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Long-term corrosion of mild steel in natural and UV-treated coastal seawater

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SUMMARY:

Highly polished coupons (25 x 25 x 1.5 mm) sourced from the same steel sheet were continuously immersion exposed either to natural coastal seawater or to seawater from the same source subjected to filtration and UV irradiation so as to eliminate microbiologically influenced corrosion as much as possible. This was continued for 943 days (2.6 years). Dissolved oxygen levels were very similar in both environments. On average the UV-treated seawater was 2°C warmer but all coupons exposed to it showed less localized corrosion than those exposed to natural seawater. The typical topographical difference was about 60% as measured by surface roughness parameter S_a . Mass losses in UV-treated seawater were about 10% higher than in natural seawater but after temperature correction were similar to natural seawater for the first year and **tended to be** lower subsequently. At all exposure periods the rusts in UV-treated seawater were less voluminous than the rusts in natural seawater. Eventually they also contained a higher proportion of magnetite.

KEYWORDS: Steel, marine corrosion, microbiological corrosion, pitting, mass loss, long-term.

INTRODUCTION

It is well-established that microorganisms including bacteria and archaea can influence the rate of corrosion of steels in water^{1,2}. It is known also that microbiologically influenced corrosion (MIC) depends on the microorganisms being present in locations likely to cause corrosion damage and on these locations having environments suitable for microbial metabolism including the availability of energy (electrons) and necessary nutrients, such as organic carbon, and, for seawater corrosion, dissolved inorganic nitrogen^{1,3}. Understanding of the role of MIC for steels has been developed largely from short-term laboratory experimental exposures in small test vessels seeded with selected microorganisms and doped with relatively high levels of nutrients^{1,2,4}. These studies have been very successful in showing the importance of microorganisms on steel corrosion and in improving understanding of the factors involved, particularly the importance of necessary nutrients. This work also has shown that pitting may be enhanced by MIC, particularly for steels with passive films⁵.

For short-term exposures under field conditions the severity of corrosion has been correlated with nutrient availability.⁶ However, for long-term exposures only a limited amount of attention has been given to the effects of microorganisms on corrosion.^{7,8} sufficient to propose models for their longer-term effect,^{9,10} but quantification largely has remained elusive. One exception is the correlation between localized corrosion in the tidal zone (the special case of so-called accelerated low water corrosion) and the concentration of dissolved inorganic nitrogen in the bulk seawater adjacent to sheet and other unprotected steel piling.^{11,12}

The possible effect of microorganisms on pitting (or localized) corrosion of steels is of particular interest. Herein the term pitting is used also in the context of mild or structural steels, consistent with classical usage.^{13,14,15} Initiation and the progression of pitting of such steels has been given considerable practical attention¹⁴ including for extended exposure periods¹⁶ and has been used to develop semi-empirical models for maximum pit depth.¹⁷ It has been observed that pit growth is limited in depth¹⁴ and that pits then tend to grow laterally, creating pit coalescence and eventually the initiation of newer pitting.¹⁸ This led to the proposition that the changes with time in topography of the corroding surfaces and in particular the pitting of mild steel could be influenced by microbial activity. This possibility is of particular interest for infrastructure applications for long-term (multi-year) exposures.

The present paper describes the results of a project designed specifically for examination of the changing topography and mass loss of the corroded surfaces of mild steel plates as exposure time increases, both for natural seawater and for seawater with as much as possible of the biotic material removed or rendered ineffective. The next section describes the experimental protocol adopted, the equipment used and the conduct of the experiment. This includes a description of the technique used to eliminate as far as practically possible the influence of microbiological activity. It is followed by a selection of photographs and scanning electron microscope (SEM) images both for steel plates exposed one or other of the exposure environments, at various exposure periods. The scientific and practical implications are discussed briefly also.

EXPERIMENTAL DESIGN AND PROCEDURES

The most direct way of ascertaining the possible influence of microorganisms on the corrosion of mild steel is to compare corrosion effects in natural seawater and in seawater from which microbiological activity is eliminated (or at least very much reduced) but all other properties, including the physical and chemical characteristics of typical seawater are retained as much as

possible. One approach to reduce microbiological effects is to eliminate (or control) the supply of nutrients essential for microbiological activity and survival. However, there are practical limitations on the control of nutrient concentration in natural seawater. Physical removal of live microorganisms and other biota such as by extremely fine filtering as has been used in some laboratory experiments (e.g. reference 19) but the volumes of water so produced are very small. A third approach is to attempt to eliminate live biota including microorganisms such as through chemical sterilization, ozone injection or autoclaving of the seawater. However, these techniques may alter the normal chemical and physical characteristics of the seawater.

The approach adopted for the present work was to (i) reduce turbidity through settlement in sedimentation tanks, (ii) physically remove as much biotic material as possible using fine filtering and (iii) to kill as much as possible of any remaining biota using UV irradiation. To ensure also that the laboratory experiments replicated field conditions closely to ensure the results are not potentially misleading when applied to practical situations,²⁰ a flow-through rather than a recirculating system or a closed system was adopted (Fig. 1). For the same reason, the use only of fresh seawater was adopted together with the use of corrosion coupons broadly consistent in size and with generally similar characteristics to those used in previous field studies. The system as designed, constructed and employed consists of two parallel streams of low velocity seawater for immersion corrosion testing, one stream being natural coastal seawater and the other using seawater from exactly the same source except that it was subjected to a sequence of settlement, filtration and ultraviolet (UV) radiation in a specially designed pumped system (Fig. 1). In the sequel these water streams are abbreviated as N-SW and UV-SW respectively.

UV irradiation has been shown in the UV literature and in industry to have no observable effect on the chemical or physical properties of waters so treated.²¹ Also, its efficiency is relatively insensitive to temperature and to differences in bulk water pH. It works by the UV rays penetrating the cell walls of living organisms and disrupting cell genetic material.²² High levels of destruction of biota in flowing water systems requires optimal conditions of water flow rates, small distances for water penetration of UV rays, low water turbidity and low shadowing and other effects.²¹ The system shown in Fig. 1 was specifically over-designed, with water flow rates much lower than theoretically necessary. Nevertheless, since in practice slight departures from theoretical optimal operation conditions are inevitable, it is recognized that the UV irradiation process may not always have produced truly sterile seawater. The effectiveness of the system was monitored periodically (see below).

