Corrosion of carbon steel in presence of mixed deposits under stagnant seawater conditions

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Abstract

Channelling corrosion of steel pipelines used for offshore water injection pipelines can be severe. Both microbiologically influenced corrosion and under-deposit corrosion are suspected. Half-pipe steel specimens with mixed deposits of magnetite, calcium carbonate and sea sand exposed to near-deoxygenated seawater for 180 days showed more severe pitting corrosion under the deposits than elsewhere. Less severe under-deposit pitting occurred for seawater treated with filtration and ultraviolet (UV) irradiation. Nitrate addition, used in practice to control bacterial H₂S production in oil reservoirs, resulted in the most aggressive localized corrosion under the deposits. This has implications for water injection pipeline management.

Keywords: A. Carbon steel; B. Water injection pipeline; C. Channelling corrosion; D. Under-deposit corrosion; E. Microbiological corrosion.

1. Introduction

Pipelines are widely used in oil and gas industry as it is the most economic and feasible choice for transporting materials such as oil and gas, hydrocarbons, seawater, produced water and other materials associated with the process of exploitation, transportation, refining and storage in oil and gas industry (Shahriar et al., 2012). A big threat to the safety management of pipelines in oil and gas production is corrosion that represents approximately 20% - 40% of recorded pipeline failure incidents (Palmer and King, 2004), more specifically, 81% of the corrosion failures are caused by internal corrosion. The internal corrosion could cause severe thickness reduction and reduce the mechanical capacity of pipelines (Chen et al., 2014). In addition, pitting corrosion is regarded as one

of the most hazardous form of corrosion in offshore structures. The development of pitting corrosion could also result in the perforation of pipelines 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 offshore oil industry to inject seawater (and other waters) into oil reservoirs to promote secondary oil recovery. The water injection pipelines (WIPs) typically are carbon steel. The internal pressure usually is in the range of 200-250 bar, water flow velocity in the range of 1-5 m/s and temperature in the range 10-60°C. Internal corrosion is a potentially serious issue and for pipelines often is associated with microbiologically influenced corrosion (MIC). To attempt to control corrosion, the water usually is deoxygenated, prior to injection, to around 20 ppb oxygen. It also is filtrated and treated with biocides. Typically the pipelines are pigged, regularly or irregularly, in an attempt to remove internal surface rusts and a proportion of any microbiological deposits. However, field experience shows that these techniques do not eliminate corrosion completely. Of most concern is that some pipelines, but certainly not all, eventually show severe internal corrosion at the bottom or 6 o'clock position, often extending along most of the length of the pipeline (Heidersbach and van Roodselaar, 2012). This type of corrosion, if it occurs, is much more severe than elsewhere around the circumference of the pipeline. It is known variously as channelling corrosion, 6 o'clock corrosion, bottom of the line corrosion, or grooving corrosion. The failure cases caused by channelling corrosion are not rare. 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 the channelling corrosion at the 6 o'clock position. The perforation of pipelines was also observed although these pipelines were serving for 4-15 years even though the design life is typically 20-25 years.

Field observations during pigging operations show evidence of accumulation of deposits at the 6 o'clock position. This suggests that under-deposit corrosion (UDC) may be involved and that this may be responsible for channelling corrosion. Observations on flush-disk coupons, mounted on the walls of pipelines near the up-stream end, usually show pronounced evidence of bacterial species and thus support the proposition that channelling corrosion maybe associated also with MIC (Heidersbach and van Roodselaar, 2012). However, at this time no agreed mechanism exists to explain the channelling corrosion phenomenon, although an initial proposal has been made (Comanescu et al., 2016).

Under normal operations the water flow conditions are likely to be turbulent, unlikely to permit the deposition of suspended solids. However, during maintenance or replacement work, the water velocity may be very low or even stagnant, thus permitting deposition of suspended solids at the bottom of pipelines. The deposits typically contain corrosion products (magnetite and iron sulphides), calcium carbonate and sea sand (Comanescu et al., 2012). As noted, these are considered to create conditions suitable for under-deposit corrosion and also local environments suitable for microbiological activity and potentially for MIC (Durnie et al., 2005).

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

MIC usually is attributed to the sulphate reducing bacteria (SRB) (Little and Lee, 2007). However, other species may be involved, including sulphur 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 pitting and crevice corrosion (Little and Lee, 2007; Beech and Sunner, 2004). The accumulation of corrosion products on the metal surface usually is considered to provide the anoxic conditions necessary for anaerobic bacteria (Jeffrey and Melchers, 2003; Melchers, 2007).

The 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 produced oil (or gas). A common practice to control the SRB within the confines of the reservoir is to add nitrate (NO₃⁻), such as calcium nitrate (Ca(NO₃)₂) or sodium nitrate (NaNO₃), to the injected water (Stott, 2012). The extra nitrate boosts the metabolism of the nitrate reducing bacteria (NRB) within the reservoir and potentially allows them to outcompete the SRB for organic electron donors (Eckford and Fedorak, 2002). The NO₃⁻ reduction products inhibit the SRB (Greene et al., 2003; Nemati et al., 2001) or cause the functionality of SRB to switch 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 up-stream end of the WIP has been linked to increased corrosion of the pipeline (Schwermer et al., 2008). This possibility is supported by reports from several failure cases (Beeder et al., 2007; Halim et al., 2011; Stott, 2012) and also by recent field data from North Sea WIPs that indicated that pipelines conveying seawaters with nitrate treatment suffered more severe channelling corrosion than those without nitrate injection (Comanescu et al., 2016). More generally, this scenario is consistent also with findings for mild steel samples exposed to natural seawater that showed long-term corrosion loss increased in the presence of dissolved inorganic nitrogen (DIN) (Melchers, 2014a).

The surface of the pipe interior also may be a factor. For corrosion experiments steel coupons generally are given a well-defined surface topography (for example, highly polished surfaces) so as to obtain repeatable and reproducible experimental results. However, such surfaces may not represent

those of in-service materials (Hinds et al., 2013). For stainless steels, surface roughness is a known factor influencing pitting initiation and propagation (Burstein and Pistorius, 1995; Hong and Nagumo, 1997; Sasaki and Burstein, 1996). For carbon steels exposed to natural seawater, surface roughness affects corrosion only in the early stages of exposure (Melchers and Jeffrey, 2004). In biotic environments, surface condition could influence biofilm adhesion and thereby influence MIC (Hilbert et al., 2003). This suggests that surface roughness may be a factor also for channelling corrosion. Also, 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 under abiotic conditions as a result of aggressive autocatalytic reactions under anoxic conditions (Melchers, 2014b).

