

pH Measurement Under A Simulated Disbonded Coating Using An Optical Fibre Chemical Sensor

Maftah H. Alkathafi , Robert A. Cottis, Ramaier Narayanaswamy

Abstract— The present paper is concerned with pH measurement under a disbonded coating on steel, pH was monitored at different locations down the crevice using an optical fibre chemical sensor. A physical model was developed to understand the chemical and electrochemical conditions that are created within the crevice beneath a disbonded coating. The physical model used a polyethylene film covering a crevice of controlled thickness, and exposed to a gas of controlled Composition (air with 1%CO₂) on the exterior of the film. The crevice was filled with a simulated ground water and pH measurement was carried out at a controlled potential at the mouth of the crevice of -900 mV (SCE). The gas permeability of the coating played an important role in controlling the conditions at the end of the crevice, as the gas transport through the coating creates a more alkaline solution inside the crevice, the generation of hydroxyl ions due to the oxygen reduction reaction increasing the pH.

Keywords: optical fibre sensor, pH, physical model

1 INTRODUCTION

A special rig was constructed to study pH under a disbonded coating of steel. The rig consists of two steel plates, a polyethylene tape and silicone rubber to create the crevice gap and abrasive paper to provide a path for the gas flow (air with carbon dioxide). Perhaps counter-intuitively the crevice solution is situated above the polyethylene tape, so that the pressure of the solution holds the tape against the abrasive paper sheet. The upper plate of steel contains a simulated holiday, together with five holes at different distances from the mouth of the disbonded coating. An optical fibre chemical sensor was developed to measure the pH beneath the disbonded coating by using the reflectance technique. In the reflectance technique, light passes to a reagent retained at the fibre tip of one arm of a bifurcated fibre bundle, and the reflected light is taken to the detector by a second arm. This reflected light is analysed, giving information about the colour of the reagent. The change in colour is employed to determine the variation in pH. The corrosion system studied was selected because of its relevance to carbonate-bicarbonate SCC [1,2]. It has also been modelled numerically, as has been reported in an earlier paper [3].

2 EXPERIMENTAL PROCEDURE

The rig consists of two steel plates, 900 x 100 x 25.4 mm, a polyethylene tape of 0.8 mm thickness, silicone rubber of 0.52 mm thickness and abrasive paper of 900 mm length x 75 mm width, as illustrated in Figure 1 and 2. The two steel plates were surface ground to ensure that the two surfaces were parallel. A rectangular hole was machined through the top plate at one end to provide a solution reservoir and to simulate a holiday in the coating. The dimension of the holiday was 81.5 x 25 mm and a gas vent 8.30 mm diameter was situated at the far end of the crevice to facilitate gas removal during filling of the crevice with a solution. The latter was sealed with a screw during the experiment. Five holes, of 25mm diameter, were drilled part-way through the upper steel plate at 25, 75, 150, 300 and 600 mm from the holiday. Each hole contained two small holes that penetrated through the plate (this was done to avoid problems with drilling small diameter holes through the thick plate), one for the placement of a salt bridge, 2.4 mm diameter, that was used to connect to a reference electrode to measure the local potential of the steel plate, and the other, of 4.25 mm diameter, that was used to measure the pH of the crevice solution. The crevice between the upper steel plate and the polyethylene film was filled with a simulated ground water; Table 1 illustrates the chemical composition of the simulated ground water that was used in this study. The crevice was open to the air at the holiday, and the potential of the steel was potentiostatically controlled at this point.

- Maftah H. Alkathafi, Faculty of Engineering, Sirte University
P.O.Box 565, Sirte-Libya, maftahok@hotmail.com
- Robert A. Cottis, Corrosion and Protection Centre, School of Materials, University of Manchester, Sackville Street, Manchester, M13 9PL, UK
- Ramaier Narayanaswamy, School of Chemical Engineering and Analytical Science, University of Manchester, Sackville Street, Manchester, M13 9PL, UK

TABLE 1
Chemical Composition of Simulated Ground Water

Compound	Concentration, mg/l
NaHCO ₃	32.676
Na ₂ CO ₃	64.453
NaCl	292.50
NaOH	13.3885