Figure 1 here

The test rig is located inside a small laboratory building on the site of the Port Stephens Fisheries Centre at Taylors Beach, located on a tributary of Port Stephens, a very large coastal water body on the East coast of Australia. The Centre is used for fish breeding and fisheries research and has a large pumped fresh seawater supply. The seawater for the experiment was taken directly from this source.

Fig. 1 shows that the seawater taken from the pumped fresh seawater supply is split into two streams, one piped directly into the natural seawater exposure tank. The tank is constructed in fiberglass as a single moulded unit. Its internal dimensions are 1.5 x 0.58 m in plan, with a water depth of 235 mm at the inlet end. The tank floor slopes upward with flow direction towards the overflow at the outlet end. The water capacity is 102 litres. Water enters the tank past an overflow weir followed by an underflow weir to achieve uniform flow across the tank in an attempt to

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2
3 minimize as much as possible dead spots in the water body. The water velocity in each tank is kept
4 constant at approx. 1-1.5 mm/s. This is considered sufficiently low to obviate velocity effects that
5 might interfere with the corrosion processes but high enough to obviate concentration control
6 limitations on the rate of corrosion. The water discharges through a piped system back to the
7 estuary. The tank is fitted with a moulded fiberglass non-airtight lid to reduce entry of dust and light
8 and to achieve exposure conditions generally similar to those of the second tank.
9

10
11 The second seawater stream passes through a settling tank followed by a series of filters consisting
12 of primary (AMIAD Automatic Filter, 80 micron) and secondary (Diatomaceous earth filter
13 Performa CV 962f TC) filters and a succession of 10, 5 and 1 micron filter bags (FSI). The primary
14 and secondary filters are backwashed and the filter bags replaced in accordance with manufacturer's
15 recommendations. The water then passes through two 85 diam. uPVC tubes each with an axially
16 placed UV lamp (Smart UV sterilizer Model 02040, 40W, UV-C, 254nm wavelength) around which
17 the water flows at low velocity (less than 0.5 mm/s) before entering an exposure tank similar to the
18 natural seawater tank except that it is covered with a moulded fiberglass lid that is fitted internally
19 with a third UV lamp. The purpose of this lamp was to prevent secondary microbiological growth
20 inside the tank. For personnel safety reasons this tank is fitted with a more substantial lid than the
21 natural water tank. The lid is fitted with a biological airfilter (Osmonics Inc.) to minimize entry of
22 atmospheric bacteria and to permit limited access of fresh air. After passing through the tank the UV-
23 treated water is discharges to the estuary.
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28 The effectiveness of the filtration and UV irradiation system in destroying biota was monitored at
29 regular intervals. Samples of seawater were taken from the water stream immediately after the
30 filtration unit, after the two UV units and from inside the UV exposure tank. The water samples were
31 tested for sulfate reducing bacteria (SRB) and iron related bacteria (IRB) using commercial test kits
32 (BART™). The protocol for these kits is based on the time taken to reach a noticeable change in
33 color of the solution in the test tube. The tube contains nutrients for necessary for bacterial
34 metabolism. Material suspected of containing the bacteria of interest is introduced into the tube,
35 which is then sealed. Visible detection of a change in color after 24 hours is quoted as equivalent to
36 6×10^6 cfu/ml (colony forming units / milliliter) and detection after 7 days (the standard maximum
37 observation period) as equivalent to about 500 cfu/ml. The latter usually is considered a negligible
38 presence of background bacteria.²³ This is equivalent to a limit on the probability of detection of
39 10^{-4} .
40
41
42

43 Independent testing of the effectiveness of the filtration and UV irradiation process also was carried
44 out. This was done by testing for microbiological content within the rusts of steel coupons exposed
45 for 239 days in the natural seawater exposure tank and also for the rusts on coupons exposed in the
46 UV-treated seawater exposure tank. In addition, microbiological testing was done for the rusts on a
47 coupon exposed in the natural seawater tank for 943 days. The coupons were withdrawn from the
48 exposure tanks and immediately and while still wet placed in sterile plastic sample tubes, sealed and
49 then express couriered to an independent testing laboratory in Canada. The coupons were sent
50 'blind' and identified only by code letters. At the laboratory, tests were conducted on the rusts for
51 IRB, SRB, HAB (Heterotrophic Aerobic Bacteria), SLYM (Slime Forming Bacteria) and DN
52 (Denitrifying Bacteria) using the BART™ system and for ATP using third generation modification
53 of the Luminultra™ total ATP methodology.²⁴
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57 Periodic water quality testing was performed during the whole of the test program. This included
58 salinity, pH, dissolved oxygen concentration and nutrient concentrations. An independent water
59 quality laboratory (Hunter Water Australia) performed the water quality analyses. The water
60

temperature was monitored using Tinytag Aquatic TG-3100 data loggers in both tanks continuously for a twelve-month period during the test program. In addition, subsequent to the present test program but as part of a research program using the same rig as in Fig. 1, open circuit potentials were measured on carbon steel samples²⁵ at 4 hour intervals throughout the 90 day test program in each of the two streams. The corrosion potential E_{corr} was measured against a portable Ag/AgCl reference electrode (CCS1-PORT, Silvion Ltd., accuracy $-5\text{mV}\pm 5\text{mV}$ vs. SCE in 3% NaCl at 20°C).

The corrosion coupons were laser cut from one 1.3 mm thick low carbon steel plate (C 0.08, Mn 0.21, S 0.017, Ni 0.03, Al 0.059, Cu 0.03, Sn 0.02, others < 0.01, bal Fe, % weight). The plate surfaces were hand polished using 1200 grit paper then further polished to a mirror finish using a series of fine abrasives finishing with a 1 micron polishing paste. Each coupon was 25 mm x 25 mm, a dimension chosen to allow direct access to the stage of the SEM. Immediately prior to being exposed, all coupons were sterilized with denatured alcohol for approximately 10 minutes and air-dried. They were kept in desiccated conditions for short-term storage until installed in the exposure tanks. The coupons were each suspended from a polyvinylchloride cross-member using nylon ties with a unique numbered identification tag. All coupons were immersed vertically with the top edge at least 25 mm below the water surface such that in the UV tank any residual UV radiation was confined to the upper edge of coupons only.