To date, the causative mechanism of the channelling corrosion phenomenon is still not fully understood although it is frequent found in practice and leading to major threat to the safety of oil and gas production. It is well known for carbon steel materials exposed to seawater, various operational factors (oxygen, temperature, biological activities) are considered to lead to specific types of corrosion. In some cases, the single theory is insufficient to explain the complex corrosion phenomenon, especially regarding long-term corrosion in specific environments (Bhandari et al., 2015). Therefore the investigation of corrosion phenomenon by taking consideration of the thorough influence factors to improve the understanding of the principles of corrosion has practical implications for ensuring safety and reliability of the equipment and for corrosion management of industry (Thodi et al., 2010).

The present project aims to distinguish the relative contributions to the channelling corrosion phenomenon under simulated stagnant conditions for a water injection system. It is a pilot laboratory study using carbon steel specimens under mixed deposits and near-deoxygenated seawater conditions. The presence of mixed deposits (magnetite, calcium carbonate and sea sand), nitrate treatment, filtration and ultraviolet (UV) irradiation of seawater and surface roughness of steel specimens are considered. The next section describes the test rigs and the design details of the half-pipe steel specimens that were exposed to simulated field conditions for 180 days. The following section reports Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) observations of the corrosion products and the surface morphology of the steel specimens as characterized by optical microscopy. The pit depths were measured by digital Linear Variable Differential Transformer (LVDT). The final section discusses the findings and their implications towards better understanding of the channelling corrosion process and the influencing factors. Some comments are made about WIP corrosion management in practice.

2. Experimental

2.1 Test rigs and test environments

Identical test vessels were constructed for exposing half-pipe specimens to four different test environments (Table 1). Each test vessel was constructed from two steel drums (Drum Reconditioners, Australia) placed end to end and welded together to obtain vessels 1.7m high, 0.58m diameter and of 400 litres seawater capacity. The interior surface of each vessel was coated with International[®] epoxy paint (KGB Pty Ltd, Australia) to avoid internal corrosion. The inside surface of the test vessels and the lids were sterilised using dilute ethanol (Chem-Supply[®], Australia) and deionized water before being filled with testing seawater. 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 at the top exterior wall with a thermocouple (Type T, Omega[®], USA) attached to the outside of the vessel as input.

2.2 Half-pipe steel specimens

The half-pipe specimens were 90 mm long, cut from 60 mm diameter and 3.9 mm thick API 5L carbon mild steel pipeline (Arrium Steel, Australia) spilt length-wise across the diameter. The chemical composition of the steel specimens is shown in Table 2 (as reported certified by the manufacturer). A steel plate was welded across each end of the half-pipe specimens. 5mm diameter mounting holes were drilled in the plates to accommodate a fishing line lifting rig to facilitate deploying and recovering the half-pipe specimens to and from the bottom of the test vessels. The exterior surface of the specimens and both sides of the steel end plates were coated with International[®] epoxy paint (KGB Pty Ltd, Australia) to avoid corrosion. All specimens were uniquely identified using clean plastic numbered tags.

Two types of surface treatment were applied to the interior surfaces of the half-pipe specimens. The acid cleaning approach is using 16% dilute hydrochloric acid (HCl) (RCI Labscan, Thailand) with 3% hexamethylene tetramine inhibitor $[(CH_2)_6N_4]$ (Chem-Supply[®], Australia) to clean the interior surfaces of half-pipe specimens. 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 specimens were rinsed in deionized water to remove the residue acid solution followed by dilute ethanol (Chem-Supply[®], Australia) sterilization and air-drying. The remainder of the specimens were commercially grit blasted (KGB Pty Ltd, Australia) to achieve Sa 2.5 class (ISO 8501-1:2007) surfaces. To do this uniformly across all specimens, they were laid out and grit blasted together by experienced staff. The specimens were then cleaned by deionized water and sterilized using dilute ethanol followed by air-drying. All specimens were stored in a desiccator for a short period prior to being exposed in the test vessels.

The surface characteristics of typical acid cleaned and grit blasted 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 with conventional surface finishes obtained by polishing with grit abrasive papers. The acid cleaned surfaces are visually smoother than the grit blasted surfaces. The latter show a coarsely textured surface with localized deformation resulting from the grit blasting process.

2.3 Test media

The seawater used in the test vessels (Table 1) was collected from the test rig at Port Stephens Fisheries Centre located at Taylors Beach, East coast of Australia. The water quality here (Table 3) is very similar to neighbouring Pacific Ocean seawater based on long-term monitoring (Machuca et al., 2014; Melchers and Jeffrey, 2014). The test rig consists of two streams. The natural seawater was obtained from the first stream, pumped directly from the seawater source without treatment. The collected seawater was transported to the laboratory in sealed sterile drums. Filtrated and UV irradiated seawater was obtained from the second stream, in which seawater was passed through a settling tank and followed by a series filtration system, including primary (AMIAD[®], 80 µm, Australia) and secondary (Autotrol[®], USA) filters and a series of 10, 5 and 1 micron filter bags (FSI[®], USA). The water then flows through two uPVC tubes each with an axially installed 254 nm wavelength ultra-violet lamp (Model 02040, 40W, Emperor Aquatics Incorporated, USA) through which the water velocity is extremely low (less than 0.5mm/s) before collection. This treated seawater was transported to the laboratory in air-tight sterile plastic container immediately after collection. In the rig as shown in Fig. 2, fine filtration and settling physically removes much of the biotic materials such as sediments, larger organisms and other organic matter (Machuca et al., 2014; Melchers and Jeffrey, 2014). The irradiation of ultraviolet light causes irreversible cellular and molecular changes and is considered to damage the genetic material of, and to kill, the majority of microorganisms (Elasri and Miller, 1999). To minimize the contamination by unexpected factors, the tools used to sample the filtrated and UV irradiated seawater were sterilised by ethanol. Nevertheless, due to some inevitable factors, such as secondary growth of small numbers of some shielded microbes surviving after UV irradiation or unexpected invasion by aerial bacteria, it is possible that the water produced in the second stream was not perfectly sterile (Melchers and Jeffrey, 2014). To assess the effectiveness of filtration and UV irradiation in removing microorganisms, biological activity tests were conducted immediately after sampling the seawater from the test vessels. Commercial microbiological test kits (BART[®], Canada) were used to test for sulphate-reducing bacteria (SRB) and iron-related bacteria (IRB). In these, the sampled seawater is sealed in test tubes which contain nutrients for specific species to grow. The identification of biological reaction is obtained by the time taken to reach a noticeable colour change in the test solution. Noticeable colour change after 24 hours of introduction is quoted as equivalent to 6×10^6 CFU mL⁻¹ (colony forming units per millilitre) while a time of 7 days