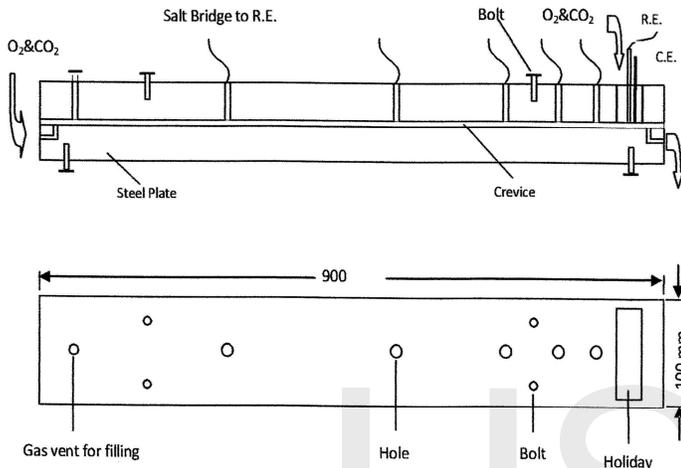


Figure 1: Schematic of the test cell used to simulate disbonded coating on steel.

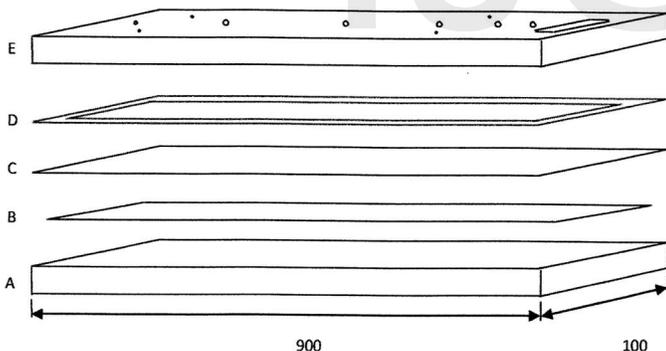


Figure 2: Test cell used to simulate disbonded coating on steel

Legend:

- A: The lower steel plate
- B: Abrasive paper (silicon carbide paper)
- C: Polyethylene film
- D: Silicone rubber
- E: The upper steel plate

2.1 Optical Sensor

The main materials used in the optical fibre chemical sensor were as follows:

Chemical Reagent. Bromothymol Blue is an indicator, a substance that changes colour as the pH of a solution changes. Bromothymol blue (BTB) is yellow in acidic solutions and blue

in basic solutions. Using BTB as the indicator in the pH sensor, it was expected that the pH value can be determined between 9 and 12 [4].

Copolymers. XAD-2 polymer beads are made from a copolymer of styrene and divinylbenzene and are used as substrates for optical fibre sensors. XAD2 is a non-ionic adsorbent with an average pore diameter of 90Å, a particle size of 20-60 mesh and a surface area of 300 m²/g.

Buffer Solution. Buffer solutions with pH values 6.0-12.0 ± 0.02 were used to create the calibration curve.

2.2 Immobilisation Procedure

1. XAD-2 polymer beads were washed thoroughly with deionised water, then with acetone using a filter paper, glass funnel and 400 mL conical flask.
2. The polymer was dried in a vacuum desiccator and stored for use.
3. 0.1 g of indicator dye (Bromothymol blue) was inserted in a 100 mL volumetric flask.
4. Methanol was added to the volumetric flask make up 100 mL of indicator solution, the flask was stoppered, then shaken.
5. 10 mL of the indicator solution was withdrawn with a pipette, and inserted in a small glass bottle.
6. 1g of XAD-2 polymer was placed in 10 mL of indicator solution and allowed to soak for 4-to 6 hours.
7. The XAD-2 polymer with adsorbed indicator dye (BTB) was washed with deionised water using filter paper until the water remained clear.
8. The dyed XAD-2 samples were left to dry in a vacuum desiccator for a few hours.

In solution Bromothymol blue is yellow at pH values below 7 and changes to blue at higher pH. On addition of hydrochloric acid the colour of the immobilised Bromothymol blue is reported in the literature to be yellow and then changed to dark blue on the addition of sodium hydroxide solution [5].