One coupon was recovered from each of the exposure tanks after 1, 4, 7, 14, 50, 100, 135, 190, 280, 360, 534, 726 and 943 days continuous exposure. All such coupons were examined externally immediately upon recovery and the nature of the rust formation noted and photographed. Samples of the rusts were taken for microbiological analysis as close as possible next to the metal surface. They were tested immediately using BART™ test-kits for SRB and IRB. Samples were taken also for immediate analysis of rust composition. Coupon rusts were analyzed using XRD (Philips X'Pert MPD) and quantified phase analysis (Rietveld refinement) for estimating the quantities of crystalline and amorphous components of the rusts.

Immediately after these samples were taken the coupons were cleaned of corrosion products. In many cases washing under a stream of fresh laboratory tap water for two minutes was sufficient to remove all the corrosion products to reveal bright steel. In some cases, particularly for exposures of more than 200 days, the inner rust layer was found to be more difficult to remove. These were removed using dilute inhibited hydrochloric acid (16%wt HCl with 2% hexamine) and then rinsed in clean tap water and alcohol before drying, following conventional ASTM standard procedures.²⁶ The coupons were then weighed for mass loss analysis (to 0.1 mg accuracy). Coupons were examined also on both sides by low powered microscope (x60) and photographed. Some coupons were selected for more detailed examination using a SEM (Philips X'Pert MPD). Consistent with standard practice, these coupons were gold coated. Both sides were examined. All coupons were stored in desiccated conditions at all times when not being examined or processed, for the whole of the experimental program.

At the end of the complete exposure program the surface roughness of a selected set of coupons was measured using a 3D optical profilometer (Contour GT-K1, Bruker, Germany). The phase shift interference mode was used to characterize the polished surfaces. For each coupon face 5 different locations were selected at random and more than 5 mm away from edges. Ten measurements were made at each location. Each location covered an area of 0.588 x 0.441mm. A combination of x20 and x0.55 lenses was used, with a vertical resolution of approx. 0.1nm and lateral resolution < 1 micron. The data were filtered and processed using VISION 64™ software (v5.30, Bruker,

Germany). A Gaussian regression filter was applied to remove general surface waviness. The surface roughness values were then calculated.

At the end of the experimental program all the corroded coupons were held together face-to-face and the edges and their associated rusts removed using a milling machine. This was to attempt to eliminate edge effects. Typically only about 0.3 mm of metal was removed from each edge. The carefully controlled process ensured all coupons were of the same finished size. Blank (i.e. uncorroded) coupons were included in the process. Following this operation all coupons were weighed and new mass losses determined. These were compared to the mass of the blank (and also machined) coupons. The mass losses were converted to corrosion losses using a steel density of 7.88g/mm^3 .

EXPERIMENTAL OBSERVATIONS

Environmental conditions

Table 1 shows a typical set of results from water quality analyses. Similar results were obtained at various stages throughout the test program. The water temperature at any time in the UV-SW tank was approximately 2°C higher than in the N-SW tank. This is attributed to the heat generated by the two UV tubes causing the water temperature to rise prior to entering the tank. The contribution from the heat generated in the water by radiation from by the UV tube in the roof of the tank is considered negligible. The error involved in temperature readings is estimated to be less than $\pm 2\%$.

Table 1 shows that both exposure tanks had similar dissolved oxygen (DO) concentrations. Similar results were obtained at other sampling times. This is consistent with both exposure tanks being supplied from the same bulk seawater used in the experiment with the result that the DO of the waters in the tanks is governed by the DO in the bulk seawater. Variation in DO within the tanks depends on factors such as water temperature and water agitation and possibly water composition. All such factors are very similar (e.g. DO, sulfates, total phosphorous) or negligible (e.g. nitrates) for both tanks. The long-term variation in DO is estimated to be less than $\pm 5\%$ around the values shown in Table 1, based on the data underlying the typical values shown in column 4.

Table 1. Typical concurrent averages (and long-term range of) water quality results at Taylors Beach.

Water Quality Parameter	Units	Natural seawater (N-SW) (typical)	UV treated seawater (UV-SW) (typical)	Taylors Beach long-term range*
Column	(1)	(2)	(3)	(4)
Water temperature	$^\circ\text{C}$			
Minimum-maximum		10.3-31.3	11.3-33.6	
Average		19.5	21.5	~ 20
Typical diurnal range		1.0-2.0	1.0-2.5	
Salinity	ppt	30.9	30.2	25.7-31.3
pH		7.9	7.7	7.7 - 8.1
Dissolved oxygen	% sat.	83.6	81.3	
Ammonia	mg N/L	0.035	0.054	< 0.03 -0.08
Nitrite	mg N/L	0.005	< 0.003	< 0.003 -0.034
Nitrate	mg N/L	0.015	0.082	0.017-0.05

Total oxidized nitrogen	mg N/L	0.020	0.082	
Sulfate	mg/L	1800	1800	1600-2750
Total phosphorous	mg P/L	0.014	0.018	< 0.003-0.07
Calcium	mg/L	355	341	

* Range taken over the 10 years 2000-2009 for surface waters.

Microbiological analyses

For the seawater in the UV-SW tank testing for SRB and for IRB produced negative results, [at 7 days incubation](#), throughout the entire exposure program period. In contrast, for the seawater in the natural seawater tank positive test responses were obtained (within 1 day) for SRB and for IRB and this continued throughout the whole exposure program.

