipelines, but certainly not all, eventually show strong internal corrosion in the lower position or 6 hours, often extending along most of the length of the pipeline (Heidersbach and van Roodselaar, 2012).

This type of corrosion, occurs, much more serious than anywhere else around the circumference of the pipeline. It is known as several-channeled corrosion, 6-hour corrosion, lower line corrosion, or grooving corrosion. Failure caused by corrosion conduit is not uncommon. A Joint Industry Project investigated 23 North Sea water injection pipelines in 1997 (Maxwell, 2006). The analysis indicated that 9 (39%) of the pipelines failed due to corrosion channeled at the 6 o'clock position. Pipeline drilling also has been observed, although these pipelines have served for 4 to 15 years, although the design life is typically 20 to 25 years.

An observation on the ground during the decoking operations shows evidence of accumulation of deposits at the 6 o'clock position. This suggests that sub-deposit corrosion (UDC) may be involved and that it may be responsible for channeling corrosion. Observations on discharge disc coupons, mounted on the walls of pipelines near the flow end, usually shows pronounced evidence of bacterial species and thus support the proposal that channel corrosion perhaps also associated with MIC (Heidersbach and van Roodselaar, 2012). However, at the moment there is no agreed mechanism to explain the phenomenon of channeled corrosion, although an initial proposal has been made (Comanescu et al., 2016).

In normal operations, water flow conditions are likely to be turbulent, not allowing the deposition of suspended solids. However, during maintenance or replacement work, the water speed can be very low or even stagnant, thus allowing the deposition of suspended solids at the bottom of the ducts. The deposits typically contain corrosion products (magnetite and iron sulphides), calcium carbonate and sea sand (Comanescu et al., 2012). As mentioned, these are considered to be the creation of adequate conditions for the corrosion of the sub deposit and also local environments suitable for microbiological activity and potentially for MIC (Dumie et al., 2005).

The classical conditions considered responsible for the corrosion of the sub deposit include concentration cells (Hinds and Turnbull, 2010), defects in protective coatings, failure of corrosion inhibitors that reach the metal surface, metabolism of aggressive microorganisms (Tan et al., 2011) and galvanic action between the previous corrosion product and the metallic surface (Han et al., 2013). As a result, most studies considered the efficiency of corrosion inhibitors in deposits (de Reus et al., 2005; Turnbull et al., 2003) or galvanic effects (Pedersen et al., 2008; Tan et al., 2011; Zhang et al., 2012). Several investigations also indicate that the physicochemical characteristics of the deposits significantly influence the corrosion process below the deposits (Boivin et al., 2011; Huang et al., 2010; Standlee et al., 2011; Xue et al., 2011). These studies largely considered CO₂ environments, such as oil production pipelines.

MIC is usually attributed to sulfate reducing bacteria (SRB) (Little and Lee, 2007). However, other species may be involved, including sulfur oxidizing bacteria (SOB), iron reducing bacteria (IRB) and manganese oxidizing bacteria (MOB) (Zhang et al., 2003). All are known to contribute to localized corrosion, including slit beading and crack corrosion (Little and

Lee, 2007; Beech and Sunner, 2004). The accumulation of corrosion products on the metal surface is generally considered to be providing the anoxic conditions necessary for anaerobic bacteria (Jeffrey and Melchers, 2003; Melchers, 2007).

Oil and gas reservoirs subjected to water injection often generate H₂S, as a result of the presence, inside the reservoirs, of SRB. This tends to inhibit the water injection process as well as being an undesirable component of the oil produced (or gas). Extra nitrate boosts the metabolism of nitrate-reducing bacteria (NRB) within the reservoir and potentially allows them to overcome SRB for organic electrode donors (Eckford and Fedorak, 2002). NO₃ - reduction products that in still the SRB (Greene et al., 2003; Nemati et al., 2001) or to make the functionality of the SRB go from reducing SO₄²⁻ to H₂S to reducing NO₃ - to NH₄ + (Schwermer et al., 2008). However, the addition of nitrate to the injection water at the wip current flow end was associated with increased corrosion of the pipeline (Schwermer et al., 2008). This possibility is supported by reports of several cases of failure (Beeder et al., 2007; Halim et al., 2011; Stott, 2012) and also by recent field data from North Sea WIPs that indicated that pipelines carrying nitrate-treated seawaters suffered more severe channeled corrosion than those without nitrate injection (Comanescu et al., 2016). More generally, this scenario is also consistent with the findings of mild steel samples exposed to natural seawater that showed increased long-term corrosion loss in the presence of dissolved inorganic nitrogen (DIN) (Melchers, 2014a).

