

Article

Investigation of the Effect Chloride Ions on Carbon Steel in Closed Environments at Different Temperatures

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Abstract: This paper investigated carbon steel corrosion in an enclosed environment, where one set of steel was immersed in 3.5 wt.% NaCl solution and another exposed to humid (condensation) conditions. The study employed electrochemical noise and electrochemical impedance spectroscopy techniques to monitor real time corrosion behaviour. The samples were evaluated with surface characterisation techniques including optical light microscope, scanning electron microscope with energy dispersive X-ray spectroscopy, and Raman spectroscopy. The results showed that carbon steel immersed in the liquid phase at a constant temperature exhibited the highest weight loss. However, the carbon steel exposed to water condensation (gas phase) at 80 °C manifested extensive localised corrosion. EN results agreed with the microscopy findings.

Keywords: carbon steel; SEM; EIS; EN; localised corrosion and weight loss

1. Introduction

Carbon steel is the most widely used engineering material, accounts for approximately 85% of the annual steel production worldwide [1]. Despite it is relatively limited corrosion resistance, carbon steel used in marine applications, desalinations plants, pipelines, ballast tank in ships [2]. Because carbon steels represent the largest single class of alloys in use, both cost-effectiveness and high strength.

Corrosion in carbon steel alloy is electro conductive media is influenced by the properties of the media in which they are immersed or exposed such as salt concentration [3], humidity [4], dissolved oxygen [5], and temperature [6].

In areas such as ballast tanks or insulated metals, carbon steel can be exposed to two distinct environment, i.e., immersion and condensation. Thus, different corrosion behaviours can be expected from these two scenarios. Literatures indicated that temperatures, relative humidity and chloride ion, affect the corrosion rate of materials, and complex interactions exist among these factors [7–10]. It was reported that time of wetness and chloride concentration were the critical factor determining the severity of corrosion [4]. However, Cai et al. [11] argued that the temperature and relative humidity were more important. Due to the contradiction in literature, it is thus required further investigation.

Sodium chloride (NaCl) solution is a type of typical electroconductive media, which could destroy the dense oxide layer formed by iron (Fe) via chloride ion (Cl^-) [12]. The nanometer-thick passive film on the metals resists a general corrosion, but it is susceptible to severe localised attack in certain aggressive media [13]. The best-known inducer of localised passive film breakdown is the chloride ion. Despite the enormous amount of experimental data and diverse hypothesis and models proposed [3,14–16], its influences on the corrosion product is still not sufficiently understood and the relationship between the chloride ions and temperature remains one of the most important and basic problems in corrosion science.



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The present work aims to distinguish the two environments potentially created from constant water evaporation and condensation in an enclosed space, with the effects of chloride ions in 3.5 wt.% NaCl solution. Several methods were used to characterise corrosion products, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. Electrochemical techniques such as electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS) were used to derive insight into localised corrosion activity and obtain real-time corrosion rates. Uniform corrosion rates were determined using a weight loss technique and the severity of localised corrosion was quantified using a 3D surface profilometer.

2. Experimental

2.1. Materials and Solutions

Carbon steel samples (AS 3678/Grade 250) similar to grade ASTM A 36 [17] with an nominal composition as shown Table 1 were cut to dimensions 20 mm × 20 mm × 2.5 mm.

Table 1. The chemical compositions of the carbon steel specimens (in mass).

Sample	C	Si	Mn	P	S	Fe
AS36	0.22	0.55	1.7	0.04	0.03	Bal.

All the specimens were coated with electrodeposition technique using a cationic epoxy, i.e., POWERCRON 6000 CX. Once electrocoating was applied to the sample, it was removed from the bath, and the electrocoated parts were placed in an oven to cure at 170 °C for 20 min. After the covered with the coating, a surface of each sample was wet grounded up to 600 grit SiC paper and rinsed with deionised water and ethanol. The surface was then dried with nitrogen gas and stored in a desiccator before testing. The exposed surface area of the specimens was set at 20 mm × 20 mm. before experiments; the samples were weighed with an analytical balance (0.1 mg precision). In each experiment, three samples were prepared for weight loss analysis.

The electrochemical probe was made with three identical carbon steel coupons (AS 3678/Grade250) with dimensions of 19 mm × 4 mm × 2.5 mm. Each coupon was soldered to an electrical wire; the three metal coupons were placed in parallel and mounted at 1 mm from one another using epoxy resin as shown in Figure 1. The exposed surface area of each coupon was 19 × 4 mm², which was wet ground to 600 grits on SiC paper and rinsed with deionised water and ethanol.

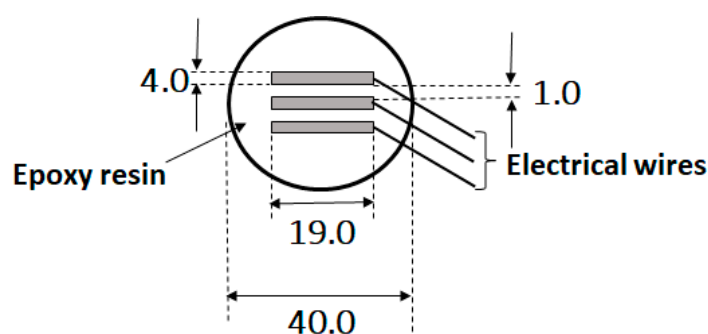


Figure 1. Schematic illustration of the three identical steel coupons mounted in resin, used for electrochemical measurements.

The test solution was 3.5 wt.% NaCl prepared from deionised water and reagent grade NaCl (99.7%). The pH of the solution was 5.5 at 22 °C (pH sensor, Hanna instrument) and was used without further adjustment.

2.2. Test Procedures

A schematic of the test setup is shown in Figure 2. Two temperature conditions were applied, namely a constant temperature of 80 °C and thermal cycling between 25 °C and 80 °C. For the thermal cycling condition, the temperature of the test solution was 25 °C for 4 h, then increased to 80 °C at 20 °C/min and maintained for 20 h. The temperature was reduced from 80 °C to 25 °C at 2.8 °C/min, and the same interval was applied when the temperature was increased from 25 °C to 80 °C. Two test durations followed, i.e., 5 and 21 d. The initial pH of the test solution phase was 7.08 after the temperature reached a steady state at 80 °C. The pH of the condensed water in the gas phase was not obtained because the liquid volume was insufficient for the pH measurement. Three weight loss specimens and the electrochemical probe (Figure 1) were placed on the top layer of the holder made from Polytetrafluoroethylene (PTFE), and the samples were then exposed to the humid gas above the solution.

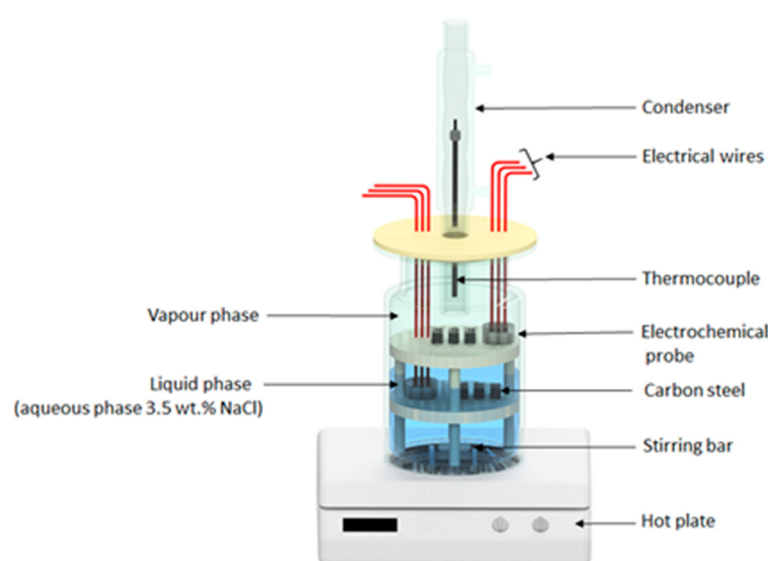


Figure 2. Schematic diagram of the experimental setup.