As noted, an independent testing laboratory performed microbiological analyses on the rusts present on coupons randomly selected from each tank. Table 2 shows the results with the coupons identified. The microbiological samples extracted from the rusts on coupons exposed in the UV-SW tank gave zero responses to standard bacterial culturing tests. There was a low response also to ATP tests. The low reading obtained from the coupon rusts in filtered and UV-treated seawater is likely to represent remnant ATP on dead cell material.²⁷

Table 2. Microbiological test results on rusts of selected (blind) coupons²⁴

Coupon Identification (Blind sample)	S	R	T
Coupon Environment	Filtered and UV radiated seawater	Natural seawater	Natural seawater
Coupon continuous exposure duration	239 days	239 days	943 days
ATP ^a (total) RLU: Mean, standard deviation ^b .	110, 49	623, 75	262, 103
Bacterial population ^b (pac/g)			
IRB	ND	1.8 x 10 ⁶	2 x 10 ⁶
SRB	ND	ND	ND
HAB	ND	ND	ND
SLYM	ND	50 x 10 ⁶	40 x 10 ⁶
DN	ND	ND	3 x 10 ⁶
Dried corrosion products and biomass (mg/m ²)	2.3	2.27	17.2

^a RLU: Relative Light Units.

^b from triplicate sampling.

Rusts on coupons

During the first 3 months there was little to distinguish between the rusts formed on coupons in the N-SW and UV-SW seawaters. At 135 days (about 3 months) the coupons recovered from the UV-SW tank showed a uniform and apparently compact rust build-up. The coupons exposed in the N-SW tank had rusts that were soft, voluminous and easily washed off.

The corrosion products at subsequent recoveries were similar in overall appearance but increasingly more voluminous, much more so for the coupons in UV-SW. For example, at 943 days (2.6 years) exposure the rusts were more voluminous and more irregular in appearance than was seen for the earlier rusts at 135 days. There also was a greater difference in the appearance between the coupons.

The coupon exposed to natural seawater shows a number of smaller tubercles and also one large orange tubercle. When removed, the larger tubercle was found to cover a layer of black corrosion product that was easily washed off to reveal bright steel underneath. Some of the long-term rusts on coupons exposed to UV-SW were slightly uneven in appearance but tubercles were not observed at any time.

Coupon rusts were analyzed using x-ray diffraction (XRD) techniques using a standard analysis package for Rietveld refinement for the estimating the quantities of crystalline and amorphous components of the rusts. Figs. 2 and 3 show the XRD traces for rusts obtained in the UV-SW and N-SW immersion exposure environments respectively. The relative occurrence of each crystalline component is shown in Table 3.

Figure 2.

Figure 3.

Table 3. Constituents of rusts and relative occurrence (%) (using Rietveld quantified phase analysis) after 943 days continuous exposure.

Environment		Natural seawater	Filtered and UV treated seawater
Constituent	Formula	%	%
Magnetite	Fe_3O_4	38	71
Goethite	$\alpha\text{-FeOOH}$	24	13
Lepidocrocite	$\gamma\text{-FeOOH}$	27	8
Aragonite	CaCO_3	7	-
Quartz	SiO_2	2	-
Sodium chloride	NaCl	1	1
Green Rust 2		trace	-
Akaganeite	$\beta\text{-FeOOH}$	-	-
Hematite	Fe_2O_3	-	8
Ferric oxychloride	FeOCl	-	trace

Mass and corrosion losses

After exposure and cleaning of each coupon the remaining mass was determined and compared with the original mass. The values of mass loss per unit area per face of coupon so determined are shown in Fig. 4 as a function of exposure period, both for coupons in both exposure environments. A best-fit non-linear trend has been drawn through each data set using a standard smooth curve fitting routine employing the Stineman smoothing function.²⁸

Figure 4.

At the end of the complete experiment the masses were determined also for all coupons after removal of their edges by a milling machine. These masses were compared with the mass of uncorroded coupons that also had been machine-milled and the corrosion losses determined. These are shown in Fig. 5. Again, best-fit trends are shown through each data set.

Figure 5.

Topography of corroded surfaces

The corroded surfaces of each coupon were photographed immediately after the rusts had been cleaned off. There were only very slight differences in the appearance of the surfaces between the two exposure environments for exposures of 14 days or less. At 50 days of exposure there is little evidence of corrosion although some pitting was observed under microscopic examination. In contrast, the corroded surface for the natural seawater exposure conditions showed obvious visual evidence of various areas localized corrosion. At 100 days the coupon exposed in UV-SW showed some localized corrosion at several locations on the surface. This was similar for both faces of the coupon. The coupon exposed in natural seawater for the same time period showed a surface that was considerably more uneven in surface texture and also was more heavily pitted. Similar but more severe differentiation in appearance of the corroded surfaces was observed for coupons exposed for successively longer periods. Examples are shown in Figs. 6 and 7 for exposures at 554 days (1.5 year) and 943 days (2.6 years) respectively. Again, the surfaces exposed in natural seawater (N-SW) show more localized and more aggressive corrosion than the coupons exposed in UV-treated seawater (UV-SW).

Figure 6.

Figure 7.

The topography of the coupon surfaces that had been exposed for more than 280 days was profiled and quantified using the conventional two-dimensional surface roughness parameter S_a . This measures the arithmetical mean height of the surface.²⁹ Fig. 8 shows that for the longer-term exposures S_a is considerably higher for the coupons exposed to natural seawater compared with the coupons exposed to filtered and UV-treated seawater. Also, for each exposure condition S_a increases with exposure period as shown by the linear trends fitted through the data.

Figure 8.

SEM observations

Optical microscopy and SEM showed considerable variation in the details of the topography of the corroded coupon surfaces between the type of seawater to which the coupons had been exposed and in each case as a function of exposure time. Areas of the most severe localized corrosion on a coupon surface were examined. Only a selection of images is given here.