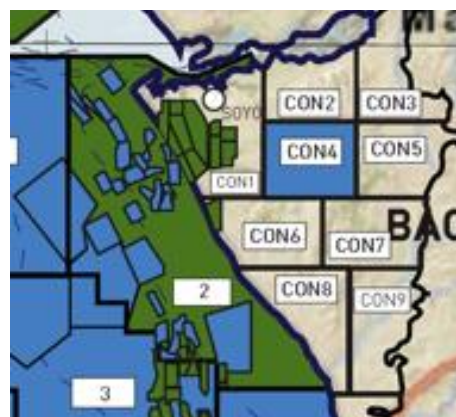


Figure 3. Block 2/05 – Map site Location (Internet: www.sonangol.co.ao)

The surface inside the tube can also be a factor. For corrosion experiments, steel coupons generally receive a well-defined surface topography (e.g. highly polished surfaces) for repeatable and reproducible experimental results. However, these surfaces may not represent those of materials in service (Hinds et al., 2013). In the case of stainless steels, surface roughness is a known factor that influences the initiation and propagation of oposures (Burststein and Pistorius, 1995; Hong and Nagumo, 1997; Sasaki and Burststein, 1996). In the case of carbon steels exposed to natural seawater, surface roughness affects corrosion only in the early stages of exposure (Melchers and Jeffrey, 2004). In biotic environments, the surface condition can influence biofilm adhesion and thus influence MIC (Hilbert et al., 2003). This suggests that surface roughness may also be a factor in channeling corrosion. In addition, for pre-corroded (i.e., rough) and rust-covered surfaces, it has been proposed that MIC may not be necessary and that very aggressive corrosion can occur in abiotic conditions as a result of aggressive autocatalytic reactions under anoxic conditions (Melchers, 2014b).

To date, the causal mechanism of the phenomenon of piped corrosion is not yet fully understood, although it is frequent in practice and leads to a major threat to the safety of oil and gas production. It is well known for carbon dioxide materials exposed to seawater, several operational factors (oxygen, temperature, biological activities) are considered to lead to specific types of corrosion. In some cases, the only theory is insufficient to explain the complex phenomenon of corrosion, especially with regard to long-term corrosion in specific environments (Bhandari et al., 2015). Therefore, the investigation of the phenomenon of corrosion, taking into account the in-depth influence factors to improve understanding of the principles of corrosion, has practical implications for ensuring the safety and reliability of the equipment and for the management of industry corrosion (Thodi et al., 2010).

This project aims to distinguish the relative contributions to the phenomenon of corrosion channeled under simulated conditions of stagnation for a water injection system. It is a pilot laboratory study using carbon steel samples in mixed deposits and nearly deoxygenated seawater conditions. The presence of mixed deposits (magnetite, calcium carbonate and marine sand), nitrate treatment and surface roughness of steel samples is considered.

The following section describes the test platforms and design details of the half-tube steel samples that have been exposed to simulated field conditions for 180 days. The following section reports electron microscopy (SEM) and X-ray spectroscopy (EDS) of energy dispersion of corrosion products and the surface morphology of steel samples characterized by optical microscopy. The pit depths were measured by the variable linear digital differential transformer (LVDT).

The final section discusses the findings and their implications for a better understanding of the channeled corrosion process and influencing factors. In practice, some comments are made on the management of wip corrosion.

2. Methodology

2.1. Test platform and test environment

Identical test vessels were constructed to expose half-tube samples to different test environments. Each test ship was constructed from two steel drums (Drum Reconditioners, Australia) placed end-to-end and welded

together to obtain vessels 1.7 m high, 0.58 m in diameter and 400 litres of seawater capacity. The interior surface of each ship has been coated with international epoxy paint® (KGB Pty Ltd, Australia) to prevent internal corrosion. The inner surface of the test vessels and lids was sterilized with diluted ethanol (Chem-Supply®, Australia) and deionized water before being filled with the seawater test. The temperature in each test environment was maintained by a temperature control system consisting of a controller (Omron E5CZ-R2, Australia) and a 500 W aquarium titanium heater (Weipro®, China). The controller, in a plastic enclosure, was fixed to the upper outer wall with a thermocouple (Type T, Omega®, USA) attached to the outside of the vessel as an entrance.

2.2. Half tube Steel Samples

The Half-tube samples were 90 mm long, cut from 60 mm in diameter and 3.9 mm thick API 5L of soft carbon steel (Arrium Steel, Australia) poured in length throughout the diameter. A steel plate was welded at each end of the half-tube samples. Mounting holes of 5 mm diameter were drilled in the plates to accommodate a lifting platform of the fishing line to facilitate the implantation and recovery of half-tube samples to and from the bottom of the test vessels. The outer surface of the samples and both sides of the steel end plates were coated with epoxyink® International (KGB Pty Ltd, Australia) to prevent corrosion. All samples were identified exclusively with clean plastic numbered labels.