Once the test cell was assembled, the test solution (3.5 wt.% NaCl) was transferred, which might contact the samples at the top section. While temperature in the liquid phase was 80 °C, the temperature on the surface of the sample in the gas phase was 75.5 °C measured by a thermocouple. The size of glass cell was 2 L and the height of the liquid was 100 mm. Three samples and an electrochemical probe were placed onto a sample holder 60 mm above the water line, whereas the other specimens and an electrochemical probe were immersed in the liquid phase to a depth of 50 mm below the water line. The test cell was fitted with a condenser to prevent loss of liquid. The test solution was mildly agitated with a PTFE-coated magnetic stirring bar to maintain the uniform temperature.

Two electrochemical methods were carried out using the same probe, as shown in Figure 1. Electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques were used to monitor corrosion activity of the steel samples. EIS was performed on the samples immersed in the liquid phase using a multi-channel potentiostat (VSP300, Bio-Logic Science Instruments, Biologic Company, Grenoble city, France). The three identical carbon steel electrodes were used as working, reference, and counter electrode. EIS was stabilised for 30 min at the open circuit potential (OCP) before an AC excitation voltage of 10 mV was applied over a frequency range of 100 kHz to 10 mHz at 10 points per decade. The impedance spectra were analysed using EC-lab software (Bio-logic. Inc.). EIS was conducted twice a day (approximately every 12 h).

EN measurements were carried out on both samples located with gas and liquid phases with a potentiostat operated in zero resistance ammeter (ZRA) mode. The sampling

frequency was 2 Hz. EN data were measured for 1 h twice a day (approximately every 12 h).

2.3. Post-Test Analysis

2.3.1. Uniform Corrosion Rate Determined Using Weight Loss Method

After exposure, corrosion products formed on the carbon steel surfaces were removed using Clark's solution (SnCl_2 20 g/L, Sb_2O_3 50 g/L, and 100 mL of 32 wt.% HCl). The specimens were then air-dried before being weighed on an analytical balance, with a precision of 0.1 mg, following the procedures described in ASTM G1-03 [18]. The specimens were then air-dried before being weighed on an analytical balance, with a precision of 0.1 mg. The corrosion rates were calculated according to

$$CR = \frac{K \times (W_0 - W_1)}{A \times T \times D} \quad (1)$$

where, CR is the corrosion rate of metal ($\text{mm} \cdot \text{y}^{-1}$), K constant in corrosion rate ($87,600 \text{ mm} \cdot \text{y}^{-1}$), W_0 denotes the initial mass of a sample (g), W_1 represents the final mass of the sample upon the removal of the rust layer (g), D is the density of carbon steel ($\text{g} \cdot \text{cm}^{-3}$), A is the exposed surface area of the sample (cm^2), and T is the exposure time (h).

2.3.2. Localised Corrosion Assessed Using Surface Profilometry

Surface profilometry was performed using a light optical microscope (Infinite Focus G4, Alicona Imaging GmbH Company, Grambach City, Austria) to determine the extent of localized corrosion, based on the maximum pit depths. For each condition, three samples were scanned to measure a maximum pit depth. Time-averaged pitting rate was calculated from Equation (2), to determine the penetration rate of the deepest pit on the metal surface in relation to the exposure time (5 and 21 days).

$$\text{Pitting rate} \left(\frac{\text{mm}}{\text{y}} \right) = \frac{\text{pit depth} (\mu\text{m})}{\text{exposure time} (\text{d})} \times 0.0365 \quad (2)$$

2.3.3. Corrosion Product Characterisation

The morphology and elemental composition of the corrosion products were characterised by scanning electron microscopy (SEM) (Mira instrument, Tescan Company, Brno City, Czech Republic) combined with energy-dispersive X-ray spectroscopy (EDS). Aztec software (Oxford Instruments, Oxford City, UK) was used to collect X-ray signals from the metal surface and analyse the elemental composition data obtained from the corrosion layers formed on the metal surfaces exposed to both the liquid and gas phases. The samples were mounting a test specimen in resin before being cross-sectioned and then cut using Accutom-50 (Struers Company, Paris City, France), and their surfaces were polished with a grit size of 4 μm using 1200 grit finish (SiC paper).

The chemical composition of the corrosion products was analysed by Raman spectroscopy (RS), (Labram 1B model, HORIBA Jobin Co., Lille City, France). The samples were excited by Helium-neon with an excitation wavelength of 632.82 nm and a laser power of 2 mW (full power). Spectra was collected through 150 μm slit, 1100 μm confocal hole (fully open), 50 $\times$ objective, 1800 lines per mm diffraction grating, and a Peltier-cooled CCD (charge coupled device) detector. Data collection time was 16 accumulations of 60 s. The Raman shift was calibrated against the Raman line of silicon (520.7 wavenumbers).

3. Results and Discussion

3.1. Uniform Corrosion

Uniform corrosion rate from weight loss measurements were obtained from triplicate samples retrieved from the test cells after 5 and 21 days of testing under the different test conditions. The results are shown in Figure 3. The error bars represent the standard deviation from the measurements at the triplicate samples.

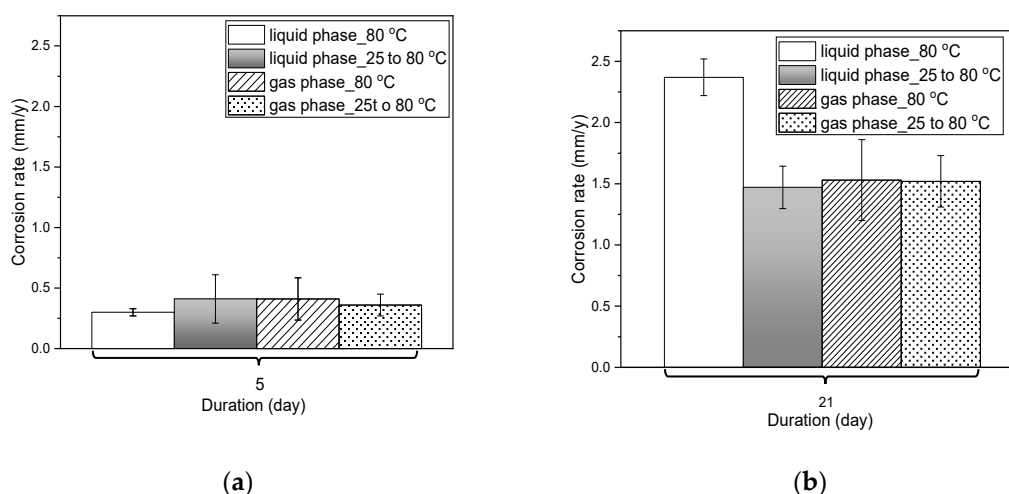


Figure 3. Uniform corrosion rate of carbon steel retrieved from the tests under various conditions after (a) 5 days and (b) 21 days. The corrosion rates were derived from weight loss measurements.

After 5 days of the exposure, the mean corrosion rate of the specimens exposed to the liquid phase at 80 °C was the lowest (i.e., 0.3 mm·y⁻¹). However, when the standard deviations were considered, corrosion rates in all conditions except the liquid phase at 80 °C were not significantly different.