Fig. 9 shows sample images of the surfaces of the coupons after 100 days continuous exposure in the two exposure environments. Both cases show localized or pitting corrosion, consistent with earlier observations.¹⁴ Both exposure environments show pits with regular and irregular plan shapes and of apparently similar pit depths. The pits in UV-SW environment appear to be somewhat larger in plan size but also somewhat more regular (curvilinear) in shape compared to those in the N-SW environment. In both cases the pitting shown suggests that the growth of the pits was limited in depth and that the pits also corroded sideways, some eventually joining to form larger depressions with similar depth to other pits on the surface.¹⁸ The surface of the coupon in N-SW shows what could be interpreted as large areas of pitting that has amalgamated but leaving some remnant

regions with lesser corrosion (Fig. 16a). In contrast, for the N-SW exposure conditions there appear to be no remnant regions. Generally similar patterns can be seen in Fig. 10 at 190 days of exposure.

Figure 9.

Figure 10.

Figure 11 shows the surfaces after 554 days (1.5 years) of exposure. In this case the coupon surface exposed to N-SW (Fig. 11b) shows a major depression that appears to be the amalgamation of pits lower centre, lower right, centre right and middle with also small pits adjacent. In contrast, the surface of the coupon exposed to UV-SW (Fig. 11a) shows numerous localized areas of corrosion (most of the area shown in the photograph).

Figure 11.

After 943 days (2.6 years) exposure the coupons in both environments show extensive corrosion plateaus (Fig. 12). Both the lower and the higher level plateaus are relatively uniform in appearance although both show areas of localized corrosion and, on close examination, very small pits on the surfaces.

Figure 12.

DISCUSSION

Whether irradiation from the single UV lamp in the tank conveying filtered and UV treated seawater could have influenced the corresponding corrosion mass loss curve in Fig. 5 or could have been involved in causing the differences in pitting corrosion (Fig. 8) requires consideration. There is some evidence that UV irradiation can affect corrosion resistance for carbon steels, but the results appear to be contradictory. Pioneering laboratory experiments³⁰ using high intensity, highly focused, laser type UV radiation on small samples of pure iron (area 0.785 mm²) immersed in borate buffered distilled water at pH = 8.4, with and without the addition of chlorides showed that the time to initiation of metastable pitting tended to be delayed by more than 12 hours. This occurred only when the radiation was applied continuously from first exposure. The effect was attributed to increased resistance of the passive film that formed during UV exposure. Subsequent investigations confirmed these observations.³¹ They are for very short observation times relative to the present experiment and were for essentially stagnant water conditions.

Contrary to these laboratory findings, Burleigh et al.³² reported increases in the mass loss of 25 x 50 mm carbon steel coupons immersed in flowing 10°C lightly chlorinated 'treated' water of undefined characteristics from a water treatment facility when irradiated by multiple (112) 27 W UV lamps. The intensity of irradiation at the coupons, any changes in water temperature and the water velocities were not reported. However, with a nominal discharge rate of 8m³/min. it is likely that the average water velocity was moderate to high and almost certainly turbulent. Two sets of experimental results are reported. In the first experiment of 3 months duration the carbon steel samples were noted as 'ruined' by severe crevice corrosion. Whether these were exposed to UV radiation and whether the crevice corrosion contributed to mass loss is not clear. For these reasons the results are not considered further. In a second experiment, the coupons were exposed initially for 3 months, then cleaned of rust products. Mass losses and properties of the rusts were not reported. The coupons were then re-immersed and UV irradiation continued for a further 2 months. At that

time (i.e. after 5 months) the total mass losses for the UV exposed coupons were some 15% greater than for coupons not exposed to UV radiation. Actual mass losses were not reported. Presumably, the double exposure protocol was applied both to the UV exposed samples and to the unexposed samples, and was an experimental device to obtain greater mass loss differentiation. The percentage mass loss increase is therefore independent of this artifice. Obviously, the effects of any hydrogen peroxide or hydroxyl radicals generated in the water by UV radiation³³ are included.

It is reasonable to assume that a sufficient build-up of rusts eventually would block UV radiation. In this case any UV effect would be only transitory. This may explain why the second exposure period was only 2 months since after the first of 3 months it had been found necessary to remove rusts. Unfortunately, with only a single observation, at 2 months in the repeated exposure, any transitory UV effect could not have been detected. However, it is of relevance to note that rust build-up also has the effect of limiting the effect of water velocity. Field results³⁴ for carbon steel immersed in seawaters at 20°C showed that increasing water velocity increases the rate of corrosion loss, but only for a period of some 20-30 days, depending in the magnitude of the velocity. Thereafter there was only an additive effect from the extra corrosion caused by water velocity in the early exposure period. For waters at 10°C this period will be about twice as long since at this temperature the rate of corrosion is about half that at 20°C. This compares with the 2 months in the second exposure used by Burleigh et al.³²

Information about the effect on corrosion loss of the single UV lamp in the tank with UV treated water is available in the corrosion loss vs. time plot (Fig. 4). For the first 50 days or so the coupons exposed to UV radiation showed greater and increasing corrosion losses compared with those in natural seawater (Fig 13). However, thereafter the difference declined, presumably because of the build-up of rusts, consistent with the effect of rusts on velocity effects. By 90 days the UV effect had disappeared. This transient behavior was not observed by Burleigh et al.³² because their experiments involved only one observation over the whole of each individual exposure period. Fig. 13 indicates that the 15% effect reported by Burleigh et al.³² may be an under-estimate compared with the peak effect.

Figure 13.

Support for the transient nature of UV irradiation on corrosion of carbon steel can be seen also in the results obtained for open circuit potentials (OCP) measured on carbon steel in each of the two exposure tanks in an experiment subsequent to the present one using the same experimental rig.²⁵ Fig. 14 shows that the OCP readings were almost identical on first exposure. After a sharp decline and a short (4 day) period of rapid active-passive peaks, a period of about 12 days followed during which the OCP in the UV exposed stream was slightly more positive (about 10 mV). The OCPs then became very similar and at 28 days the OCP for the steel in natural seawater showed greater corrosivity. This continued throughout the rest of the experiment. Of course, the OCP readings can shed no light on the relative rates of corrosion, whether corrosion is predominantly general or pitting, what component is the result of UV radiation in the tank or, importantly, whether microbiologically influenced corrosion is involved.³⁵

Figure 14.