taken to detection is equivalent to about 500 CFU mL⁻¹. The latter usually is regarded as a negligible presence of background bacteria. The biological testing results show that the seawater from the filtrated and UV irradiated stream filled in test vessel 3 revealed negative responses at 7 days of inoculation for SRB and IRB in the test tubes and continued throughout the entire exposure period. However, the natural seawater sample without treatment continuously showed positive results for both SRB and IRB after only 24 hours of detection throughout the experiment. This approach was used for various research projects and the protocol of the test kits has been described elsewhere (Melchers and Jeffrey, 2014).

2.4 Deposits preparation

The artificial deposit materials used in the present study were made up of magnetite, calcium carbonate and sea sand. The weight ratio of magnetite, calcium carbonate and sea sand was 4.9: 2.71: 2.65 with the same volume placed to a level surface between the 4 o'clock and 8 o'clock position of the half-pipe specimens. The total amount of deposits is 127.47g for each half-pipe steel specimen. Ultrafine magnetite powder (Australian Scientific[®], Australia) and technical grade calcium carbonate crystals (Chem-Supply[®], Australia) were used. The particle size of magnetite mainly is in the range 10-75 µm according to the technical data provided by the vendor. The carbonate crystals were ground into fine particles by a sterilised mortar grinder (Retsch[®], Germany) to obtain a 200-500 µm size range. The sea sand was collected from Stockton Beach, Newcastle. The size of the sand particles ranges from 0.2 mm to 0.6 mm. The sea sand was washed in 5M hydrochloric acid solution followed by deionized water to remove possible microorganisms. Prior to placing in the specimens, the deposits were mixed and stirred using a sterile glass rod for 10 mins on a clean tinfoil plate to ensure the deposits were mixed evenly.

2.5 Chemical treatment

Typically in offshore water injection systems, dissolved oxygen is much reduced by gas stripping de-aerators and most of the residual dissolved oxygen is removed by injection of chemical oxygen scavengers (Heidersbach and van Roodselaar, 2012). The practical residual oxygen range is about 10-200 ppb O₂ with 20 ppb an ideal target (Comanescu et al., 2016). For the present experiment, sodium bisulphite (NaHSO₃) was used as the oxygen scavenger. 100 mg L⁻¹ sodium bisulphite (ACROS[®] Organics, Belgium) was added to each vessel to remove most of dissolved oxygen and thereby to obtain a near-deoxygenated environment. In test environment 4, a practical dosage of 0.25mM NO₃⁻ in the form of calcium nitrate (Chem-Supply[®], Australia) was added to the seawater to simulate practical nitrate addition as used in some real water injection systems. After the addition of the oxygen scavenger, the vessels were sealed and left for 90 mins and then a DO meter (Horiba[®] OM-51, Japan) was used to monitor the concentration of dissolved oxygen. The results demonstrated that dissolved oxygen was < 0.08 mg L⁻¹ (approximate 80 ppb) in all four vessels after oxygen scavenger treatment.

The half-pipe steel specimens were then carefully placed to the bottom of the test vessels away from the heater. The vessels then were sealed using a sterilized airtight lid and O ring. Also, the gap between lid and vessel was covered with sealant. The temperature for the first 12 days was maintained at room temperature, approximately 21 °C. After that, the temperature was increased gradually over a period of two weeks and then maintained by the heating system at 30 °C for the remainder of the experiments. All four test vessels were located standing at a secure and clean place in the laboratory to avoid any disturbance. The dissolved oxygen was monitored after 180 days of exposure by the DO probe, the data indicating that the DO levels in all four test environments were below 80 ppb for the entire period of experiment.

2.6 Analytical methods

After 180 days' exposure, two acid cleaned and two grit blasted specimens were recovered from each vessel. They were photographed immediately upon recovery by a digital camera (IXUS 120, Canon®, Japan) and then fixed using 2.5% glutaraldehyde (Scharlau, Spain) containing 0.2M phosphate buffered saline (PBS) (pH 7.4) for 2 hours in a desiccator. Corrosion products and any biofilm on the steel surfaces were removed using a sterile scalpel blade. In test environments 2, 3 and 4, the corrosion products of approximately 2-3mm thickness were sampled immediately next to the metal at the very bottom of the specimen. The samples of corrosion product were then dehydrated by immersing them in a graded series ethanol (Chem-Supply®, Australia) (15 min 30%, 15 min 70%, 15 min 90%, 15 min 100%). The dehydrated samples were then critical point dried (CPD) in liquid carbon dioxide using a critical point drier (FL-9496, Balzers Union Ltd, Liechtenstein). The dried corrosion product samples were then mounted on aluminium stubs using adhesive carbon tape and gold coated by a SPI Module Sputter Coater (SPI supplies, USA). SEM images were obtained by a Sigma VP FESEM (Zeiss, Germany) and Energy-dispersive X-ray spectroscopy (EDS) distribution maps were performed on light element SSD EDS (Bruker, USA) detector.