Weight loss corrosion rates increased with time for all the samples under different exposure conditions. However, the largest increase in corrosion rate was observed on the steel samples exposed to liquid solution at a constant temperature of 80 °C for 21 days. In this condition, corrosion rate was 2.37 mm·y⁻¹. As corrosion kinetic is influenced by the exposure temperature, the difference in corrosion rate of the steel in the liquid phase at constant and thermal cycling conditions could be attributed to the duration at which the steel exposed to high temperature. Several factors affect the rate and extent of corrosion, including time, temperature, and ionic species such as NaCl. The loss of metal increases over time; and the concentration of the ionic species and temperature accelerate the corrosion process.

In comparison, the steel samples placed in the gas phase had similar weight loss corrosion rates, regardless of the temperature conditions.

3.2. Localised Corrosion Analysis

Figure 4 shows microscopic images of samples after 21 d exposure. The variation in colour indicates surface morphology, where red indicating the deepest area of the pit on the metal surface. Pitting corrosion was apparent on the samples in the gas phase (80 °C), liquid phase (80 °C) and gas phase (25 °C to 80 °C), except the liquid phase under thermal cycling (25 °C to 80 °C). The most aggressive localised corrosion was manifested in the gas phase at both temperatures' conditions as shown in Figure 4a,c, summarised in Table 2.

Pit depth increased with the test duration. For instance, the maximum pit depth found on the sample exposed to the gas phase at constant temperature of 80 °C was 51 µm after 5 d of exposure as shown in Figure 5. When the exposure time at this condition increased to 21 d, the maximum pit depth increased to 185 µm. The results suggested a continuing pit growth.

Pitting rates were determined from the pit depth and the exposure time. The pitting rates (as shown in Table 2) were lower in the immersion condition. For instance, the pitting rate was 1.1 mm·y⁻¹ under the immersion condition at 80 °C while a rate of 3.7 mm·y⁻¹ was measured on the samples in the gas (condensation) condition at the same temperature. A decrease in pitting rate with time was apparent in all conditions, except in the gas phase with temperature cycling where the pitting rate increased with time from 1.6 to 2.2 mm·y⁻¹.

Table 2. Summary of maximum localised corrosion (in μm) and localised corrosion rate (in $\text{mm}\cdot\text{y}^{-1}$) measured at various conditions.

Condition	Exposure Time	
	5 d	21 d
	Depth (μm)/Localised Corrosion Rate ($\text{mm}\cdot\text{y}^{-1}$)	Depth (μm)/Localised Corrosion Rate ($\text{mm}\cdot\text{y}^{-1}$)
Liquid phase ($80\text{ }^{\circ}\text{C}$)	15/1.1	43/0.7
Liquid phase (80 to $25\text{ }^{\circ}\text{C}$)	6/0.4	16/0.3
Gas phase ($80\text{ }^{\circ}\text{C}$)	51/3.7	185/3.2
Gas phase (80 to $25\text{ }^{\circ}\text{C}$)	22/1.6	124/2.2

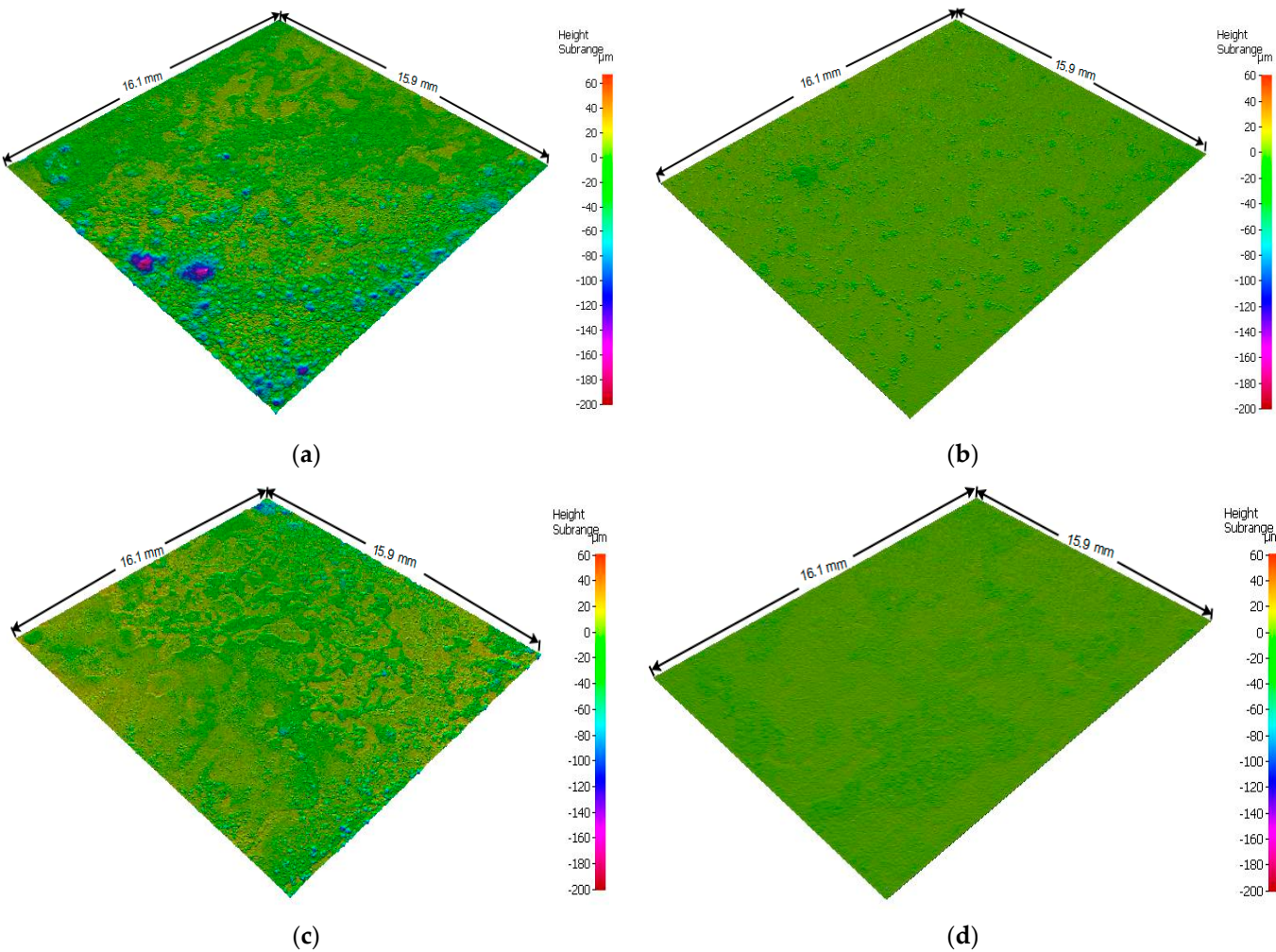


Figure 4. Carbon steel surface morphology after 21 d of exposure to different temperatures and phases: (a) gas phase ($80\text{ }^{\circ}\text{C}$), (b) liquid phase ($80\text{ }^{\circ}\text{C}$), (c) gas phase ($25\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$) and (d) liquid phase ($25\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$).