A quantitative but conservative estimate of the effect of UV irradiation from the lamp in the tank conveying UV treated seawater is to assume the 15% increase observed by Burleigh et al.³² at 2 months is applicable also for the present experiment, even without considering the actual intensity

of UV radiation or the effect of water velocity. Assuming, as indicated above, that the effect is transitory, let it be taken that the 60 days (2 months) period also applies for the present experiment. Fig. 5 shows that the corrosion loss at that time is about 25-30 μm . Thus the 15% UV effect is equivalent to 3.75-4.5 μm . This amount is an estimate for the additive corrosion loss for all corrosion subsequent to 60 days or so, caused by the (earlier) UV irradiation. In other words, after 60 days or so the trend for corrosion loss in UV treated seawater in Fig. 15 is higher, by up to 4.5 μm , than it might have been without the UV lamp in that tank. Clearly, the error is small. The overall conclusion is that the UV lamp in the tank with coupons exposed to UV treated seawater had only a negligible effect on corrosion mass losses and on localized corrosion.

The observations in Fig. 4 show that the trends for corrosion losses for steel coupons in filtered and UV-treated seawater are similar, overall, to those observed previously in natural seawater.¹⁰ Fig. 5 shows the overall trends for corrosion loss as a function of exposure time for coupons from which the edges, and hence the effects of edge corrosion, have been removed. Again, the trends are similar although the trend for UV-SW in Fig. 5 is slightly higher overall compared to the N-SW trend. Also, the coupon views Figs. 6 and 7 and the SEM views Figs. 9-12 show that differences in localized corrosion and pitting have developed 100 days after first exposure and that these differences remain with longer exposure time (Fig. 8). Possible reasons for these observations are addressed below.

The difference between Figs. 4 and 5 shows the comparative influence of edge rusts on mass loss and that this is slightly greater for exposures in natural seawater. As expected, in the early stages of corrosion and before rusts build-up the effect of the edges is unlikely to be large and this is indicated by the initial corrosion rate r_0 . It is similar for both exposure environments, governed by oxygen diffusion limitations, and in the case of N-SW possibly by MIC influences.¹⁰ It is easily shown that the average rate of (initial) corrosion r_0 for the first 50 days in the UV-SW environment is 225 $\mu\text{m}/\text{y}$ and 255 $\mu\text{m}/\text{y}$ in the N-SW environment.

As shown in earlier studies at the same exposure site used for the present study and also for other sites, corrosion losses to about 350 days exposure at 20°C average seawater temperature largely are governed by oxygen diffusion rate limitations.^{9,10} During this period the corrosion loss trend is characterized by the distinctive gradual reduction in the instantaneous corrosion rate (the slope of the trend curve). This is consistent with Figs. 4 and 5. Also, it is known from previous observations, and from interpretations of the results reported by others, that during this time period the influence of MIC on overall corrosion is of negligible importance except for the first few days immediately after first exposure.¹⁰ It follows that in Fig. 5 the difference in the trend curves for the exposure period after a few days to about 350 days largely must be the result of factors other than microbiological activity.

Monitoring of dissolved oxygen (DO) concentration during the experiment showed that it was very similar in the two exposure media (Table 1). Because this is a practical experiment, slight variations and differences in DO concentrations could have occurred from time to time, despite the common seawater feed to both exposure tanks. However, because corrosion is a long-term process, such short-term variations are unlikely to have any noticeable influence on longer-term corrosion. Only consistent and continued differences in DO between the two exposure environments could cause a noticeable difference in corrosion loss between them when oxygen controls the corrosion rate (i.e. over the exposure period to about 350 days).³⁶ It follows that differences in DO can be discounted as a causative factor for the difference in the corrosion loss trends shown in Fig. 5 for the exposure period to 350 days, and, because subsequent corrosion loss magnitude depends on earlier corrosion

loss, also subsequently. A more likely causative factor is the difference in average seawater temperatures.

As noted, the water temperature for UV-SW typically was 2°C higher than for N-SW (Table 1). Water temperature will affect corrosion kinetics and may influence the rate of metabolism of microorganisms. Microorganisms usually are sensitive to temperature but typically are relatively insensitive to variations in temperature (typically $\pm 5^\circ\text{C}$) around the temperature corresponding to optimal microbiological activity. Gradual adaptation by microorganisms to higher or lower temperatures is known to occur, provided the temperature (and other) changes are very gradual in time.³⁷ Water temperature monitoring recorded only diurnal and seasonal changes in seawater temperature well within the tolerance limit and consistent with the source of the seawater and the design of the experiment. It follows that the corrosion loss differences in Fig. 7 are unlikely to have been the direct result of water temperature on any microbiologically influenced corrosion.

In contrast, water temperature does have an effect on electro-chemical and chemical corrosion reaction kinetics. It also has an effect on diffusion processes.³⁸ Previous investigations have included the effect of seawater temperature on the corrosion of mild steel for extended periods. These show that a rise of 2°C in average seawater temperature around 20°C increases the rate of corrosion by around 7-10% depending on the length of exposure.⁹ Using this estimate, the corrosion losses in UV-SW seawater environment at 21.5°C (average) were downward corrected by 10% to those in the N-SW seawater environment at 19.5°C (average). The result is shown in Fig. 15. It is seen that now the corrosion losses and the loss trends are closely similar for both exposure media during the first 350-400 days. This also reinforces the observations of closely similar DO concentrations in the two exposure environments (Table 1).

Figure 15.