Figure 4. General Map Oil & Gas Angola and Congo (Internet: www.apposecretariat.org)

Table 1: Test Environments for exposure of half-pipe specimens (Internet: www.elsevier.com)

Environment	Coupon surface preparation	Water type	Deposit	Chemical treatment
1	(a) acid cleaned (b) grit blasted	Natural seawater	No deposits	Oxygen scavenger
2	(a) acid cleaned (b) grit blasted	Natural seawater	Magnetite, calcium carbonate, sea sand	Oxygen scavenger
3	(a) acid cleaned (b) grit blasted	Filtrated and UV irradiated seawater	Magnetite, calcium carbonate, sea sand	Oxygen scavenger
4	(a) acid cleaned (b) grit blasted	Natural seawater	Magnetite, calcium carbonate, sea sand	Oxygen scavenger, Calcium nitrate

Two types of surface treatment were applied to the interior surfaces of the half-tube samples. The acid cleansing approach is using 16% dilute hydrochloric acid (HCl) (RCI Labscan, Thailand) with 3% tetramine hym ethylene inhibitor [(CH₂)₆N₄] (Chem-Supply®, Australia) to clean the inner surfaces of half-tube samples. This procedure is defined in the corrosion testing standard ASTM G1-03 (2011) and is described elsewhere (Melchers and Jeffrey, 2004). After this treatment, the samples were rinsed in deionized water to remove the residual acid solution followed by diluent ethanol (Chem-Supply®, Australia) sterilization and air drying. The remaining specimens were marketed (KGB Pty Ltd, Australia) to reach Sa 2.5 class surfaces (ISO 8501-1:2007). To do this evenly on all specimens, they were placed and sand blown together by experienced personnel. The samples were then cleaned by deionized water and sterilized with diluted

ethanol, followed by air drying. All samples were stored in a desiccator for a short period of time before being exposed in the test vessels.

Table 2: Chemical composition of steel specimens in wt% (balance Fe) (Internet: www.elsevier.com)

C	Si	Mn	P	S	Cr	Ni	Mo	V	Al
0.12	0.29	1.01	0.017	0.014	0.001	0.017	0.010	0.001	0.022

The Surface characteristics of typical clean and sand-busted surfaces were captured by scanning electron microscopy (SEM) (XL30 Philips®, Netherlands). Fig. 1a and Fig. 1b show that these surfaces are different in characteristics compared to conventional surface finishes obtained by polishing with gr abrasive it papers. Acid-cleaned surfaces are visually smoother than sand surfaces. The latter shows a thick textured surface with localized deformation resulting from the sand detonation process.

2.3. General features of the Corrosion Product Layer

2.3.1. Stratification of the Corrosion Product layer

After several years in natural seawater, a corrosion product layer itself covered by bio fouling covers the surface of carbon steel structures permanently immersed in natural seawater. Figure 1 displays the main features of the layers formed on carbon steel coupons after 6 to 11 years of immersion.

The corrosion product layer can be several millimetres thick, reaching locally a thickness of 1 cm or more. Under the biofouling layer that may incorporate mineral compounds (sand, clay, fragments of shells) and macro-organisms, an orange-brown corrosion product layer is generally seen. This is the outer stratum, mainly composed of Fe(III)-oxyhydroxides (FeOOH). Lying underneath is found the inner stratum, characterized by a black color, that is in contact with the steel surface.

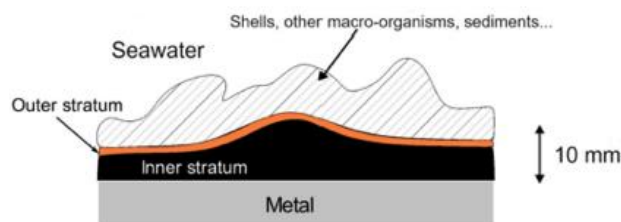


Figure 5. Schematic representation (cross-section) of the layer covering a carbon steel coupon after 6-11 years of permanent immersion in natural seawater

This inner stratum is mainly composed of Fe(II)-based corrosion products, mixed with magnetite Fe₃O₄.

The Fe(II)-based compounds are reactive towards oxygen and the Fe(III)-oxy hydroxides that constitute the orange brown outer layer are the end products of their oxidation by dissolved O₂. After 6–11 years in natural seawater, the inner black stratum is much thicker than the orange-brown outer stratum. This demonstrates that the steel surface and the main part of the corrosion product layer are no more reached by dissolved oxygen, i.e., that anoxic conditions are met. This explains why anaerobe microorganisms develop systematically inside the corrosion product layers and influence necessarily the corrosion process, as perfectly illustrated by the phenomenological model proposed by Melchers et al. [17,22]. Dissolved oxygen cannot reach the inner part of the corrosion product layer because the aerobic microorganisms that colonize the biofouling layer and the orange-brown outer stratum consume it. The little oxygen that could possibly reach the dark inner stratum would then react with the Fe(II)-based corrosion products to form FeOOH phases and/or magnetite.

The stratification of the corrosion product layer can be clearly observed as soon as 1 to 2 months of immersion.