After sampling for corrosion products, the half-pipe steel specimens were prepared for detailed surface examination. Firstly, the specimens were cleaned by rinsing in 16% dilute hydrochloric acid (HCl) (RCI Labscan, Thailand) with 3% hexamethylene tetramine inhibitor (Chem-Supply®, Australia) for 30 s. The specimens were then immediately washed using deionized water. Any residual surface deposits were removed using a fine brush. This was followed immediately by gentle blotting with paper towel and overnight storage in a desiccator. The surface topography of the steel specimens was inspected and imaged using stereo zoom microscopy (SZ60, Olympus®, Japan) with a Pixelink® camera. All images were obtained with oblique lighting. The relative depth of pits of each specimen was measured by a microscope (Axio.A1, Zeiss, Germany) focused successively on the base of pits and on the surrounding surface, measurements were recorded by means of digital Linear Variable Differential Transformer (LVDT), thereby obtaining the relative pit depth with 1 micron sensitivity. For the steel specimens covered with deposits, the deposit-covered surfaces were examined by the

optical microscopy first and the most severely corroded areas with deep pits were located. The depths of these deep pits were then measured and recorded. In each test environment, four coupons were examined with two acid cleaned coupons and two grit-blasted ones. The depth of each pit was measured five times and the average value was applied. Multiple pit depths were measured for each specimen and then these readings were compared and finally the depth of the deepest pit on the specimen surface was reported as the relative maximum pit depth. Each set of data consists of 10 deepest pit depth readings on each of the duplicate coupons thus obtaining 20 maximum pit depth readings per test environment per initial surface roughness. In this study, only the (relative) maximum pit depth was presented. Because the primary aim of the project was to evaluate the pitting development under different test environments, bacterial community testing such as DNA analysis to identify the microorganisms in the corrosion products was not conducted. Such work has been done previously by others (Stipanicev et al., 2014).

3. Results

3.1 Characterization of the corrosion products

All specimens recovered from each of the 4 test environments showed similar wet surface conditions as shown in Fig. 3. The SEM micrographs of the corrosion products removed from the acid cleaned specimens in all four test environments, with some spots emphasized, are shown in Fig. 4. New scale bars were inserted to facilitate reading. Table 4 summarizes the EDS results of the emphasized spots in Fig. 4. The various proportion and amount of specific elements indicates different corrosion products formed on the steel surfaces. Some microorganisms were found intertwined with the corrosion products in test environment 2 (red arrows, sp2 of Fig. 4b). For all four test environments after 180 days of exposure, Fe and O are the dominant elements of the corrosion products. Specifically, in test environment 4 with nitrate addition, the corrosion products show higher amount of Fe (74 wt.%) and lower amount of O (4.59 wt.%) (sp4 of Fig. 4d) than that in the other ones. The S peaks in test environments 1, 2 and 4 are significantly higher than that in test environment 3 (filtrated and UV irradiated seawater). The nitrate-added test environment (4) contains the highest proportion of S (17.87 wt.%). At the same time, EDS reveals higher amount of Cl in test environment 3. The simultaneous presence of Fe and O of sp3 is an indication of iron oxides. The image also shows overlapping hexagonal platelets in Fig. 4c which is a representative morphology of sulphated green rust ($\text{GR}(\text{SO}_4^{2-})$) (Duan et al., 2008; Refeit et al., 2003). Moreover, Mn, Na, Si, Al and Mg peaks were detected with various proportions, however, the difference is considered not significant.

The characterization of the corrosion products of the grit blasted specimens from all 4 test environments is shown in Fig. 5. The EDS results of corrosion products are given in Table 5. The general composition of the corrosion products is similar with to that found in acid cleaned specimens. High weight percentage of Fe and O is detected in the deposition of corrosion products from all 4 test

environments. Moreover, S is also found in a higher proportion in test environment 1 (7.68 wt.%), 2 (5.09 wt.%) and 4 (15.86 wt.%) than test environment 3 (1.17 wt.%). The morphological examination of the corrosion products in test environment 1 (sp1 of Fig. 5a) reveals overlapping hexagonal platelet structure together with globular particles. An example of SEM image with lower magnification is also given in top right of Fig. 5a. Numerous microorganisms are found attached on the globular particles in sp1 of Fig. 5a (red arrows). This representative morphology has been extensively found in marine corrosion influenced by SRB and is attributed to iron sulphides and to $\text{GR}(\text{SO}_4^{2-})$ (Duan et al., 2008; Pineau et al., 2008; Refeit et al., 2003). This is also supported by the EDS results which show the simultaneous presence of Fe, S and O. The hexagonal platelets are also found in sp2 of Fig. 5b. Minor presence of other elements such as Na, Si, Mg, Al, Mn and Cl are also present. It is also found that the Ca peak in test environment 3, although has minor presence, reveals higher possession than other three test environments both for acid cleaned and grit blasted specimens. This suggests the higher amount of calcareous deposition such as CaCO_3 in test environment 3 (Stipanicev et al., 2013).

3.2 Surface topography

The corroded surface of each half-pipe steel specimen was examined by optical microscopy and recorded immediately after the corrosion products were cleaned off. The surface topography of the steel specimens in all four test environments is shown in Fig. 6. For test environment 1 having deoxygenated natural seawater, it is clear that numerous small individual pits are present on the acid cleaned steel surface. Some of the smooth pits appear to have coalesced with their neighbours, the connected pitted areas having a diameter of approximately 1mm (middle of Fig. 6a). The grit blasted specimens reveal an uneven surface texture with small pits scattering on the surface. In addition, the areas of the acid cleaned surfaces free from visible pitting appear to be smoother than those of the grit blasted specimens. Compared with environment 1, for which there were no deposits, the surfaces of both acid cleaned and grit blasted steel specimens in test environment 2 in which deposits were present show more severe and clear pitting corrosion. For the acid cleaned surface, Fig. 6b shows large areas of localized corrosion having the appearance of irregular shaped “valleys and plains”. This type of corrosion is likely to be the result of the coalescence of developed pits. The photographs can be interpreted as showing the pits being in the process of coalescence. An example is shown at top right in Fig. 6b. Additionally, what would appear to be new single and deep isolated pits can be seen in the floor of shallow broad pits (bottom right part of Fig. 6b). The parts of the original metal surface remaining after general corrosion also can be seen, such as at the top of Fig. 6b. For the grit blasted specimens the surfaces show topographies much more corroded than seen in Fig. 6e for test environment 1. Large pits are evident. Some of these clearly appear to have coalesced, thereby forming larger or broad pits with obvious benches inside (Fig. 6f). Similarly, the right side of Fig. 6f shows some isolated large pits that can be interpreted as being in the process of coalescing. Such an interpretation can be made also for the acid cleaned samples (Fig. 6b). In test environment 3 (seawater