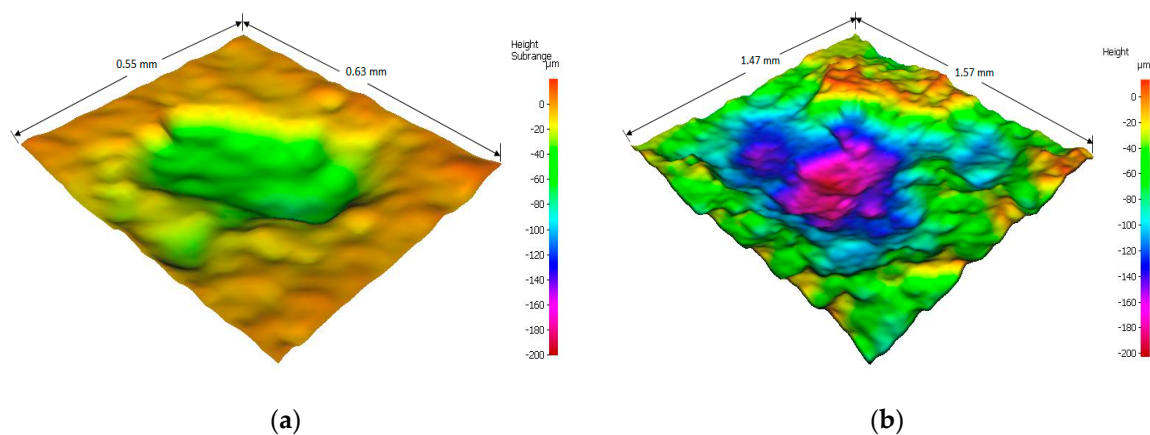


Figure 5. Surface morphologies of carbon steel clarified the pit depth measurements to the largest pit occurred on the metal surface after specimens were exposed to the gas phase at a constant temperature of 80 °C; (a) sample at 5 d and (b) sample after 21 d.

The pitting factors after 21 d exposure were 1.04 and 1.02 for the tests under immersion conditions at constant temperature and thermal cycling, respectively. It was calculated per ASTM G46 [19], as shown in the following equation:

$$\text{Pitting Factor} = \frac{\text{Pitting rate}}{\text{Weight loss corrosion rate}} \quad (3)$$

A pitting factor of one indicates uniform corrosion. As such, it may be concluded that the samples exposed to immersion conditions were subject to uniform corrosion. For the exposure to condensation, the pitting factors were 1.96 and 1.32 for constant temperature and thermal cycling, respectively. Thus, it is evident that the samples exposed to the condensing conditions were more prone to localised corrosion than those under immersion conditions.

3.3. Corrosion Product Layer Characterisation

SEM/EDS Results

Figure 6 shows the SEM images of the cross-sectioned steel after the tests. Circles highlight the areas with localised corrosion, which was evident in all samples except the one that was retrieved from the liquid phase under thermal cycling conditions. On this sample, a uniform rust layer covered the metal surface with no observable pits. Three layers of corrosion product were apparent. Inner and outer layers appeared to be uniform and compact. In contrast, an intermediate film was porous. The thickness of the corrosion product was approximately 75 to 100 μm, which was markedly greater than the corrosion product formed in other conditions. An SEM image showing the top surface of this sample is presented in Figure 7. Corrosion products were uniformly distributed, thereby creating a physical barrier against the diffusion of oxygen and corrosive ions. These effects, in turn, reduced the corrosion rate and the tendency of localised corrosion.

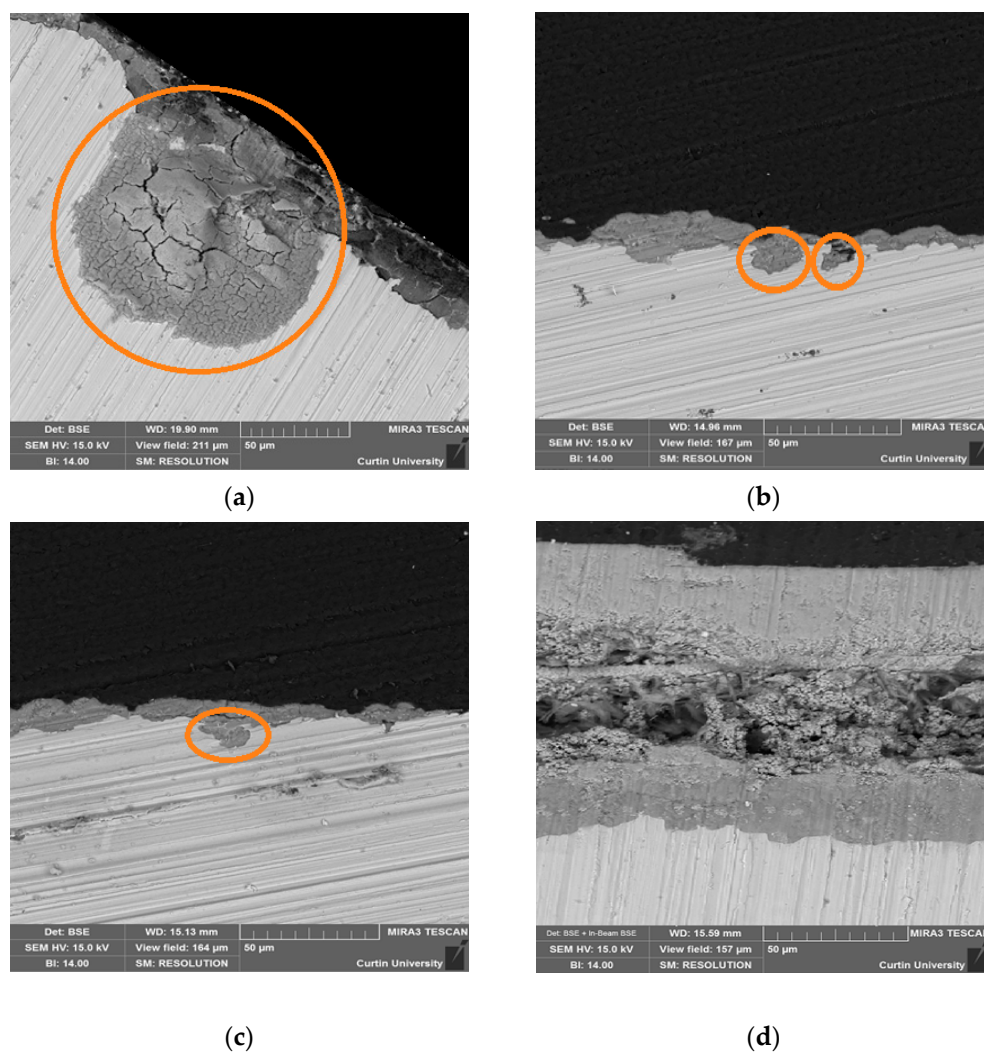


Figure 6. SEM of corrosion products, specifically the cross-sections of sample surfaces at different temperatures and phases after 21 d: (a) gas phase (80 °C), (b) liquid phase (80 °C), (c) gas phase (25 °C to 80 °C) and (d) liquid phase (25 °C to 80 °C). Circles highlight localised corrosion areas.

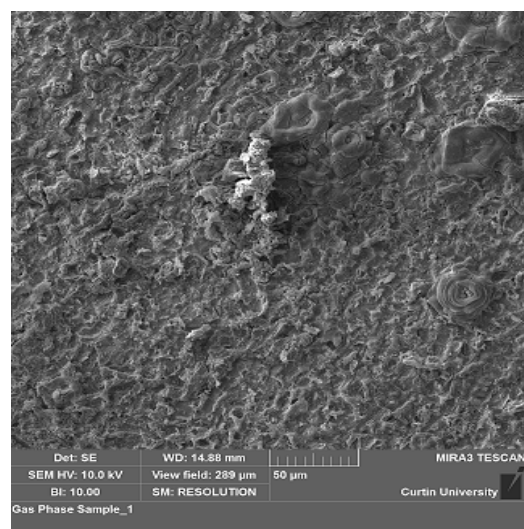


Figure 7. Scanning electron micrographs of corrosion products on the sample surfaces after 21 d of immersion in 3.5 wt.% NaCl under thermal cycling between 25 °C to 80 °C.

For other test conditions, the cross-section SEM images demonstrated that the corrosion product layers were thinner. The thickness varied from a few μm to 20 μm . There were also some areas where the corrosion product was in absence. In addition, cracks can be observed in the corrosion product layer, as shown in Figure 8. While cracks could also be developed due to the drying out of the samples, it is worth noting that all the specimens were prepared and processed the same way. No cracks were found on the sample that had no localised corrosion.