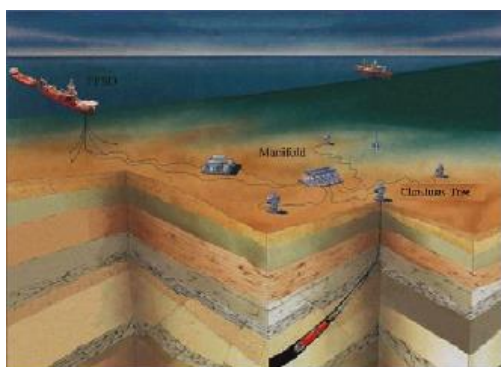


Figure 6. Offshore Field

2.4. Composition of the Corrosion Product Layer

Figure 7 shows the XRD pattern of the corrosion product layer that covered a carbon steel coupon immersed 6 months in natural seawater (Les Minimes marina exposure site, La Rochelle, Atlantic Ocean). The main crystalline solid phases that constitute such corrosion product layers are all detected here. Two Fe(III)-oxyhydroxides, namely goethite -FeOOH and lepidocrocite -FeOOH, are identified.

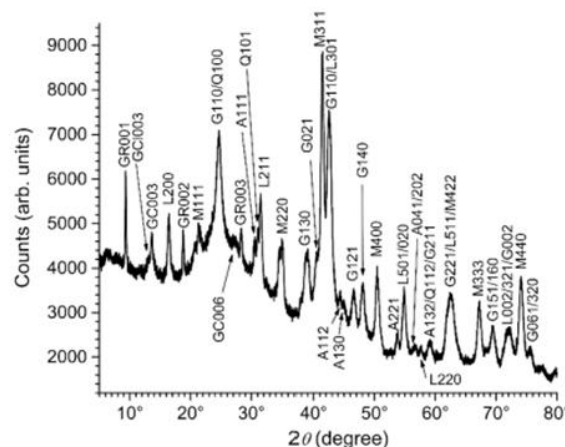


Figure 7. XRD analysis of the corrosion product layer covering a carbon steel coupon after 6 months in natural seawater (Internet: www.elsevier.com)

They constitute the orange-brown outer stratum. Magnetite, the Fe(II,III) mixed-valence oxide Fe₃O₄, is identified too. It is present in the inner dark layer. Magnetite can form in anoxic conditions as shown by thermodynamic data e.g., [49,50]. The overall reaction involves the oxidation of three Fe(0) atoms to one Fe(II) cation and two Fe(III) cations, and the reduction of four water molecules to hydrogen. It can be written as.

This first process explains the formation of magnetite on or close to the metal surface. However, magnetite can also be obtained indirectly as an oxidation product of Fe(II)-based corrosion products at very low oxygen flow rates [51]. This second process explains why magnetite was in some cases mainly detected at the interface between the inner dark stratum and the outer orange stratum [41], where a small amount of oxygen can access after having crossed over the outer parts of the biofouling/corrosion product layer.

3. Results and Discussion

3.1. Formation of Corrosion Products

In-depth research was carried out on carbon dioxide corrosion products under anoxic seawater conditions (Duan et al., 2008; Jeffrey and Melchers, 2003; Lee et al., 2004; Pineau et al., 2008; Refeit et al., 2003; Sherar et al., 2011; Stipanicev et al., 2013). Steel samples in previous work have been exposed to an anoxic test environment created in a laboratory or in natural seawater environments.

The anoxic condition in natural seawater is typically caused by the accumulation of corrosion products that slow the rate of oxygen diffusion to the metal surface for long-term effects (Melchers and Jeffrey, 2008). It should also be noted here that the outer layer of corrosion products immersed in natural seawater contains different minerals compared to the inner layer due to the ingress of O₂ in the outer layer.

Under anaerobic conditions, the structure and evolution of corrosion products are mainly influenced by the local physiochemical environment (pH, temperature and redox potential) (Lee et al., 2004), dissolved oxygen content and possibly microbiological activities (Lee et al., 2004); Melchers and Jeffrey, 2008; Pineau et al., 2008).

In the present work, the results of the EDS of the composition of corrosion products in the environments, regardless of surface roughness, show the dominant presence of Fe, O and S and this is likely to reflect the formation of characteristic iron oxides (magnetite and iron oxyhydroxides), iron sulphides and GR(SO₄2-). These iron minerals are typical of steel corrosion products. Of particular interest is the proportion of S in corrosion products.



Figure 8. Christmas Tree - Subsea Equipment (After 20 years submerge) (Internet: www.cortecvci.com/cortec-corrosion-solutions-available-around-the-globe)

3.2. Industrial Importance

Severe corrosion of the conduit, sometimes observed in offshore water injection pipelines, is presumed to be associated with microbiologically influenced corrosion and that much attention has been paid to this possibility in the practices adopted by the industry (Comanescu et al., 2012; Comanescu et al., 2016; Heidersbach and van Roodselaar, 2012). The potential influence of sub-deposit corrosion has been given much less attention, although there is circumstantial evidence for it from field observations (Heidersbach and van Roodselaar, 2012). The results of current experiments show that the presence of deposits on the metal surface resulted in more severe corrosion and that it also seems to have accelerated the coalescence of the options. This is consistent with previous observations for well development (Jeffrey and Melchers, 2007). Observations on the test environment 3 show that, even in an almost sterile environment, corrosion of steel surfaces covered in mixed deposits was more severe than that which had no deposits and caused deeper fossa. In addition, under

laboratory conditions with the presence of deposits, the addition of nitrate resulted in more severe localized corrosion. In terms of corrosion channeling, the coalescence mechanism of the pits and the development of wells is considered the most likely main cause of the formation of channeled corrosion. Current results also show that MIC may be involved in mixed deposits and with the addition of nitrates. Similar experimental observations were not previously reported.