filtrated and UV irradiated) the surfaces of the specimens show a high density of individual pits, irrespective of the original difference in surface finish (Fig. 6c and 6g). Fig. 6c (middle) and Fig. 6g (bottom right) show what can be interpreted as incipient coalescence of isolated pits. The number and size of such incipient coalescence appears slightly higher on the acid cleaned surfaces than on the grit blasted surfaces, however, the difference is not pronounced. The surfaces of steel specimens exposed to seawater with added nitrate (test environment 4) for 180 days are shown in Figs. 6d and 6h. For the acid cleaned specimens (Fig. 6d) the corroded surface shows distinct large and irregular shallow depressions. There is evidence of newer pits on the base of these shallow depressions. The patterns of corrosion attack observed on grit blasted surfaces (Fig. 6h) are only slightly different compared with the acid cleaned specimens. Fig. 6h shows numerous isolated pits. These appear rounded. Again, the patterns of the developed broad pits at the right part suggest coalescence of pitting.

Additionally, for the specimens exposed to test environment 4 (deoxygenated natural seawater with deposits and nitrate addition), severe and irregular localized corrosion what might be termed stepped bench marks were observed along the boundary of the deposits of both acid cleaned and grit blasted specimens. The height difference of the bench is clearly observed in Fig. 7b and Fig. 8b. This indicates that more metal loss occurred. In addition, the height difference of the bench of the grit blasted specimen is approximately 0.35 mm and is larger than that of acid cleaned steel specimen which is approximately 0.2 mm. The cross-section micrographs of the steel surfaces under the deposits with higher magnification (200x) (Fig. 7c and Fig. 8c) show the characteristics of pitting corrosion under deposits. Regardless to the size and depth of pits with different surface roughness, the profiles of the pitting corrosion are consistent with the observations in Fig. 6d and Fig. 6h that some pits appear to have grown laterally and to have coalesced with neighbouring pits to form broader and deeper pits. The stepped bench marks were not observed on specimens exposed to any of the other test environments after 180 days of exposure.

3.3 Maximum pit depth

The depth of the deepest pits obtained from the steel specimens exposed in different test environments for 180 days is shown in Fig. 9. Apparently, despite the initial surface treatment, the maximum pit depth in test environments 2, 3 and 4 where the mixed deposits were present is higher than that in test environment 1 without deposits. There is a slight difference of pit depth between acid cleaned and grit specimens in test environment 1, 3 and 4 but this is considered to be not significant. However, the maximum pit depth of grit blasted specimens in test environment 2 (natural seawater with deposits) is clearly higher than acid cleaned ones. The deepest pit was found from a grit blasted specimen in test environment 2 (0.394 mm). For acid cleaned coupons, the deepest pit is 0.335 mm from acid cleaned coupon 2 in test environment 4 (nitrate added seawater with deposits). The deepest pits on the surfaces of acid cleaned and grit blasted specimens were located and are shown in Fig. 10. It is noted

that the maximum pit depth demonstrated herein is the relative maximum pit depth since the mass loss of the total specimen is not considered.

Table 6 shows the comparison between test environments of standard deviation of the 20 recorded maximum pit depth data observed on the steel specimens after 180 days of exposure. It is evident that the standard deviations have varied between test environments. This means the variability of the maximum pit depths are different between test environments. However, generally, the standard deviations of the maximum pit depth data recorded on the specimens in test environments 2, 3 and 4 where deposits were present are greater than that without deposits. This is consistent with optical images showing considerably difference of surface morphology of steel specimens in different test environments.

4. Discussion

4.1 The formation of corrosion products

Extensive investigation of the corrosion products of carbon steel under anoxic seawater conditions has been carried out (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). The steel specimens in previous work have been exposed to either a created anoxic test environment in a laboratory or to natural seawater environments. The anoxic condition in natural seawater typically is caused by the accumulation of corrosion products slowing down the rate of oxygen diffusion to the metal surface for long-term effect (Melchers and Jeffrey, 2008). It has been proposed that magnetite (Fe_3O_4), Fe(III) oxyhydroxides (α - FeOOH and β - FeOOH), iron sulphides (Fe_xS_y), $\text{GR}(\text{SO}_4^{2-})$ and calcareous minerals (CaCO_3) mixed with other minerals are the typical compositions of the inner layer of corrosion products under anoxic conditions (Duan et al., 2008; Pineau et al., 2008; Stipanicev et al., 2013). It should also be noted here that the outer layer of corrosion products immersed to natural seawater contain different minerals compared with inner layer because of the ingress of O_2 to the outer layer. Under anaerobic conditions, the structure and evolution of the corrosion products are mainly influenced by the local physiochemical environment (pH, temperature and redox potential) (Lee et al., 2004), the content of dissolved oxygen and possibly by microbiological activities (Lee et al., 2004; Melchers and Jeffrey, 2008; Pineau et al., 2008).

In the present work, the EDS results of the composition of corrosion products in test environments 1, 2, and 4, irrespective the 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 $\text{GR}(\text{SO}_4^{2-})$. These iron minerals are typical of steel corrosion products. Of particular interest is the proportion of S in the corrosion products, noting that the proportion of S in test environment 1, 2 and 4 is clearly higher than that in test environment 3. The corrosion products in test