Figures 7 and 8 show the different corrosion morphologies of carbon steel with different concentrations of the NaCl solution and temperature. The corrosion product became heavier and thicker in higher concentrations of NaCl and thermal cycling. The corrosion morphologies showed consistency with the test results for corrosion rates and localised corrosion depth. In the condition where the corrosion product morphology exhibits cracks and becomes thinner, the highest corrosion rate was observed.

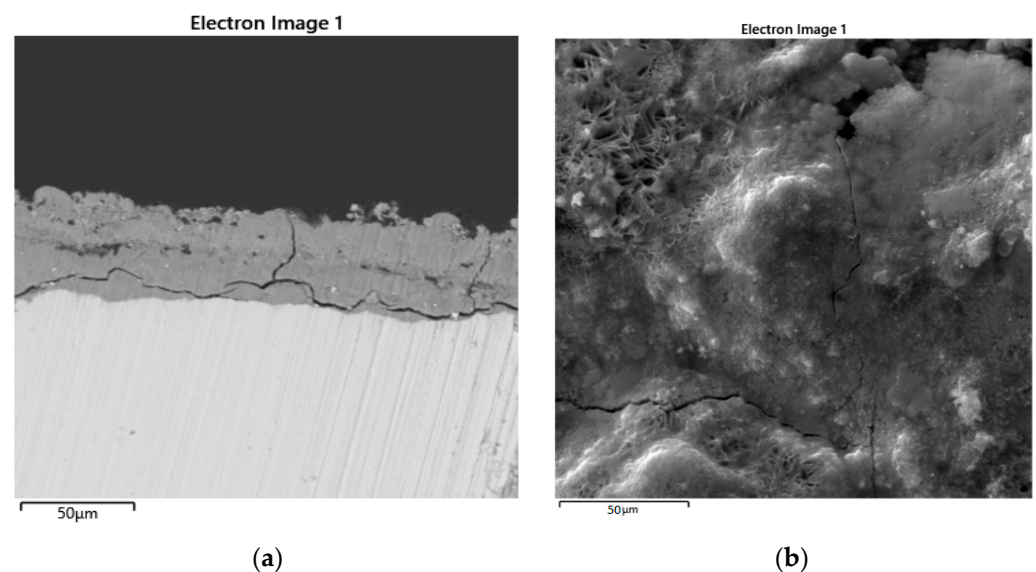


Figure 8. SEM image of carbon steel after 21 d of immersion in 3.5 wt.% at constant temperature 80 °C showing cracks present: (a) cross section and (b) sample surface.

Elemental mapping of the corrosion product formed on the samples exposed to the liquid and gas phase at constant temperature of to 80 °C are shown in Figure 9a,b respectively. The concentration of elements in the analysed region is associated with the intensity of the colour. In both conditions, the corrosion product layer consisted of only iron and oxygen, consistent with iron oxide. Chloride was found only inside of the pits and its concentration was highest at the cavity bottom and decreased gradually along the path going outward. Ye Wan et al. [4] found that during pitting corrosion in carbon steel exposed to chloride ions, FeCl_3 accumulated in the centre of the pit cavity and was laterally walled by iron oxides. The diffusion of iron ions away from the active pit surface controls further pit growth. Iron oxides form the core's exterior wall, create a diffusion barrier for mass transport and maintain the concentrated local chemistry, thereby providing a suitable condition for pit growth.

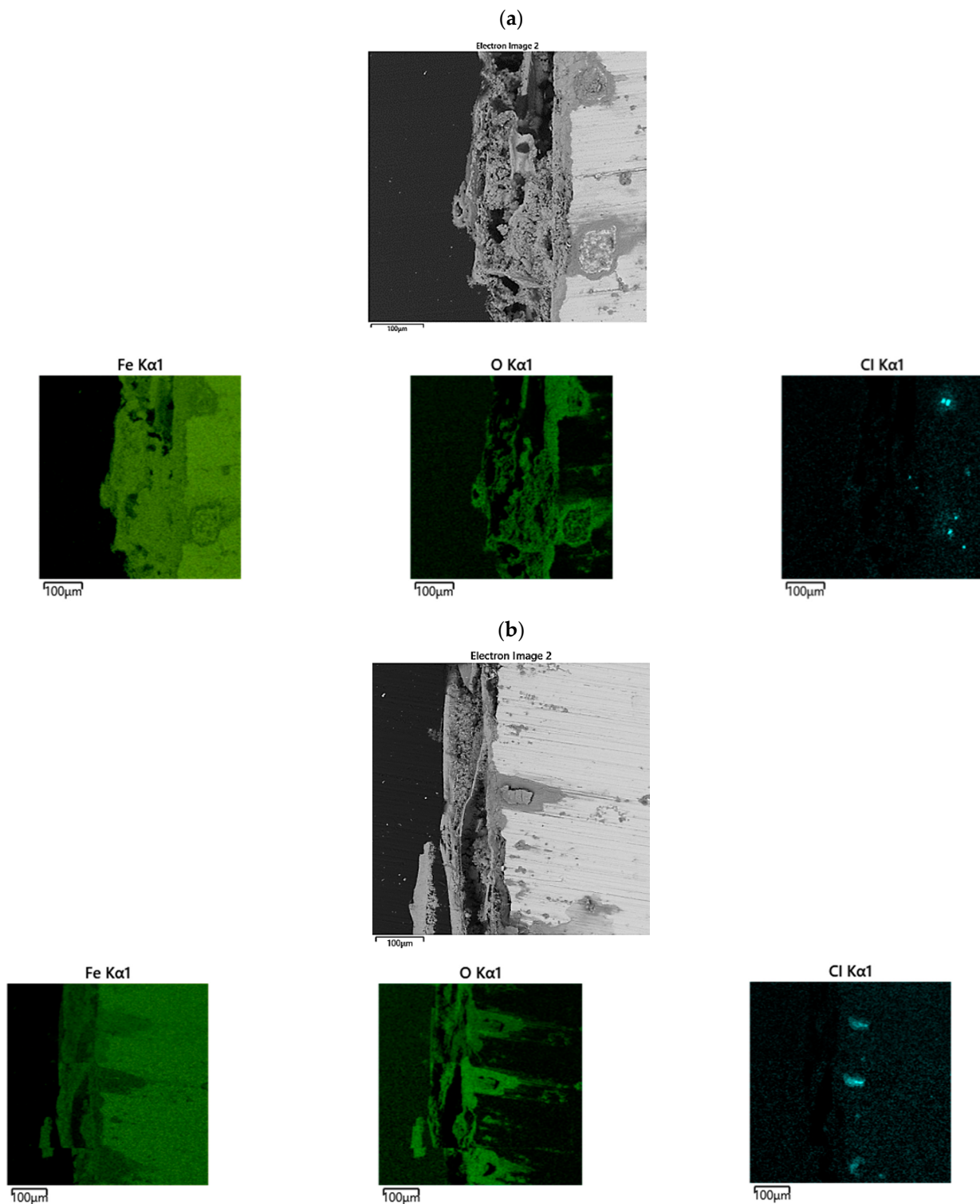


Figure 9. EDS map of corrosion products on the sample surfaces exposed to the (a) liquid and (b) gas phases at 80 °C for 21 d.

3.4. Raman Spectroscopy

Figure 10 shows the Raman spectra of top layer of the corrosion products formed on the surfaces' specimen after exposure to the gas and liquid phases for 21 days under different temperature conditions. Strong peaks were observed at 225, 250, 290, 293 and 379 cm^{-1} , and medium peaks were found at 411, 412, 528, 611 and 650 cm^{-1} . Overall, the

Raman spectra reflected that hematite ($\alpha\text{-Fe}_2\text{O}_3$) and lepidocrocite ($\gamma\text{-FeOOH}$) were the major compounds of corrosion products that dominated the metal surfaces [20–24].