Although maximum pit depth data obtained from steel samples in current studies only provide information during a single point in time, it clearly shows that the variability of maximum pit depths varied between test environments. As far as industrial practice is concerned, the long-term progression of the maximum pit depth is of particular interest, as the harmful effect of the pits leads to insufficient drilling of pipelines.

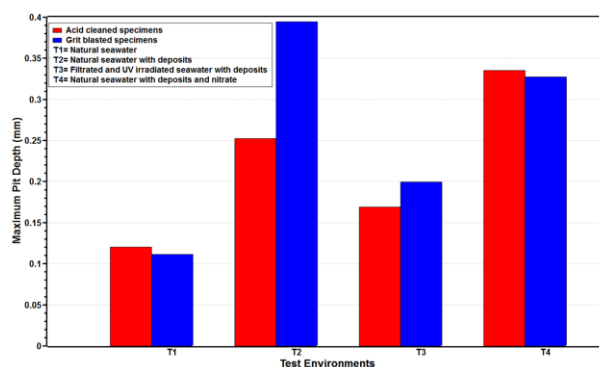


Figure 9. Test Environments (Internet: www.elsevier.com)

Previous studies have shown that the maximum depth of carbon steel exposed to natural seawater for long-term effects follow specific models of extreme value distribution, which is significant for risk assessment of existing corrosive structures (Chaves et al., 2015). However, this is not the focus on the current role and needs further investigation.

Table 3. Typical seawater composition at Taylors Beach (Internet: www.elsevier.com)

Parameter	Units	Typical value	Parameter	Units	Typical value
Alkalinity (CaCO ₃)	ppm(wt)	409-419	Nitrite	ppm (wt)	<0.003-0.011
Ammonia	ppm(wt)	0.017-0.090	pH		8.1-8.3
Calcium	ppm(wt)	374-409	Salinity	ppt (wt)	25.7-31.3
Chloride	ppm(wt)	21,000	Sulphate	ppm (wt)	1600-2,750
Nitrate	ppm(wt)	0.017-0.050	Total phosphorous	ppm (wt)	<0.003-0.07
Temp.(annual mean)	°C	20			

*Long-term range taken over the 10 years, 2000 through 2009, for surface waters (Chaves et al., 2015; Machuca et al., 2014; Melchers and Jeffrey, 2014). Data is obtained from an independent water quality laboratory (Hunter Water Australia).

3.3. Operation and Integrity Management

The function of submarine pipeline systems is to transport a variety of fluids, the submarine pipeline system's ability to operate safely and withstand the loads imposed efficiently and safely during the pipeline lifecycle. If a system loses this ability, a failure has occurred.

• Pipeline integrity is:

Established during the concept, design and construction phases. Transferred from the development phase to the operations phase. This interface involves transfer of vital data and information about the system.



Figure 10. The Integrity Management (IM System)

Maintained in the operations phase:

Risk based pipeline integrity management takes into account:

- Identification of threats and failure modes;
- Estimation of probabilities of failure (PoF);
- Estimation of consequences of failure (CoF);
- Estimation of risk level (CoF × PoF).

Risk assessments are used to focus on the right issues at the right time. It is used to prioritize and schedule activities:

- Provides long-term plans / high level plans.

Inspection and Monitoring:

- Are activities carried out to collect parameter data and information that give indications to the condition / state of the equipment;
- Testing;
- Are activities carried out to test if the system or inherent safety systems have the required structural integrity or are working properly;
- The "Inspection, Monitoring and Testing" activity includes:
 - Detailed planning;
 - Execution;
 - Evaluation;

- Reporting and documentation.

Potentially unacceptable mechanical damage or other abnormalities detected shall be reported as input to the Risk Assessment and Integrity Management Planning activity (where overall plans for more detailed integrity assessments re-qualifications shall be developed).

Within the Integrity Management Process cycle, the “Integrity Assessment” step comprises:

- Planning;
- Data Management;
- Evaluation of integrity;
- Evaluation/identification of corrective actions;
- Report.

3.4. Characterization of corrosion products

All samples recovered from each of the 4 test environments presented wet surface conditions. The SEM micrograms of corrosion products removed from clean acid samples in the four test environments, with some pointed spots, are indicated in Fig. 14.

The scientific term “pitting corrosion” is associated with a local rupture of metal’s passive film in aggressive environment and formation of a pit due to metal dissolution inside, while the rest of the surface remains free of corrosion. For carbon steel, which does not form a protective oxide layer, “pitting” is a localised corrosion attack that takes a form of a cavity on the metal surface. These pits can be originated from pitting corrosion, MIC or erosion corrosion.