environment 4 with nitrate addition reveal the highest amount of S. It is well known that in natural seawater conditions, the presence of S comes mainly from sulphates, biotic sulphides and abiotic sulphides (Lanneluc et al., 2015). Taking into consideration the natural seawater environment and the results of the biological culture testing, the appearance of blackish deposits and the presence of microorganisms are not inconsistent with previous observations (Refeit et al., 2003; Stipanicev et al., 2013; Lee et al., 2004) that the corrosion products from test 1, 2 and 4 are microbiologically influenced. In test environment 3 with its filtered and UV irradiated seawater, there is only small amount of S after 180 days of exposure. The presence of hexagonal platelet structures in sp3 of Fig. 4c suggests the S is mainly from $\text{GR}(\text{SO}_4^{2-})$. This possibility is supported by previous observations that $\text{GR}(\text{SO}_4^{2-})$ is the first deposit to form on the metal surface during the anaerobic period from the purely electrochemical (i.e. abiotic) corrosion process (Lanneluc et al., 2015; Refait et al., 2011). In addition, the high amount of Fe and O in test environment 3 is an indication of iron oxide minerals, more likely to be magnetite or iron oxyhydroxides. The mixed structure of green rust and magnetite without sulphides that compose the main parts of inner layer of corrosion products under natural seawater conditions also has been reported (Refait et al., 2011). In addition, the trace of S in test environment 3 is also likely to be from abiotic sulphides. Recent observations suggest that under anoxic abiotic conditions, sulphide species can originate from MnS inclusions which are typical in carbon steel (Avci et al., 2013; Stipanicev et al., 2013). The detection of Mn in corrosion products consolidates this point.

Moreover, the addition of nitrate in test environment 4 was designed to simulate the industrial practice to suppress the growth of SRB in the reservoirs and further the production of H_2S . However, the results for the specimens used in the present work show that larger proportion of sulphur was detected both for acid cleaned and grit blasted specimens after 180 days compared with that in the other three test environments. Homogeneously combined with Fe, the presence of S is an indication of the production of Fe_xS_y compounds (Jeffrey and Melchers, 2003). This suggests that the nitrate addition in the current work promoted the production of sulphide or elemental sulphur. In regards to the side effect associated with nitrate injection, various mechanisms have been proposed and most of them are correlated with complex microbiological activities (Stott, 2012). For example, in a nitrate added environment, the microbial disproportionation of sulphur and the metabolism of specific sulphur-reducing species such as *Desulfuromonas* have been found to promote higher sulphate reduction rates to produce sulphides and cause high rates of corrosion (Drønen et al., 2014). Some previous findings indicate that SRB may be inhibited by nitrates when the effective dosage of nitrate is 17 mM (Hubert et al., 2003), this is much higher than the dosage used in present study (which was equivalent to 0.25mM). However, since bacterial community analysis to identify the microorganisms was not part of the present research scope, these hypotheses are not conclusive. This is a matter for further investigation.

4.2 The effect of test environments on pitting corrosion

The present work demonstrates that after 180 days exposure, the surfaces of steel specimens covered with deposits in test environment 2, 3 and 4 had developed more severe localized/pitting corrosion and deeper pit depth than those without deposits (test environment 1) irrespective of the differences in initial surface roughness. This correlates directly with the difference in test environments. The main difference between test environment 1 and test environments 2, 3 and 4 is the presence, throughout the experiment, of mixed deposits. It is not correlated with the fact that in test environment 3 the seawater was filtrated and UV irradiated as opposed to test environment 1, 2 and with test environment 4 having nitrate addition. Thus it is reasonable to suggest that the enhanced corrosion and the development of pitting is the direct reason of the presence of deposits. Further, in test environments 2, 3 and 4 the deposits consist of granular materials and while they were well-mixed prior to placing, it is reasonable also to speculate that there was some difference in the degree of local contact with the steel surface, permitting the development of oxygen concentration cells even under the very low dissolved oxygen concentrations test conditions. This would allow initiation of pitting corrosion (Tan et al., 2011). Gradual localized depletion of oxygen would then occur. As noted earlier, previously it was proposed that the pitting corrosion that occurs under anaerobic conditions is likely to be the result of aggressive microorganisms such as SRB flourishing within the biofilms (Beech, 2004; Lee et al., 2004; Mansfeld, 2007). The pitting patterns of steel specimens in test environment 1 (deoxygenated natural seawater) certainly appear to be similar to those reported previously in the literature (Lee et al., 2004; Stipanicev et al., 2013) but such similarity cannot be taken as conclusive. However, the possibility that MIC is involved in the corrosion observed in the present experiments has some support by the presence of microorganisms in the corrosion products and the EDS results and with the biological testing results (test environment 4). It also is broadly consistent also with observations in the literature and with some investigations of the corrosion of WIPs (Bødtker et al., 2008; Drønen et al., 2014; Stipanicev et al., 2014; Stott, 2012).

In terms of test environment 2 with presence of mixed deposits, microscopy images show more severe pitting corrosion than that in test environment 1. It is well known that the presence of mixed deposits on the steel surface can cause under-deposit corrosion. The mechanism of UDC is mainly ascribed to the galvanic effect caused by a large cathode to anode surface ratio (Tan et al., 2011). It is noted earlier that the presence of deposits and oxygen initiate pitting corrosion as a result of oxygen concentration cell (Hinds and Turnbull, 2010). However, it is also found that even in deoxygenated conditions, localized corrosion expands due to the galvanic effects between the edge of the corrosion product ring and the product-covered steel areas and pitting corrosion initiates and propagates (Han et al., 2013). The presence of deposits also influences MIC. It has been proposed the presence of deposits damages the integrity of biofilms which could accelerate localized corrosion (Beech, 2004).

This suggests that it is possible to have a synergistic effect between UDC and MIC, allowing the formation of more severe localized corrosion. This could explain the difference in pitting severity between test environments 1 and 2.

On the other hand, the pitting that can be observed for the specimens exposed to test environment 3 is more severe and deeper than that in test environment 1. This can be seen also in optical images which show “broad pits” of larger size and also pit density greater than those in test environment 1. Taking the near-sterile consideration into account, it follows that microbiological influences (such as SRBs) alone are unlikely to explain the greater severity of pitting and corrosion in test environment 3. Recently, it has been proposed (Melchers, 2014b) that aggressive autocatalytic pitting can occur under anoxic abiotic conditions on nonhomogeneous corroded surfaces covered with sufficient deposits. This is the result of purely abiotic electrochemical processes facilitated by MnS inclusions typically present in steels (Wranglen, 1974). It has been proposed (Melchers, 2014b) that microbiological activities play an additional rather than essential role in the pitting corrosion process by providing additional (i.e. biotic) sulphide species to contribute to the severity of corrosion. Based on the features of deposits and near-abiotic test conditions, this mechanism may explain the pitting patterns seen in test environment 3. Also, it has been proposed that sand and other particles on the metal surface can establish electrochemical cells that can contribute to localized corrosion, even under anoxic conditions (Han et al., 2013). These mechanisms indicate that even under near abiotic conditions, pitting corrosion beneath the deposits can initiate and develop due to an aggressive autocatalytic reaction and other galvanic effects. Under biotic conditions, bacterial metabolism also may be involved in the corrosion process, leading to the idea of a synergistic effect of MIC and under-deposit corrosion. This is considered to be the reason for the more severe pitting corrosion in test environment 2 (natural seawater with deposits).