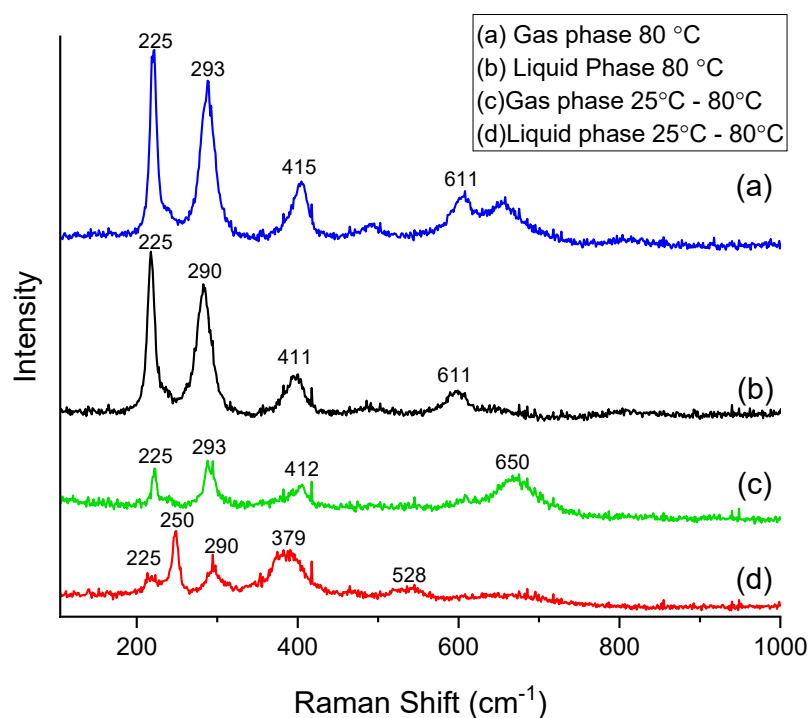


Figure 10. The Raman spectra of iron oxide at different conditions; measurement conditions at spectral ranges 100–800 cm^{-1} after 21 d.

In the gas phase (constant temperature and thermal cycling) and liquid phases (constant temperature), the Raman spectra of the narrow doublet showed that the strongest peaks at 225, 290 and 293 cm^{-1} , and that weak and broadened peaks formed at approximately 411, 412 and 415 cm^{-1} . These findings indicated that corrosion product on the steel specimens was $\alpha\text{-Fe}_2\text{O}_3$ [21,22].

At thermal cycling in the liquid phase (Figure 10d), additional characteristic peaks were detected at 250, 379 and 528 cm^{-1} , indicating the presence of $\gamma\text{-FeOOH}$ [20–24]. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) was also present, as indicated by the bands at 225, and 290 cm^{-1} . Our study probably did not detect some iron corrosion products because they could be formed in the inner layer of the corrosion product or near the metal surface.

It was also noted that when the solution temperature was kept constant, the pH in the liquid phase measured at the end of the experiment at 80 °C was 5.19, showing an increase in acidity of the test solution with time. On the contrary, when the temperature fluctuated from 25 to 80 °C, the solution pH was 6.43 at 80 °C at the end of the experiment. A difference in the solution acidity was apparent at different temperatures (constant or cyclic temperature), which may be attributed to the localised corrosion tendency.

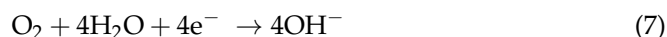
From the pitting analysis and corrosion product characterisation, the corrosion reactions could occur as follows:

Anode region:

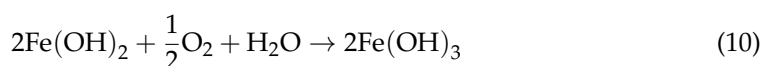
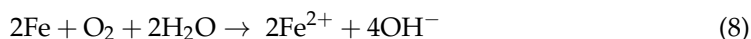


Cathode reactions usually involve three different reactions (Equations (5)–(7)). At neutral pH and at open circuit potential, water, and hydrogen reduction reactions (Equations (5) and (6)) may be neglected. Thus, oxygen reduction was the dominated cathodic reaction under the conditions in this study. The formation of corrosion product ($\text{Fe}(\text{OH})_2$) led to H^+ being

produced [25,26]. $\text{Fe}(\text{OH})_2$ was then further oxidised in the presence of dissolved oxygen (Equation (11)):



Equation (8) is equivalent to Equations (4) and (7)



Then, the reaction takes place to form an initial rust layer composed of $\gamma\text{-FeOOH}$:



On the initial rust layer, $\gamma\text{-FeOOH}$ steadily form in a solution containing NaCl component. $\gamma\text{-FeOOH}$ rust layer in the wet condition has been played a major role in determining and developing rust. Akaganeite ($\beta\text{-FeOOH}$) started to form after the formation $\gamma\text{-FeOOH}$ in the presence of chloride ions [27]. Cl^- was detected, in the centre of pits as shown in Figure 9. Local acidification in the microenvironment due to chloride ions diffusion to balance positive charge of Fe^{2+} from corrosion [14]. The microenvironment in the pit is characterised by low pH and a high concentration of Cl^- which created a very aggressive microenvironment in the pits [28].

Eventually, $\gamma\text{-FeOOH}$ transformed into more stable oxide, $\alpha\text{-Fe}_2\text{O}_3$ [29,30].



3.5. Electrochemical Measurements

3.5.1. Electrochemical Impedance Spectroscopy (EIS)

The Nyquist curves in Figure 11 illustrate only one double-layer capacitance semicircle, which varied significantly as a function of immersion time. At the thermal cycling condition, the impedance magnitude of the semicircle and the impedance magnitude Figure 12 increased gradually suggesting a decrease in the corrosion rate, which could be attributed to a thicker rust layer, as confirmed in Figure 6. It could be inferred that the corrosion rate of carbon steel in a 3.5 wt.% solution during thermal cycling was determined by limiting the diffusion of the electrolyte through the rust layer. The effect of the rust layer appeared significantly after 9 d when the impedance was high, as shown in Figure 11. The product of corrosion was not effective in reducing the corrosion rate through 5 d. However, the result appeared after 21 d of the experiment, when the reduction was around 0.8 mm/y compared with the carbon steel immersion in 3.5 wt.% NaCl at a constant temperature, as illustrated in Figure 3.

At a constant temperature, the impedance fluctuation between 14 and 21 d could indicate change in the corrosion layer, such as the cracks in the corrosion layer, as shown in Figure 8. As the rust layer under this condition was porous and thin, it could be inferred that the corrosion layer could not effectively hinder the diffusion process, resulting in localised corrosion.