Pits initiate and propagate at different moments in time; the propagation rate also varies from pit to pit; and pitting mechanism may differ with time due to local change of conditions, e.g. biofilm and rust layer development, micro-environment formation, etc

The mechanism of pitting attack is still widely uncertain. However, the fact that Melcher’s model also works for corrosion in fresh distilled water, raises an interesting point that degradation of metal occurs according to bi-modal behaviour regardless of availability of microorganisms and chlorides in water. In abiotic water during oxygen-controlled mode, a non-uniform rust layer is forming on the surface causing formation of oxygen-depleted zones within the layer. Pitting corrosion in these anoxic regions. In case of biologically active waters, the localised corrosion is worsening by anaerobic microorganisms flourishing in anoxic nooks. Moreover, research by suggests that pits form in areas with high tensile residual stresses that act as anodic regions.

Table 4. EDS results of emphasized spots on corrosion products removed from acid cleaned specimens in different test environments (wt element) / % after 180 days of exposure (Internet: www.elsevier.com)

Spot	C	O	Na	Mg	Al	Si	P	S	Cl	Ca	Mn	Fe
<i>Test environment 1</i>												
Fig. 4a												
sp1	9.84	22.11	3.82	1.99	0.02	0.3	9.19	9.9	0.09	0.74	0.14	41.84
<i>Test environment 2</i>												
Fig. 4b												
sp2	3.95	28.75	3.52	2.89	0.11	0.14	0.31	10.40	0.60	0.12	0.22	48.97
<i>Test environment 3</i>												
Fig. 4c												
sp3	2.58	23.23	0.75	1.00	0.01	/	1.83	1.06	4.54	1.91	0.47	62.54
<i>Test environment 4</i>												
Fig. 4d												
sp4	0.45	4.59	/	0.45	/	/	1.58	17.87	/	/	0.31	74.76

The characterization of corrosion products of busted sand specimens from all 4 test environments. The overall composition of corrosion products is similar to that found in clean acid samples. The high weight percentage of Fe and O is found in the deposition of corrosion products from all 4 test environments. In addition, it is also in a higher proportion in the teste environment. Morphological examination of corrosion products in the test environment reveals an overlapping hexagonal structure, along with globular particles.

This representative morphology was extensively found in marine corrosion influenced by RBS and is attributed to iron sulphides and GR(SO42-) (Duan et al., 2008; Pineau et al., 2008; Refeit et al., 2003). This is also supported by the results of the EDS that show the simultaneous presence of Fe, S and O. Lower presence of other elements such as Na, Si, Mg, Al, Mn and Cl are also present. It was also found that the peak in the test environment, although it has a smaller presence, shows a greater possession than three other test environments, both for clean acid and grain samples. This suggests the higher amount of calcareous deposition, such as CaCO3 in the test environment (Stipanicev et al., 2013).

3.5. Surface topography

The corroded surface of each half-tube steel sample was examined by optical microscopy and recorded immediately after cleaning the corrosion products. For the test environment with deoxygenated natural seawater, it is clear that there are numerous small individual pits on the clean steel acid surface.

Some of the flat pits to be reconnected with their neighbors, the opposite areas connected with a diameter of approximately 1mm. The busted sand specimens reveal an irregular surface texture with small pits scattered on the surface. In addition, areas of surfaces cleaned of acids free of visible pits appear to be smoother than those of sand-busted samples. Compared to the environment, for which there were no deposits, the surfaces of both the clean acid steel samples and the steel samples busted in a test environment where the deposits were present show a more severe and clear corrosion. For the clean acidic surface, it shows large areas of localized corrosion with the appearance of irregularly shaped “valleys and plains”. This type of corrosion is likely to be the result of coalescence of the developed wells.

The photographs can be interpreted as showing the pits that are in the process of coalescence. In addition, what appears to be new individual and deep insulated wells can be seen on the floor of shallow wide pits. The parts of the original metallic surface that remain after general corrosion. For grain-busted specimens, the surfaces show much more corroded topographies for the test environment. Large graves are evident. Some of these seem to clearly have to co-connect, thus forming larger or wide Pits with obvious seats inside. Similarly, it shows some large insulated wells that can be interpreted as being in the process of coalescing. Such interpretation can also be made for samples cleaned with acid. They show what can be interpreted as incipient coalescence of isolated wells. The number and size of such incipient coalescence appears slightly higher on clean acid surfaces than on sand-busted surfaces, however, the difference is not pronounced. For acid-cleaned samples, the corroded surface presents distinct large and irregular shallow depressions. There is evidence of more recent wells at the base of these shallow depressions. The corrosion attack patterns observed on sand surfaces are only slightly different compared to clean acid samples. These look rounded. Again, the patterns of the broad wells developed on the right part suggest pitting coalescence.

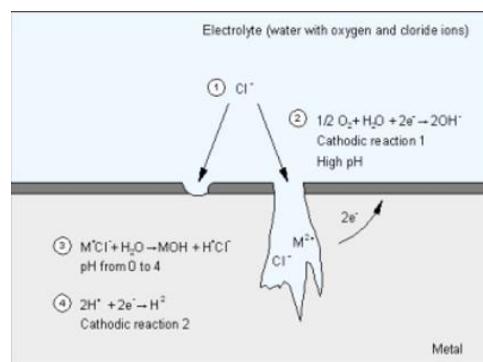


Figure 11. Pite formation occurrence.