The steel specimens in test environment 4 with nitrate addition show more severe localized corrosion and higher amount of S, this indicates that nitrate addition failed to inhibit the production of sulphides to control corrosion. The example of “stepped benches” at the boundary also indicates more metal loss. In practice, the cases of increased pitting corrosion caused by nitrate addition are not rare. It has been proposed that nitrate reduction provides energy for NRB respiration and cause more severe pitting corrosion than typical for SRB reported in MIC laboratory investigations under strict anaerobic conditions (Xu et al., 2013). It is also been found a particular microorganism named Nitrate or nitrite reducing sulphide-oxidizing bacteria (NRSOB) is known to use nitrate or nitrite to re-oxidize produced sulphide to elemental sulphur and sulphate, creating a sulphur cycle involving NRSOB and SRB (Hubert et al., 2003). The presence of sulphur on metal surfaces also is well-known to be severe localized corrosion facilitator (Boivin et al., 2011). In addition, previous observations indicate elevated concentration of dissolved inorganic nitrogen (DIN) (nitrate as the main component)

increases both general and pitting corrosion in natural seawater (Melchers, 2014a). Therefore it is possible that the nitrate addition in the present work promoted MIC by providing the necessary nutrient for the growth of SRB. Further, there is also the possibility that the components of the mixed deposits on the metal surface damaged the integrity of the biofilms that usually form there, thus having some effect on the early layers of corrosion product and on local physicochemical conditions such as pH, redox potential (Zhang et al., 2012), thereby causing acceleration of pitting corrosion (Halim et al., 2011; Drønen et al., 2014). None of this is inconsistent with the proposed mechanism of the synergistic effect of UDC and MIC causing severe localized corrosion.

4.3 The effect of initial surface roughness

Comparison of those specimens that had been prepared to obtain acid-cleaned surfaces with those having grit blasted surfaces shows that for each of the test environments 1, 2 and 4 there is relatively little difference in surface morphology and maximum pit depth of the corroded steel and as a result of these two surface treatments after 180 days exposure (Figs. 6 and 9) despite the deepest pit was found on a grit blasted specimen from test environment 2. At that time, all the surfaces that were initially acid cleaned show pronounced shallow depressions within which small pits can be observed on the floor of the depressions. The areas around these depressions appear to be relatively smooth compared to corresponding areas for the grit blasted surfaces. For these it can be observed that some of the larger pits show evidence of having coalesced. These observations may be compared with the localized corrosion seen on steel coupons exposed to natural oxygenated seawater (Melchers, 2006). For these, initial surface roughness was found to be an influence only for a short duration, associated with the time required for the corrosion process to change the form of the surface and for the rusts to build-up (Melchers and Jeffrey, 2004). In the present experiment the oxygen content is extremely low and thus the period of oxygen controlled corrosion is likely to be relatively short. This may explain why the effect of initial surface roughness is still evident after 180 days exposure. Whether this difference continues with longer exposure remains a matter for further investigation.

As noted earlier, the severity of pitting varies with the exposure environment and in particular with the presence of deposits, the use of nitrate and with whether the seawater was subjected to filtration and UV irradiation. Except for test environment 3 (filtrated and UV irradiated seawater) all the other test environments produced similar relative differences in surface morphology between acid cleaned and grit blasted surfaces. The difference in the severity of these for any exposure environment must be attributed to the effect of the presence of surface deposits. Whether this relative difference continues with longer exposure also remains a matter for further investigation. A potentially important aspect of initial surface roughness is that it may have an effect on biofilm formation for those specimens exposed to natural seawater. This is known to lead to variations in the eventual development of MIC (Hilbert et al., 2003; Cote, 2013). This possibility is consistent with the optical microscopy results for

test environment 3 (filtrated and UV irradiated seawater) for which microbial activity would have been very low or negligible. Fig. 6c and Fig. 6g show very little difference in the morphologies of the corroded surfaces, both for acid cleaned or grit blasted specimens, after 180 days exposure.

4.4 Industrial significance

The severe channelling corrosion sometimes observed in offshore water injection pipelines is assumed to be associated with microbiologically influenced corrosion and much attention has been given to this possibility in the practices adopted by industry (Comanescu et al., 2012; Comanescu et al., 2016; Heidersbach and van Roodselaar, 2012). The potential influence of under-deposit corrosion has been given much less attention even though there is circumstantial evidence for it from field observations (Heidersbach and van Roodselaar, 2012). The results from the present experiments show that the presence of deposits on the metal surface resulted in more severe pitting corrosion and that it appears also to have accelerated the coalescence of pitting. This is consistent with earlier observations for pit development (Jeffrey and Melchers, 2007). The observations for test environment 3 show that even in a near-sterile environment, pitting corrosion of steel surfaces covered with mixed deposits was more severe than that without deposits and caused deeper pits. In addition, under laboratory conditions with the presence of deposits, the addition of nitrate resulted in more severe localized corrosion. In terms of channelling corrosion, it is considered that the mechanism of pit coalescence and the development of pits is the most likely primary cause of the formation of channelling corrosion. The present results also show that MIC may be involved under mixed deposits and with nitrate addition. Similar experimental observations have not been reported previously.

Although the maximum pit depth data obtained from steel specimens in current work only provides information for a single point in time, it clearly shows the variability of the maximum pit depths have varied between test environments. For industrial practice, the long-term progression of maximum pit depth is of particular interest as the detrimental effect of pits leading to perforation failure of pipelines. Previous studies have shown the maximum pit depth of carbon steel exposed to natural seawater for long-term effect follow specific extreme value distribution models and this is significant for risk assessment of existing corroded structures (Chaves et al., 2015). However, this is not the focus in current paper and it needs further investigation.