2.3 pH Probe Construction

A plastic fibre bundle 2.8 mm diameter was used as a bifurcated optical fibre bundle. It contained 32 optical fibres. A 1.475 m length of the fibre bundle was stripped of 0.11 m of sheathing at one end. The 32 fibres exposed were separated into two bundles of 16 fibres each. The fibres in each bundle were selected to give a random distribution at the other end. This is important for efficient collection of reflected radiation. One half of the bifurcated bundle was employed to transmit visible radiation to the sensing tip and the other was used to conduct a proportion of the radiation reflected from the sensing tip to the detector. The probe construction is shown in Figure 3; the two bundles of 16 fibres were pro-

tected by heat shrink tube. Then, terminal connectors were fitted to each of the two bundles for connection to matching bulkhead connectors at the radiation source and on the detector system. At the other, unbifurcated end, shown in detail in Figure 4, 2 mm was cut from the fibres of the bundle and polished using aluminium oxide lapping film. In addition 12mm of the sheathing was stripped away from this end. The exposed fibres were inserted into a 2.5mm PTFE tube. The purpose of this tube was to retain the fibres with XAD2 polymer beads. The copolymer with immobilized Bromothymol blue was retained in position at the end of the fibre bundle using a porous membrane (NY 41 HC, white polyamid, Switzerland). A 50 x 50 mm membrane square was used to make a seal around the PTFE tube. The complete assembly was inserted into heat shrink tube of sufficient length to hold the membrane in position against the tube and to cover the probe sensing end up to the fibre sheathing and 5-10 mm beyond.

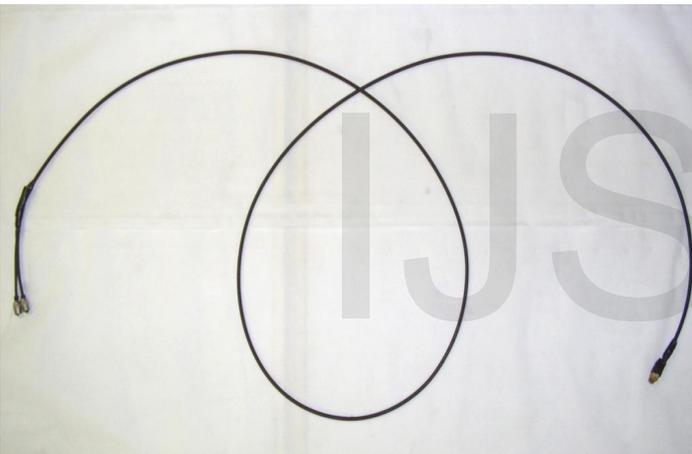


Figure 3: Bifurcated optical fibre chemical sensor

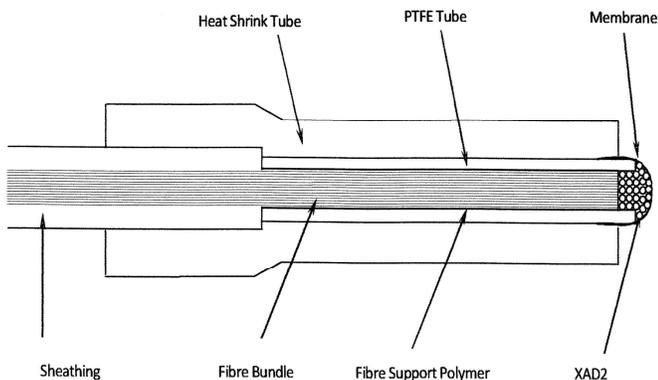


Figure 4: Cross-section of optical fibre chemical sensor

2.4 Instrumentation for Optical Fibre Chemical Sensor

A schematic diagram of the experimental instrumentation system employed in this work is shown in Figure 5. A tungsten-halogen bulb (12V,50W) was applied as a source. The power supply used (0-12V,10A) provided as stabilised DC supply to the lamp (Farnell Instrument). The lamp was housed in a diecast box with a fan providing a cooling air flow through the box. The light path was periodically interrupted by a chopper. The light from the lamp is coupled onto one arm of the bifurcated optical fibre bundle, while light reflected from the reagent phase is then collected by the other arm of the bifurcation and transported to the photomultiplier tube detector via a monochromator. The signal from the photomultiplier tube (PMT) detector is enhanced using a current amplifier and a lock-in amplifier. The lock-in amplifier is synchronized with the chopper frequency, which effectively removes interference effects from ambient light. The output is recorded on a monitor.