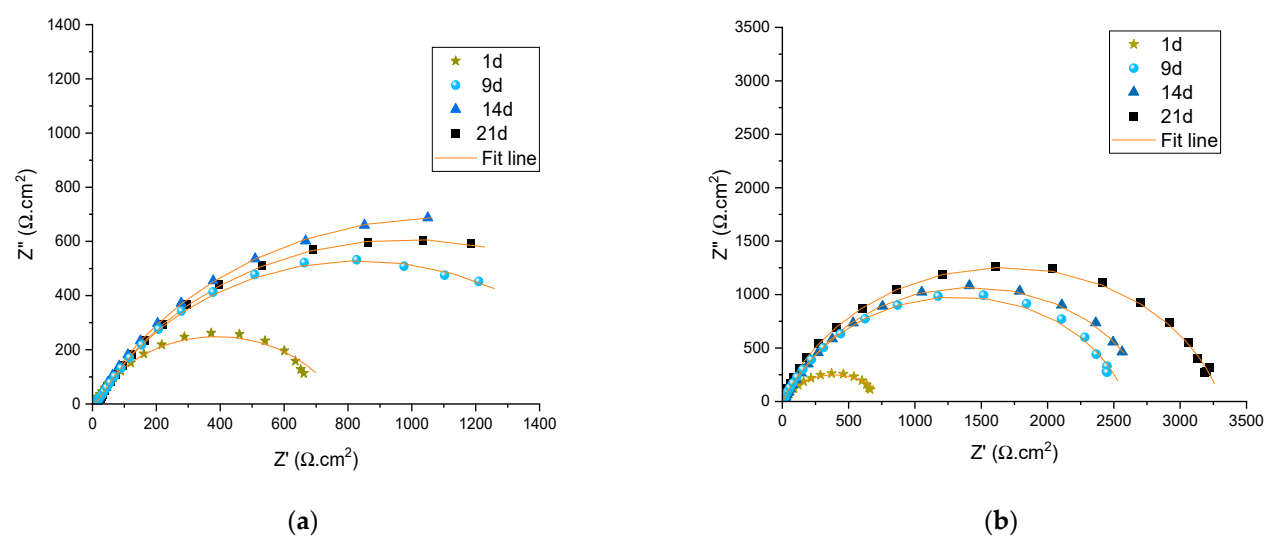


Figure 11. Nyquist plots of rusted steel at different corrosion times and immersion in 3.5 wt.% NaCl solution: (a) constant temperature at 80 °C and (b) thermal cycling 25 to 80 °C.

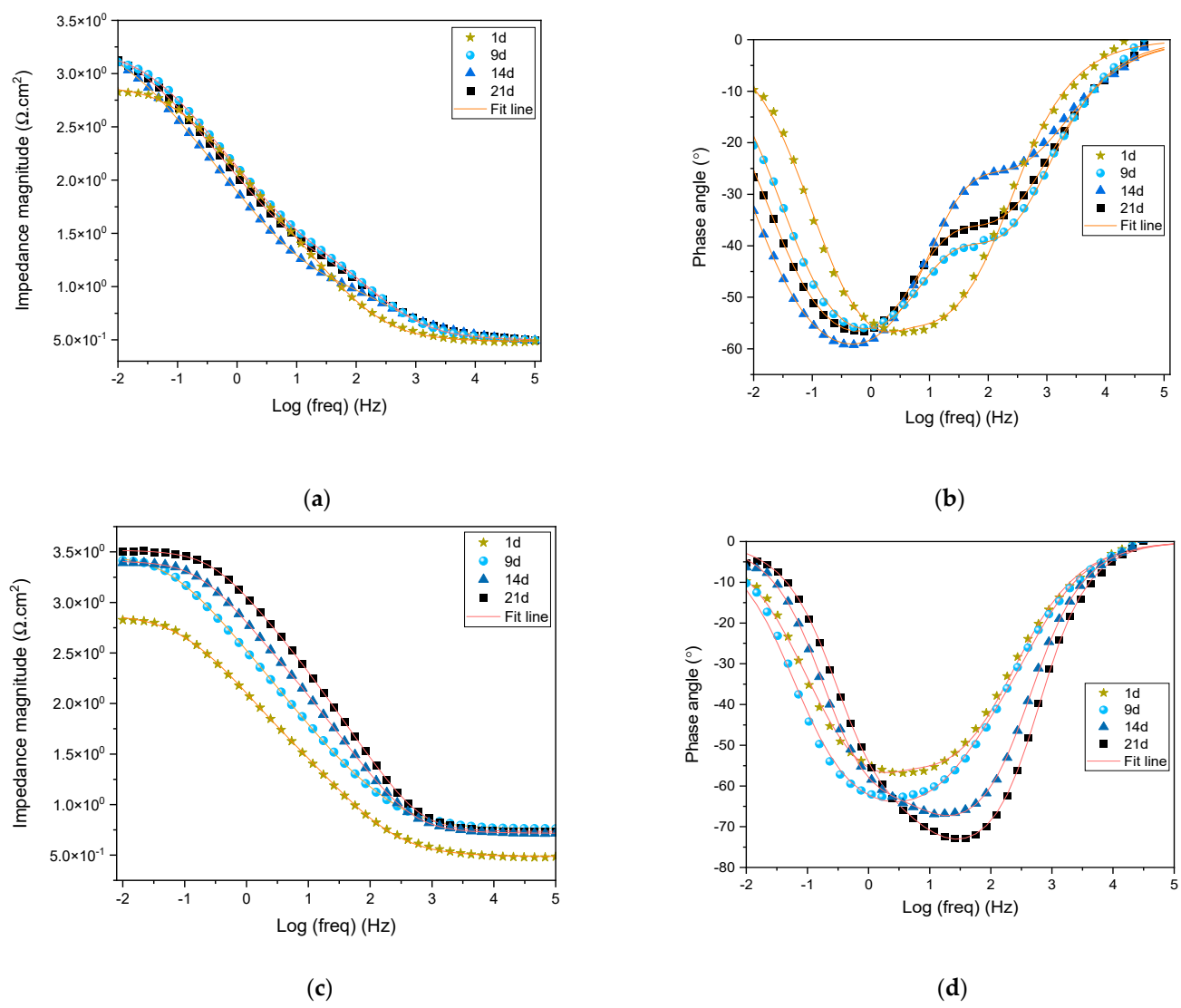


Figure 12. Bode plots of rusted steel at different corrosion times and immersion in 3.5 wt.% NaCl solution: (a,b) constant temperature at 80 °C and (c,d) Bode thermal cycling 25 to 80 °C.

The fitting results proved that the electrical equivalent circuit (EEC) Figure 13 was suitable [31,32], and the analytical results were listed in Tables 3 and 4, respectively.

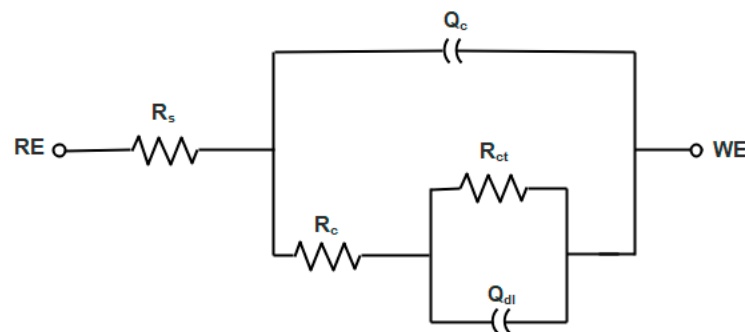


Figure 13. The equivalent circuit used for the electrochemical impedance spectra fitting.

Table 3. Fitted parameter of the EIS at thermal cycling between 25 °C to 80 °C.

Duration (Day)	R_s ($\Omega \cdot \text{cm}^2$)	Q_c ($\text{F} \cdot \text{s}^{\alpha-1} \cdot \text{cm}^{-2}$)	n_c	R_c ($\Omega \cdot \text{cm}^2$)	Q_{dl} ($\text{F} \cdot \text{s}^{\alpha-1} \cdot \text{cm}^{-2}$)	n_{dl}	R_{dl} ($\Omega \cdot \text{cm}^2$)	X^2
1	5.05	0.18×10^{-2}	0.76	296.2	0.27×10^{-3}	0.71	478.4	0.104
9	5.21	0.24×10^{-3}	0.84	737	0.151×10^{-3}	0.82	1854	0.044
14	5.81	0.39×10^{-3}	0.85	300	0.41×10^{-3}	0.84	2470	0.027
21	5.42	0.114×10^{-3}	0.89	1132	0.125×10^{-3}	0.74	2177	0.036

Table 4. Fitted parameter of the EIS at constant temperature of 80 °C.