Microbiological monitoring carried out as a routine part of the test program and also by independent analyses shows that the UV-SW exposure environment produced almost no response to any of the standard culturing kit tests and a much lower result for ATP (Table 2). These results show only that there were insufficient numbers of the specific microorganisms with the capacity to respond to the microbiological tests employed. However, often the meaning of such results is extended to apply to other microorganisms present and active in the same location and thus the same environment. The rationale is that under field exposure conditions microbiological activity nearly always occurs in microbial communities and that typically there is a high degree of inter-microbial dependence. As a result a low response by well-established and widely occurring species usually is taken as indicative of a similar state for other species in the community.³⁷

On the basis of the above observations and the data in Table 2 it is reasonable to conclude that the UV-treated seawater had a very low and probably negligible active microbiological content. As a result it had a very low to negligible capacity for microbiologically influenced corrosion (MIC). In contrast the natural seawater showed strong positive responses to most microbiological tests (Table 2). It should therefore be capable of MIC despite the relatively low concentration of critical nutrient (dissolved inorganic nitrogen, usually mainly nitrates^{6,8,11,12}) in the water (Table 1). The low availability of nutrients would suggest that any noticeable MIC could develop only under longer-term exposures. Such a conclusion is consistent with the trends for corrosion loss shown in Fig. 15. It can be interpreted as showing that corrosion loss is slightly greater in the natural seawater after about 350-400 days, increasing to some 12-15% greater at 726 and 943 days. To make a statistical comparison of the latter two readings, recourse can be made to statistical data collected earlier at the

same seawater site (Taylors Beach).³⁹ This work showed that the spread of observations, even at 2 and 3 years of exposure, is relatively constrained, with standard deviations around 20 μm estimated from 18 samples. Using the observed corrosion losses at 726 and 943 days (Fig. 15) as sample means, and applying standard statistical tools⁴⁰ shows that the (sample means for these) trend curves at both these exposure times are significantly different at less than the 2.5% probability level. This conclusion remains unchanged if the observed corrosion losses at 726 and 943 days are taken as (unfavorable) 90 percentile values. By inspection, there is no significant difference between the trends for shorter exposure periods. Overall, the results are consistent with earlier observations that showed increased corrosion losses for longer-term exposures in nutrient polluted seawater.^{3,6,8,10}

The development of localized corrosion with time follows a pattern different to that described for corrosion loss. Almost immediately from first exposure and then throughout the subsequent 2.6 years the natural seawater environment produced more severe localized corrosion and pitting than did the UV-treated seawater environment. This can be seen at the macro-scale (Figs. 6 and 7) and at the micro-scale (Figs. 9-12). Differences in surface topography are evident already after relatively short periods of exposure and continue, showing distinct difference between the two environments. Fig. 8 summarizes the longer-term trends in surface topography for each exposure environment in terms of the surface roughness parameter S_a . Grouping the data for 300-943 days exposure for each exposure environment and determining the sample statistics and then applying standard statistical tools⁴⁰ shows there is a probability of only about 2.5% that they are from the same population. From this it may be concluded that the two main trends for the localized corrosion as indexed by S_a in Fig. 8 are statistically significantly different at the 2.5% level.

Turning now to the development of corrosion with time, Figs. 9-12 give what are essentially instantaneous views of the coupon surfaces for different points in time. They may be interpreted using earlier observations. For 9a and b and Figs. 12a and b show that the pits at all points on the corroding surface have reached a similar pit depth.¹⁴ Some can be interpreted as having grown sideways and having joined with adjacent pits. This interpretation is consistent with earlier observations of the longer-term growth of pit depth for mild steel in natural seawater.¹⁸ Moreover, such development of pitting is consistent also with theoretical analytical models for pit growth. These predict sideways growth of pits once a critical pit depth has been reached, sufficiently deep to deplete the potential driving pit depth growth.⁴¹ It is important to note that these models, and the experimental findings against which they were compared, do not rely in any way on MIC.⁴² The present investigation shows that this development of pit growth occurs also in UV-treated seawater. It is, therefore, not a function of microbiological influences.

The XRD traces in Figs. 3 and 4 and the XRD results in Table 3 show very considerable differences in rust composition between the composition of rusts in natural seawater and the composition of rusts in the UV-treated seawater after 2.6 years of continuous exposure. Usually, a higher presence of magnetite and maghemite in the rusts indicates a low oxygen environment relative to that necessary to form rusts such as goethite, lepidocrocite and aragonite⁴³. For the coupons exposed to UV-treated seawater, a lower oxygen availability at the corroding interface could be the result of the apparently more compact and firmer rusts observed on these coupons. This is unlikely to have been the case for corrosion to about 350 days of exposure since the corrosion loss trends in Fig. 15 indicate relatively little difference in corrosion losses in this time period. It corresponds, in the present case of an average seawater temperature of 20°C, to the period during which oxygen diffusion controls the rate of the corrosion process. More likely the formation of magnetite occurs primarily in the subsequent exposure period, when corrosion occurs under low oxygen or anoxic conditions, most likely involving pitting under anoxic conditions.⁴² Anaerobic MIC also may be

involved. Both processes can contribute magnetite to the inner rusts. The present results suggest that corrosion under (near-)abiotic conditions such as created by UV-treatment of seawater contributes magnetite at a faster rate than under natural seawater conditions. It follows that the lower presence of magnetite in (biotic) natural seawater may be the result of microbiological influences. This supposition and the mechanics involved are areas for further investigation.

It is important to note that direct and detailed investigation or observation of in-situ microorganisms was not the aim of the present study. Microbiological monitoring was used to compare the conditions in the UV-treated seawater with those for the natural seawater and to demonstrate the degree to which the filtration and UV irradiation process was successful in removing active microbiology.

It is noted that a variety of techniques exist to examine bacteria in biofilms but these are suitable primarily for laboratory investigations.⁴⁴ They were considered impractical for the present study. These techniques also may interfere with the very processes of interest, that is, those within the biofilm and within the corrosion products. Similarly, it was recognized that detailed observation, under natural conditions, of the development over time of individual pits would be very difficult experimentally, in part because it is well-known that the location of individual pits cannot be predicted with any degree of accuracy, even for small coupons or isolated surface areas.

Microbiological testing of the rusts on the coupons showed negative results for SRB both for rusts in the UV treated seawater and for the rusts on coupons in natural seawater (Table 2). This may be considered somewhat surprising as SRB usually are assigned an important role in the corrosion of steel in natural seawater.^{1,2,4} In contrast, other bacteria usually associated with corrosion of steel in seawater such as the iron oxidizing and the iron reducing bacteria were detected in the rusts of the steel coupons. These bacteria gave similar strong responses to the commercial tests, and both earlier in the experiment and at the end (Table 2). Denitrifying bacteria were detected only at the end of the experiment and only in natural seawater, consistent with denitrifying bacteria requiring anaerobic conditions for their metabolism (as well as requiring nutrients). It is clear that these observations differ in some respects from the conventional understanding of the role, particularly of SRB, in marine corrosion of steels.