In addition, for samples exposed to the test environment (natural seawater deoxygenated with deposits and addition of nitrates), severe and irregular localized corrosion that could be called stepped bench marks were observed along the boundary of deposits of clean acid and grain specimens. The cross-sectional micrograms of the steel surfaces under the larger-widening deposits show the characteristics of pito corrosion in deposits. Regardless of the size and depth of wells with different surface roughness, piting corrosion profiles are consistent that some wells seem to have grown laterally and have to connect with neighboring wells to form wider and deeper pits. The stepped bench marks were not observed in exposed samples.

3.6. Maximum well depth

The depth of the deepest pits obtained from the steel samples exposed in different test environments, there latively, despite the initial surface treatment, the maximum pit depth in the test environments where the mixed deposits were present is higher than that of the test environment 1 without deposits. There is a slight difference in pit depth between clean acid and

grain samples in the test environment 1, 3 and 4, but this is not considered significant.

Table 5. EDS results of emphasized spots on corrosion products removed from grit blasted specimens in different test environments (wt element) / % after 180 days exposure (Internet: www.elsevier.com)

Spot	C	O	Na	Mg	Al	Si	P	S	Cl	Ca	Mn	Fe
<i>Test environment 1</i>												
Fig. 5a sp1	4.42	26.52	0.76	3.00	0.14	0.19	1.13	7.68	1.91	/	/	54.23
<i>Test environment 2</i>												
Fig. 5b sp2	4.14	30.88	1.30	0.33	0.15	0.26	0.18	5.09	4.13	1.37	/	52.17
<i>Test environment 3</i>												
Fig. 5c sp3	4.83	22.14	4.73	1.16	0.17	0.23	8.83	1.17	/	1.58	0.34	54.81
<i>Test environment 4</i>												
Fig. 5d sp4	3.09	17.04	2.20	3.69	0.43	0.84	2.68	15.86	/	0.12	/	54.04

However, the maximum depth of sand samples sprouted in the test environment (natural sea water with deposits) is clearly higher than that of acid cleaning. The deepest well was found from a sample of sand burst in a 2 (0.394 mm) test environment. For acid clean coupons, the deepest well is 0.335mm of the acid clean coupon in a test environment (nitrate added sea water with deposits). The deepest pits on the surfaces of clean acid and grain specimens were.

It is noted that the maximum depth of the ditches demonstrated here is the relative maximum depth of the well, since the metal loss of the total specimen is not considered. The comparison between the test environments of the standard deviation of the 20 maximum depth data of the pits recorded in the steel samples after 180 days of exposure. It is evident that the standard deviations varied between test environments. This means that the variability of maximum pit depths is different between test environments. However, in general, the standard deviations from the maximum depth data of the pits recorded in the samples in the test environments, where the deposits were present, are higher than those of the deposits. This is consistent with optical images that show a considerable difference in surface morphology of steel samples in different test environments.

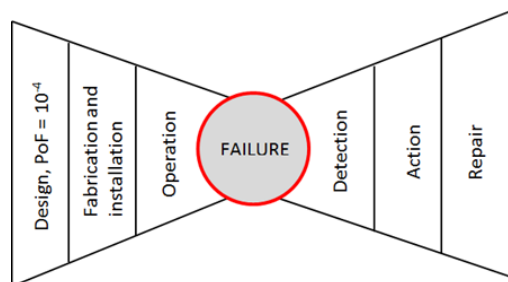


Figure 12. Integrity System

3. Conclusions

The experimental results presented here show that:

- Semi-tube steel samples covered in deposits revealed more severe corrosion than those without deposits. Seawater filtration mitigated the severity of the issue corrosion to some extent, but did not eliminate corrosion. Nitrates have been shown to promote localized corrosion and it has been found that it promoted pronounced "stepped bench" corrosion situated at the limit of the areas covered by the deposits and the discovered areas;
- The corrosion products near the steel surface exposed to untreated natural seawater presented evidence of microbiological activities and were mainly composed of mixtures of iron oxides (magnetite), iron sulphides, sulbed green rust (GR(SO₄)²⁻) and minerals based on Ca. The addition of nitrates promoted the production of iron sulphides. Corrosion products formed under filtration mainly contain iron oxides and (GR(SO₄)²⁻), the number of traces of iron sulphides may exist as a result of abiotic inclusions;
- Opposability corrosion in all test environments found on surfaces revealed a consistent trend of coalescence towards "wide fossa", regardless of the severity of pitting corrosion. This is in line with a previously proposed model for the development of long-term corrosion pits;

iv. Verified that initial surface roughness played a negligible role in the eventual morphology of corroded surfaces under filtered seawater conditions. However, under biotic conditions, the clean acid surfaces showed large shallow depressions and newly formed wells on the floor of the depressions. For the sand-busted specimens, the large, isolated wells prevailed, although some wells were connected to form large "wide pits";

v. The results show that there is potential for a synergistic effect between MIC and sub-deposit corrosion and this can cause more severe localized corrosion. This has implications for corrosion and risk management of the offshore water injection system.