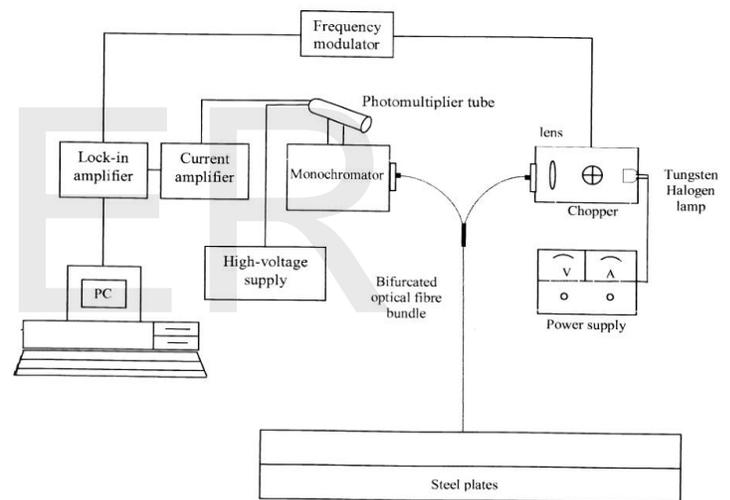


Figure 5: Instrumentation used for reflectance measurements

2.5 Reflectance Measurements

The calibration curve of reflectance versus pH was constructed as follows:

- Buffer solutions (pH6 to pH12) were prepared for calibration set points, using pre-prepared buffer sachet dissolved into 500 mL of deionised water.
- The pH of the buffer solutions were checked by pHmeter.
- The sensor probe was immersed in a 30 mL bottle containing pH 6 buffer solution.
- The probe was left to stand in the solution for 10 to 15 minutes.
- The meter was set to 380 nm and then the reflectance measured as a function of wavelength as indicated in Figure 6.

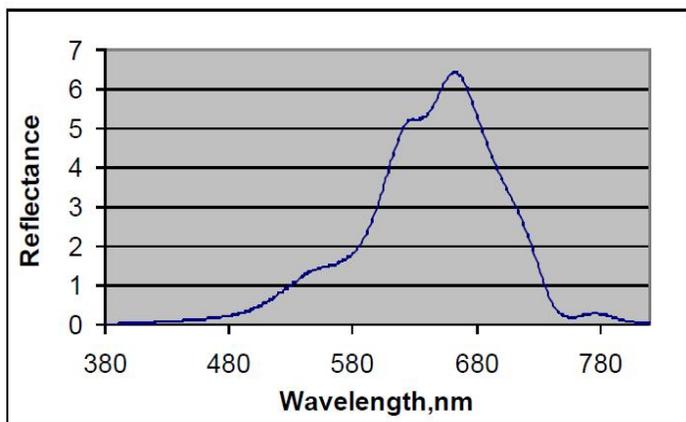


Figure 6: Reflectance with wavelength for immobilised bromothymol blue at pH 6

- Using the same procedure readings were taken in buffer solutions of pH 7, 8, 9, 10, 11 and 12. These data were logged on a PC.
- A wavelength of 653 nm was chosen for reflectance measurements as that at which the maximum change in the reflectance signal with pH was observed.
- Reflectance at 653 nm for all pH 6 to 12 was measured as shown in the calibration curve.
- The sensor probe was inserted through the hole (4.25 mm) of the upper steel plate into the solution and reading recorded after 10 - 15 minutes, see Figure 7.
- Reflectance was plotted against wavelength. Then, the reflectance value at 653 nm was plotted against pH to produce calibration curve.
- The pH of the test solution was measured at five different distances from the holiday by the same procedure. The holes were sealed by plastic bolts, 4.25 mm diameter and 23 mm long, to minimize contact with air while moving the sensor probe.

Legend:

- A: Power Supply B: Light Source
- C: Bifurcated optical fibre bundle (the sensor probe)
- D: Monochromator E: Photomultiplier Tube (Detector)
- F: 218 variable frequency optical chopper
- G: Signal Amplifier H: Monitor of Computer
- I: the Rig with two Steel Plates



Figure 7A: Rig with the sensor probe for pH measurements

3 RESULTS

The wavelength dependent reflectances from immobilised Bromothymol blue at pH 6 to 12 are plotted in Figure 8. As mentioned in previous section, the large change in the reflectance signal with pH was observed between pH7 and pH11. Consequently, the wavelength of 653 nm was used for measuring reflectance signal. Table 2 provides the reflectances obtained with pH at 653 nm, i.e. the calibration curve for the sensor, as shown in Figure 9. pH measurements along the disbonded coating at different distances and time with a controlled potential of -0.9 V are presented in Table 3. The variation of potential with distance and time at a control potential of -0.9 V are plotted in Figure 10 and 11 for physical and numerical modelling.