One aspect sometimes but not always overlooked,⁴⁵ is that the presence of biofilm and of microorganisms on steel surfaces can initiate localized differential aeration effects leading to localized concentration of corrosion,^{1,42} without a direct chemical effect such as associated with the release of metabolites from SRB. Such a scenario could explain many of the observations given herein, including the occurrence of more severe localized corrosion but not corrosion loss in natural seawater while oxygen diffusion controls the corrosion rate, and, once oxygen diffusion no longer controls the corrosion rate, the additional effect of greater mass loss for natural seawater exposures. Taken together, these observations and propositions indicate that further investigation is warranted to try to unravel the role of various bacteria in localized corrosion of steel. This should include detailed microbiological investigation closely coupled with observations of corrosion at the micro-scale. In order to obtain information directly relevant to practical applications such investigations should also include experiments done under natural conditions rather than under (artificial or accelerated) laboratory conditions.⁴⁶

CONCLUSION

Mild steel coupons cut from the same sheet of steel and immersion exposed in low nutrient, near-

fully oxygenated natural temperate coastal seawater showed very similar mass losses irrespective of whether they were immersed in natural seawater or essentially the same seawater that had been filtered and UV irradiated. This was the case for exposures up to about one year and thereafter there appeared to be a gradual increase in corrosion loss in the natural seawater relative to UV treated water and this became statistically significant at the 2.5% level at 2 and 2.6 years exposure. This latter trend is consistent with previous observations implicating microbiological influences in the increased corrosion in natural seawater.

The coupons exposed to natural seawater showed more severe localized corrosion and rougher surface profiles compared with coupons in the UV-treated seawater at all stages in the full 2.6 years of the experiment. The relative severity of localized corrosion and profile roughness in and between both exposure environments remained with longer exposure periods. For these the difference was found to be statistically significant at the 2.5% level.

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Figures

Figure 1 Schematic flow diagram for corrosion testing of steel coupons in either natural or filtered and UV-treated seawater at Taylors Beach.

Figure 2. Annotated XRD trace of rust sample from coupon exposed to filtered and UV-treated seawater for 943 days.

Figure 3. Annotated XRD trace of rust sample from coupon exposed to natural seawater for 943 days.

Figure 4. Corrosion mass per unit area as determined from mass loss observations. Best-fit trends lines are shown as functions of exposure period both for steel coupons exposed to natural seawater (full line) and to filtered and UV-treated seawater (broken line). Total surface area including edges = 13.78 cm^2 .

Figure 5. Corrosion losses determined from coupon mass losses after removal of edges and rusts on edges. Best fit trends through data as shown. The change in relative losses compared with Fig. 6 indicates the greater influence of edge rusts for exposure in natural seawater. Note that the initial corrosion rate r_0 is governed by oxygenation conditions and some short-term microbiological effect but is similar for both trends.

(a)

(b)

Figure 6. Cleaned surfaces of mild steel coupons (25 x 25 mm) after 554 days (1.5 years) of immersion. Coupon (a) exposed in filtered and UV treated seawater shows some isolated patches of pitting at lower right and localized corrosion at left. Coupon (b) exposed in natural seawater shows large areas of localized corrosion and severe edge corrosion.

(a)

(b)

Figure 7. Cleaned surfaces of mild steel coupons (25 x 25 mm) after 943 days (2.6 years) of immersion, (a) exposed in filtered and UV treated seawater and (b) exposed in natural seawater. Both show extensive localized and general corrosion, visually much more severe for case (b) that also shows corrosion plateaus, for example one large one at right and two in the upper half.

Figure 8. Surface roughness as measured by parameter S_a (microns) for longer exposure periods. Straight lines fitted to the data. Mean and standard deviation shown for collected data for (top) coupons exposed to natural seawater and (lower) filtered and UV treated seawater.

(a)

(b)

Figure 9. Most severe localized corrosion (pitting) observed on the surface of mild steel coupons after 100 days exposure (a) in filtered and UV treated seawater showing a large localized corrosion region and similar smaller shallow pitting but otherwise relatively uniform surface and (b) in natural seawater showing a surface with localized corrosion regions on a higher plateau with adjacent corroded region (at top, left). Bar = 500 μm .

(a)

(b)

Figure 10. Most severe localized corrosion observed on the surface of mild steel coupons after 190 days exposure (a) in filtered and UV treated seawater and (b) in natural seawater. The former shows what appear as amalgamated pits forming general corroded areas, leaving a remnant piece (top centre). Image (b) shows the remnant parts of pits as they have amalgamated leaving a surface resembling general corrosion. Bar = 200 μm .

(a)

(b)

Figure 11. Most severe localized corrosion observed on the surface of mild steel coupons after 554 days (1.5 years) exposure (a) in filtered and UV treated seawater and (b) in natural seawater showing large uniform depth depression relative to rest of surface. Bar = 100μm.

(a)

(b)

Figure 12. Most severe localized corrosion observed on the surface of mild steel coupons after 943 days exposure (a) in filtered and UV treated seawater and (b) in natural seawater. Both surfaces to show regions that can be interpreted as composed of laterally merged pitting. The topography is very similar in each case. Bar = 200 μm.

Figure 13. Relative mass losses for the early exposure period showing increasing mass loss for some 50 days for the coupons subjected to UV radiation from the lamp in the tank with filtered and UV treated seawater, relative to the coupons in the tank with natural seawater. After that time the relative difference declines and is reversed at about 80 days exposure.

Figure 14. Open Circuit Potentials as a function of exposure time for carbon steel exposed in the natural seawater tank and in the seawater tank with a single UV lamp. Data courtesy Laura Machuca.

Figure 15. Corrosion loss observations as in Fig. 5 but with data for UV-treated seawater reduced by 10% as an (approximate) allowance for the (about) 2°C greater water temperature. The best-fit trends lines to the data are shown.