Therefore, the experimental results demonstrated herein have implications for oil and gas industries to optimize the management strategy of rust deposition controlling and MIC controlling. A safer and more efficient approach of nitrate implementation also needs more effort. Moreover, the results have implications when applying some hazard/risk management approaches such as inherent safety approach and Process Hazard Analysis (PHA) (Khan and Amyotte, 2002; Murata et al., 2015) since a better understanding of the underlying mechanism of material deterioration of process equipment is crucial to identify and address hazards.

5. Conclusion

The experimental results presented herein show that:

1. The half-pipe steel specimens covered with deposits revealed more severe pitting corrosion than those without deposits. Filtration and UV irradiation of the seawater mitigated the severity of pitting corrosion to some extent but did not eliminate pitting corrosion. Nitrate addition was shown to promote localized corrosion and was found to promote pronounced “stepped bench” corrosion located at the boundary of the areas covered by deposits and the uncovered areas;
2. The corrosion products next to the steel surface exposed to untreated natural seawater showed evidence of microbiological activities and were mainly composed mixture of iron oxides (magnetite), iron sulphides, sulphated green rust($\text{GR}(\text{SO}_4^{2-})$) and Ca-based minerals. Nitrate addition promoted the production of iron sulphides. The corrosion products formed under filtrated and UV irradiated seawater mainly contain iron oxides and ($\text{GR}(\text{SO}_4^{2-})$), trace amount of iron sulphides may exist as a result of abiotic inclusions;
3. The pitting corrosion in all test environments found on the surfaces showed consistent trend of coalescence to “broad pits” irrespective of the severity of pitting corrosion. This is in accordance with a previously proposed model for the development of long-term corrosion pitting;
4. After 180 days of continuous exposure, the initial surface roughness was found to play a negligible role on the eventual morphology of the corroded surfaces under filtrated and UV irradiated seawater conditions. However, under biotic conditions the acid cleaned surfaces showed large shallow pitting depressions and newly formed pits on the floor of the depressions. For the grit blasted specimens, large and isolated pits prevailed although some pits connected to form large “broad pits”;
5. The results show that there is potential for a synergistic effect between MIC and under-deposit corrosion and that this could cause more severe localized corrosion. This has implications for the corrosion and risk management of offshore water injection system.

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Table 1 Test environments for exposure of half-pipe specimens.

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

Table 2 Chemical composition of steel specimens in wt% (balance Fe).

C	Si	Mn	P	S	Cu	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	0.034

Table 3 Typical seawater composition at Taylors Beach*.

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).

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.

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

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

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

Table 6 Comparison between test environments of standard deviation of the 20 recorded maximum pit depth data observed on the steel specimens after 180 days of exposure (mm).

Test environments	Acid cleaned specimens	Grit blasted specimens
1 (natural seawater)	0.0117	0.0073
2 (natural seawater with deposits)	0.0487	0.0852
3 (filtrated and UV irradiated seawater with deposits)	0.0219	0.0241
4 (natural seawater with deposits and nitrate)	0.0679	0.0461

FIGURE CAPTIONS

Fig. 1. Typical surface morphology of half-pipe steel specimens after (a) acid cleaning and (b) grit blasting. Bar=50 μm .

Fig. 2. Schematic diagram for natural and filtrated and UV irradiated seawater collection rig at Taylors Beach.

Fig. 3. Digital photograph of one representative half-pipe steel specimen recovered from the experimental vessels after 180 days of exposure: grit blasted specimen from test environment 4 (deoxygenated natural seawater with deposits and nitrate addition).

Fig. 4. SEM micrographs of corrosion products with emphasized areas subjected to EDS analysis of the steel acid cleaned specimens from test environment 1 (deoxygenated natural seawater) (a), 2 (deoxygenated natural seawater with deposits) (b), 3 (filtrated and UV irradiated seawater with deposits) (c) and 4 (deoxygenated natural seawater with deposits and nitrate addition) (d) after 180 days of exposure. Scale bars: (a), (c) and (d) =10 μm , (b) =2 μm .

Fig. 5. SEM micrographs of corrosion products with emphasized areas subjected to EDS analysis of the steel grit blasted specimens from test environment 1 (deoxygenated natural seawater) (a), 2 (deoxygenated natural seawater with deposits) (b), 3 (filtrated and UV irradiated seawater with deposits) (c) and 4 (deoxygenated natural seawater with deposits and nitrate addition) (d) after 180 days of exposure. Scale bars: (a), (b) and (c) =2 μm , (d) =10 μm . The smaller inserted SEM image in (a) has a scale bar of 10 μm .

Fig. 6. Micrographs of corroded surface of the steel specimens from test environment 1 (deoxygenated natural seawater) (a and e), 2 (deoxygenated natural seawater with deposits) (b and f), 3 (filtrated and UV irradiated seawater with deposits) (c and g) and 4 (deoxygenated natural seawater with deposits and nitrate addition) (d and h) after 180 days of exposure. Figs.6a-6d are representing the specimens with acid-cleaned surface treatment. Figs.6e-h are having grit-blasted surface treatment.

Fig. 7. Microscopy photographs and cross section view of “stepped bench” observed on the acid-cleaned half-pipe steel specimens from test environment 4 (deoxygenated natural seawater with deposits and nitrate addition).

Fig. 8. Microscopy photographs and cross section view of “stepped bench” observed on the grit-blasted half-pipe steel specimens from test environment 4 (deoxygenated natural seawater with deposits and nitrate addition).

Fig. 9. The recorded relative maximum pit depth of steel specimens from different test environments after 180 days of exposure.

Fig. 10. Located deepest pits (red circles) from (a) acid cleaned specimen (pit depth = 0.335 mm) in test environment 4 (nitrate added seawater with deposits) and (b) grit blasted specimen (pit depth = 0.394 mm) in test environment 2 (natural seawater with deposits) after 180 days of exposure. Bar = 1mm.

Figure 1

(a)

(b)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10