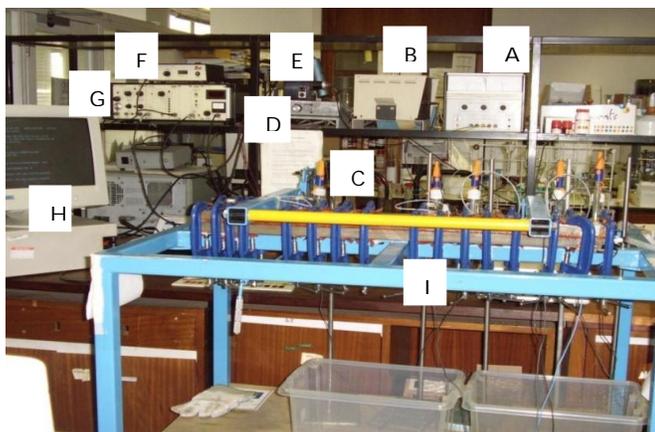


Figure 7: Rig with instrumentation and the sensor probe for pH measurements

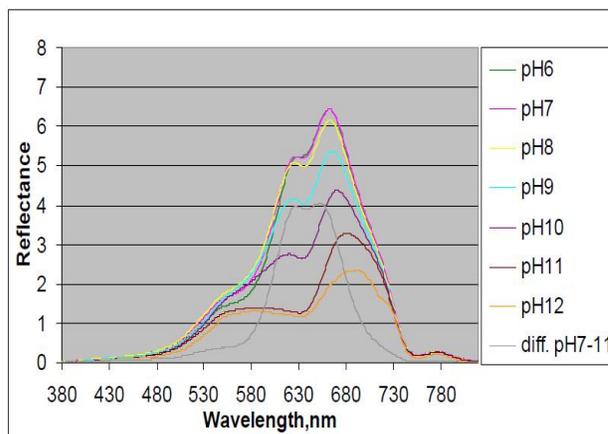


Figure 8: Reflectance with wavelength for immobilised bromothymol blue at a pH 6 to 12

TABLE 2
Reflectance Obtained With pH At 653 nm

PH	6	7	8	9	10	11	12
Refl.	6.119	6.087	5.795	4.886	3.542	2.042	1.515

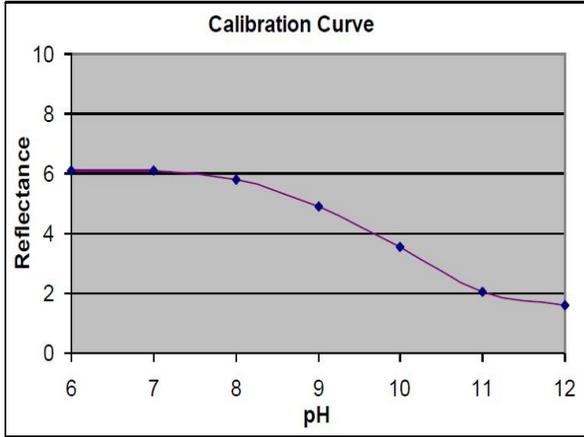


Figure 9: Reflectance signal as a function of pH at 653 nm

TABLE 3
Reflectance At 653 nm

Distance / mm	25		75	
	Refl.	pH	Refl.	pH
0	4.556	9.3	3.54	10
24	3.813	9.8	3.285	10.2
36	4.843	9	4.402	9.4
60	3.521	10	2.612	10.63
84	3.956	9.7	3.353	10.14
108	4.015	9.7	3.396	10.1
132	2.106	10.95	1.958	11.2
156	2.58	10.65	1.528	11.35
180	2.363	10.77	1.793	11.3
204	3.15	10.3	2.39	10.75

150		300		600	
Refl.	pH	Refl.	pH	Refl.	pH
4.589	9.25	5.119	8.78	4.992	8.9
3.745	9.87	4.018	9.7	4.345	9.43
2.95	10.4	3.632	10	5.111	8.8
4.229	9.52	4.224	9.5	4.051	9.63
2.947	10.4	2.539	10.68	3.496	10
2.209	10.9	3.315	10.16	2.926	10.38
2.32	10.8	2.32	10.8	2.182	10.9
2.561	10.67	2.469	10.7	2.458	10.71
2.004	11.1	2.117	10.95	2.29	11
1.66	11.6	1.79	11.45	1.94	11.2