Recognition

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Conflict of interest

The author declares that there is no conflict of interest regarding the publication of this manuscript.

References

- [1] ASTM Standard, G1-03, 2011. Standard practice for preparing, cleaning and evaluating corrosion test.
- [2] Bhandari, J., Khan, F., Abbassi, R., Garaniya, V., Ojeda, R., 2015. Modelling of pitting corrosion in Beech, I.B., 2004. Corrosion of technical materials in the presence of biofilms-current understanding.
- [3] Corrosion Conference and Expo; 2007, March 11-15; Nashville, USA.
- [4] Paper No. 07512. Bødtker, G., Thorstenson, T., Lillebø, B.L.P., Thorbjørnsen, B.E., Ulvøen, R.H., Sunde, E., Torsvik.
- [5] Burstein, G.T., Pistorius, P.C., 1995. Surface roughness and the metastable pitting of stainless steel in chloride solutions. *Corrosion* 51(5), 380-385.
- [6] Comanescu, I., Melchers, R.E., Taxen, C., 2016. Corrosion and durability of offshore steel water injection pipelines. *Ships. Offshore Struc.* 11(4), 424-437.
- [7] Comanescu, I., Melchers, R.E., Taxen, C., 2016. Corrosion and durability of offshore steel water injection pipelines. *Ships. Offshore Struc.* 11(4), 424-437.
- [8] Modeling of Heavy Nitrate Corrosion in Anaerobe Aquifer Injection Water Biofilm: A Case Study in a Flow Rig. *Environ. Sci. Technol.* 48(15), 8627-8635.
- [9] Duan, J., Wu, S., Zhang, X., Huang, G., Du, M., Hou, B., 2008. Corrosion of carbon steel influenced by anaerobic biofilm in natural seawater. *Electrochim. Acta* 54(1), 22-28.
- [10] International Corrosion Conference and Expo; 2011 March 13-17; Houston, USA. Paper No. 11229.
- [11] Heidersbach, K.L., van Roodelaar, A.C., 2012. Understanding, preventing, and identification of microbial induced erosion-corrosion (Channelling) in water injection pipelines. In: NACE.
- [12] Hong, T., Nagumo, M., 1997. Effect of surface roughness on early stages of pitting corrosion of type 301 stainless steel. *Corros. Sci.* 39(9), 1665-1672.
- [13] Chaves, I.A., Melchers, R.E., 2014. Extreme value analysis for assessing structural reliability of welded offshore steel structures. *Struct. Saf.* 50, 9-15.
- [14] Khan, F.I., Amyotte, P.R., 2002. Inherent safety in offshore oil and gas activities: a review of the present status and future directions., *J. Loss. Prevent. Proc.* 15(4), 279-289.

- [15] Melchers, R.E., 2006. Pitting Corrosion of Mild Steel under Marine Anaerobic Conditions-Part 1: Experimental Observations, Corrosion 62(11), 981-988.
- [16] Melchers, R.E., Jeffrey, R., 2004. Surface "Roughness" effect on marine immersion corrosion of mild steel. Corrosion 60(7), 697-703.
- [17] Shahriar, A., Sadiq, R., Tesfamariam, S., 2012. Risk analysis for oil & gas pipelines: A sustainability assessment approach using fuzzy based bow-tie analysis. J. Loss. Prevent. Proc. 25(3), 505-523.
- [18] Stott, J.F.D., 2012. Implementation of Nitrate Treatment for Reservoir Souring Control: Complexities and Pitfalls. In: SPE International Conference and Workshop on Oilfield Corrosion; 2012 May 28-29.
- [19] Xu, D., Li, Y., Song, F., Gu, T., 2013. Laboratory investigation of microbiologically influenced corrosion of C1018 carbon steel by nitrate reducing bacterium *Bacillus licheniformis*. Corrosion. Sci. 77, 385-390.
- [20] Xue, H., Cheng, F.Y., Zhu, Z., Tajallipour, N., Teevens, P.J., 2011. Internal Pitting Corrosion of X80.
- [21] Pipeline Steel under Deposited Sand Bed in CO₂-Saturated Solutions. In: NACE International Corrosion Conference and Expo; 2011 March 13-17, Houston, USA. Paper No. 11264.
- [20] Corrosion of Carbon Steel Marine Environments: Role of the Corrosion Product layer, Philippe Refait, anne-Marie Grolleau, Marc Jeannin, Celine Remazeilles and René Sabot.
- [21] Oil & Gas, Integrity Management of Offshore Assets, DNV-GL
- [22] Sonangol EP Home, <https://www.sonangol.co.ao/Portugu%C3%AAs/%C3%81reasDeAtividade/Explora%C3%A7%C3%A3o%20e%20>