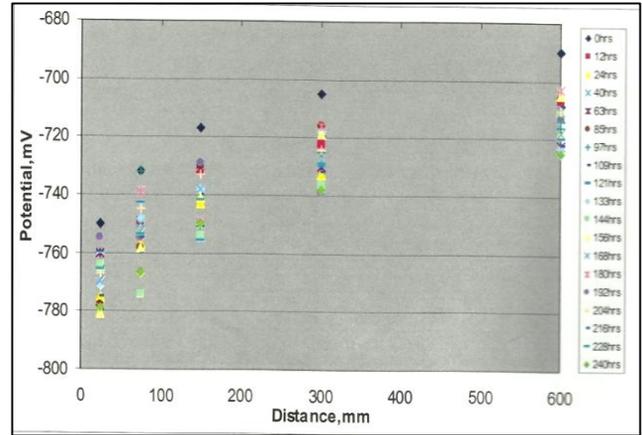


Figure 10: Variation of potential with distance from a holiday at different times and controlled potential -0.9 V – physical model results

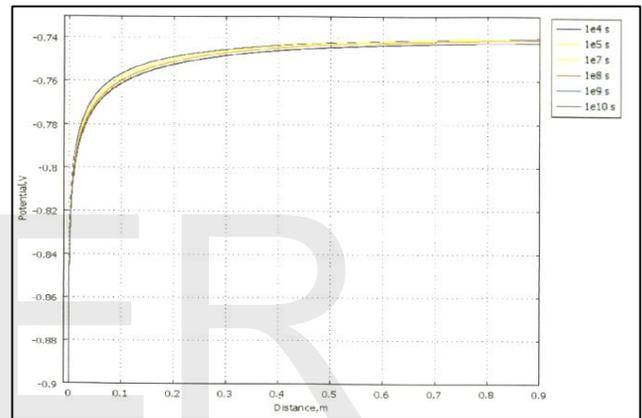


Figure 11: Variation of potential with distance from a holiday at different times and controlled potential -0.9 V – numerical model results

4 DISCUSSION AND CONCLUSIONS

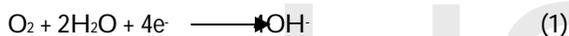
The pH was measured at different distances, i.e., at five holes from the mouth of crevice. These holes were sealed by plastic bolts (4.25 mm diameter and 23 mm length) to reduce oxygen access, but some oxygen ingress through the ports in the model crevice was possible during moving the probe sensor and closing the hole by the bolt. Although the process of moving was done as quickly as possible, it should be taken into consideration that some oxygen may have entered the crevice.

Table 3 indicates the variation of reflectance with pH for immobilized bromothymol blue at different times and distances. As indicated above, a wavelength of 653 nm was used for measuring the reflectance. At the beginning of the experiment, the mouth of crevice was more alkaline than the tip of crevice. It can be observed that the pH became less alkaline

(9.43 compared to 10.2), as illustrated in Table 3. However, the pH increased gradually to reach 10.38 at 600 mm from the mouth of crevice at 108 hrs. As the time increased, the pH became more alkaline than the mouth of the disbonded coating, where pH reached 11.2 at 204 hrs.

Figure 12 below summarizes all Table 3. The pH sensor indicated that the pH of the crevice was becoming increasingly alkaline; the maximum value of pH was 11.6 at 150 mm from the mouth of crevice. The rise in pH was fairly rapid near the holiday but thereafter only small changes were observed. The pH increased to 11.2 at 600 mm after 204 hrs.

It can be observed that the tip of crevice is very isolated from the conditions at the mouth of the crevice. This was seen very clearly from the numerical model, which also demonstrated that the conditions at the end of the crevice depend almost entirely on the permeability of the coating. There is a significant flux of oxygen and carbon dioxide into the disbonded region with a high permeability of coating. The oxygen is consumed through the cathodic reaction,



This reaction is responsible for increasing pH within the crevice through the generation of hydroxyl ions and tending to passivate the steel surface. Consequently, the deeper parts of the crevice display a net cathodic reaction, and become more alkaline than in the vicinity of the holiday. This behavior agrees with the numerical model results as illustrated in Figure 13. These results are about 1 pH unit lower than the corresponding results for the numerical model, as shown in Figure 13. Using optical fibre chemical sensor the pH at a distance of 600 mm from the mouth of the crevice was 11.02 at 204 hrs, while the pH in the numerical modelling at the same distance and time was 12.08 and this is the upper limit of pH in the numerical modelling as shown in Table 13. The reason for the difference in results may be departure from the assumptions made in the construction of the numerical model, although it should also be appreciated that the pH values are towards the upper limit of the range of the bromothymol blue indicator used.

The disbonded coating with high permeability where oxygen goes through the coating and cathodic reaction takes place (equation 1), leads to the potential inside the crevice becomes more positive or less negative with distance, as shown in Figure 10. The potential inside the crevice at a distance of 600 mm was -0.725 V_{SCE} at 240 hrs, as indicated in Figure 10. This result is in a good agreement with the nu-

merical model as demonstrated in Figure 11, where the potential inside the crevice at the same distance and time was -0.742 V_{SCE}.

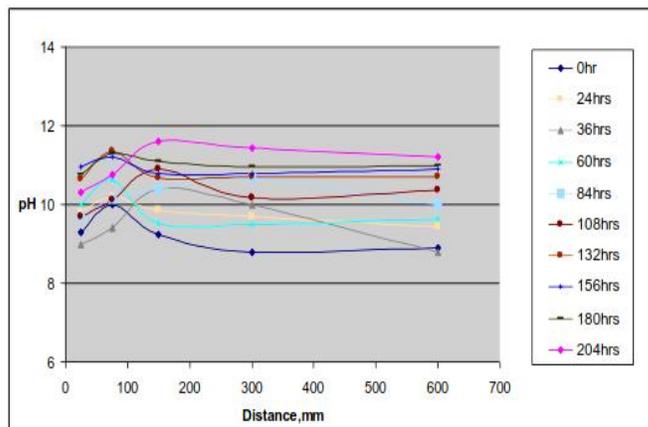


Figure 12: Variation of pH with distance from a holiday at different times and controlled potential -0.9 V – physical model

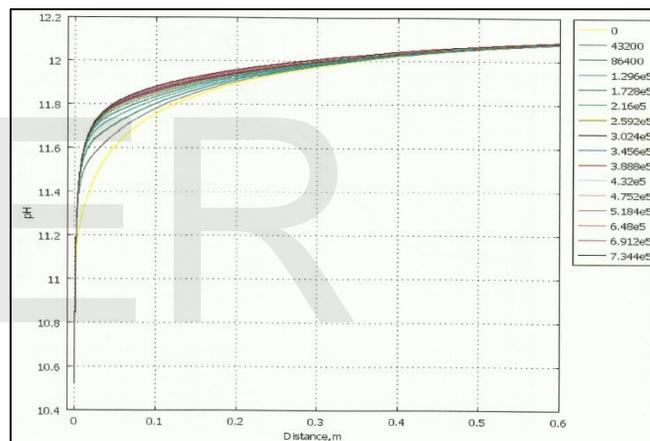


Figure 13: Variation of pH with distance from a holiday at different times and controlled potential -0.9 V – numerical model

TABLE 13

Variation of pH With Distance at 204hrs (734400 s) and -0.9V_{SCE}

Distance (mm)	25	75	150	300	600
Physical Modelling	10.30	10.75	11.60	11.45	11.20
Numerical Modelling	11.72	11.85	11.92	12.00	12.08

ACKNOWLEDGEMENT

The first author would like to thank the Ministry of Higher Education and Scientific Research-Libya and the University of Sirte to support of this study. Special thanks to corrosion and protection centre-the University of Manchester.

REFERENCES

- [1] R.L. Wenk, 5th Symp. On Line Pipe Research, AGA, 1974, T-1.
- [2] B. Fang, E. Han, Z. Zhu, J. Wang, and Wei Ke, J. Mater. Sci. Technol., Vol. 18, No. 1, 2002.
- [3] M.H. Alkathafi, and R.A. Cottis, A Study of the Chemical and Electrochemical Conditions Beneath Disbonded Coatings Using Numerical Modelling, Corrosion and Protection 2012, Australia, Paper 33.
- [4] R. Narayanaswamy, and O.S. Wolfbeis, Optical Sensors, Industrial, Environmental and Diagnostic Applications, Springer-Verlag Berlin Heidelberg, 2004, p. 287.
- [5] F.G. Kirkbright, R. Narayanaswamy, and N. A. Welti, Studies with Immobilised Chemical Reagents Using a Flow-cell for the Development of Chemically Sensitive Fibre Optic Devices, Analyst, Jan. 1984, Vol. 109, pp. 15-17.

IJSER