Duration (Day)	R_s ($\Omega \cdot \text{cm}^2$)	Q_c ($\text{F} \cdot \text{s}^{\alpha-1} \cdot \text{cm}^{-2}$)	n_c	R_c ($\Omega \cdot \text{cm}^2$)	Q_{dl} ($\text{F} \cdot \text{s}^{\alpha-1} \cdot \text{cm}^{-2}$)	n_{dl}	R_{dl} ($\Omega \cdot \text{cm}^2$)	X^2
1	3.0	0.79×10^{-3}	0.76	33.1	0.58×10^{-1}	0.97	900	0.455
9	3.01	0.12×10^{-2}	0.75	1466	0.015×10^{-1}	0.94	106.2	0.035
14	3.02	0.71×10^{-3}	0.72	1426	0.24×10^{-1}	0.86	1629	0.024
21	3.13	0.88×10^{-3}	0.703	1390	0.157×10^{-3}	0.743	885.3	0.0046

Q_c is a constant phase element (CPE) of a corrosion product, R_s is the solution resistance, and R_c denotes the resistance of a corrosion product. The CPE of the electrical double layer is denoted as Q_{dl} and the charge transfer resistance is represented as R_{ct} .

The corresponding fitting results for thermal cycling are shown in Table 3. The solution resistance was between 5.0 and 5.81 $\Omega \cdot \text{cm}^2$ and did not change significantly during the entire experiment. The comparison of R_c under the two temperatures showed that thermal cycling increased resistance to its maximum value (1132 $\Omega \cdot \text{cm}^2$) after 21 days. This finding suggests an increase in the thickness of the corrosion product. At 14 days, R_c decreased (300 $\Omega \cdot \text{cm}^2$), indicating a less homogeneous and more porous iron oxide, as shown in the middle of the cross-section of the SEM morphology in Figure 6d. However, the constant temperature fluctuated and reflected the morphology of the corrosion product (varied thicknesses of corrosion products on the metal surface), as illustrated in Figure 6b.

R_{ct} at thermal cycling increased from 478 to 2177 $\Omega \cdot \text{cm}^2$, which can be logically interpreted as a decrease in weight loss compared with the result derived at a constant temperature. At a constant temperature, R_{ct} declined at days 9 and 14, confirming a rise in weight loss (Figure 3b).

3.5.2. Electrochemical Noise Analysis (EN)

Typical EN signals obtained under various test conditions are shown in Figure 14. Different patterns were observed for different test conditions. Specifically, the magnitude of the potential signals related to the liquid phase was significantly lower than that related to the gas phase (inset of Figure 14a). As the measured potential was the potential difference

between the coupled carbon steel electrodes against a third, steel electrode with the same material and geometry, in the gas phase, the thickness of the electrolyte layer on the surface of the three electrodes was thin and the surface coverage may be different, thus leading to a larger potential difference. In contrast, when the test probe consisting of the three steel electrodes was exposed to the bulk solution, i.e., fully immersed in the liquid phase, the electrolyte coverage of the electrodes would be the same for all the three electrodes. Therefore, the potential difference among the three electrodes was expected to be small. Meanwhile, the magnitude of the current signals showed an opposite trend, i.e., a larger magnitude was observed for the current signal related to the liquid phase compared to that associated with the gas phase.

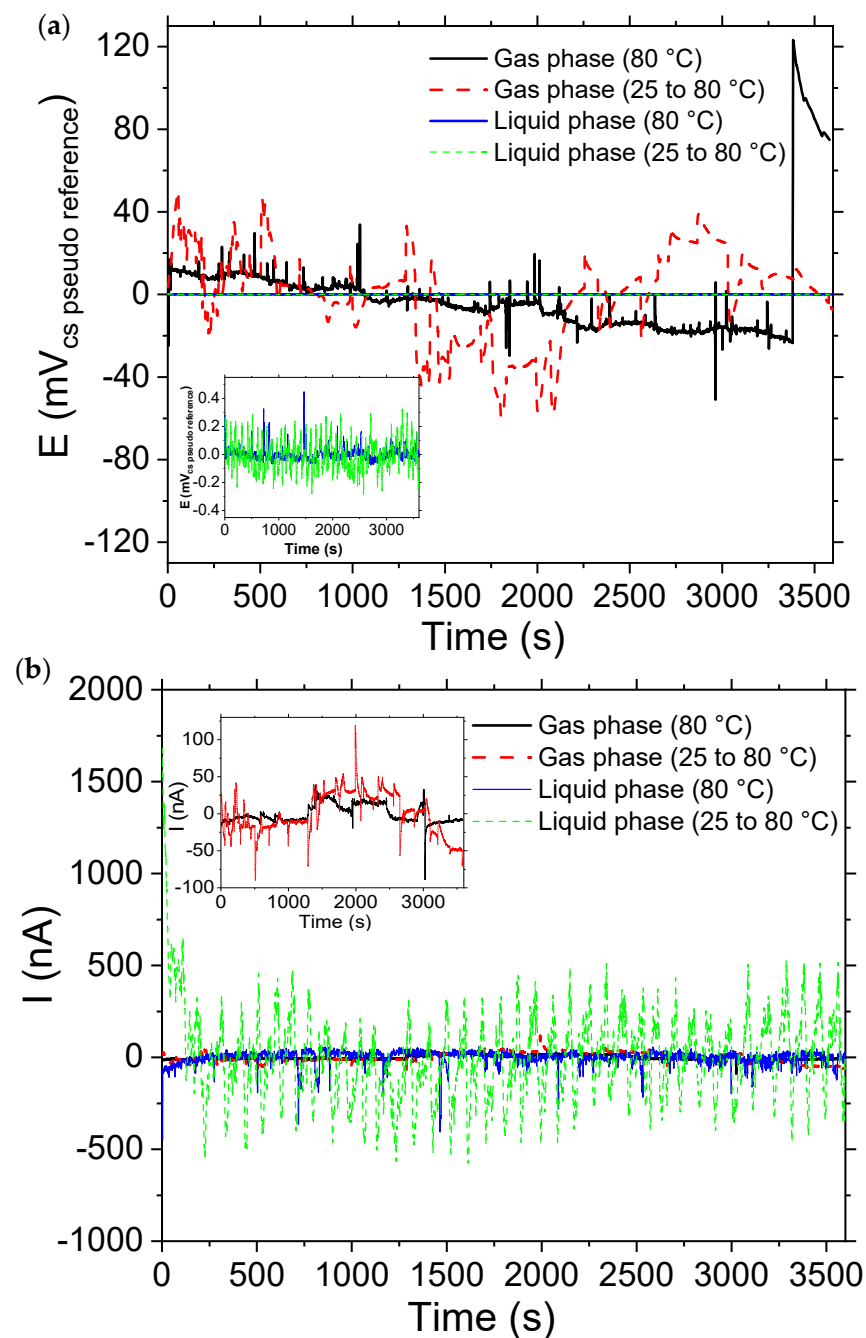


Figure 14. Electrochemical noise signals recorded on day 21 at various test conditions after linear trend removal. (a) Potential signals; (b) Current signals. The insets show the enlarged graphs of the signals corresponding to the legend shown in the main figures.

On the other hand, the shape and frequency of the transients could be correlated with different forms of corrosion. Figure 15 shows the details of the typical transients extracted from the EN signals displayed in Figure 14. The sharp increase/decrease followed by a slow decrease/increase in current and potential indicate the initiation and propagation of pitting [33]. This type of transients was observed for all the test conditions (Figure 15a–c) as indicated by the green box, except for the liquid phase under thermal cycling (Figure 15d). Therefore, it is inferred that the steel samples exposed to liquid phase under thermal cycling mainly underwent uniform corrosion [34], while the other systems were dominated by localised corrosion for the recording period. In the liquid phase at constant temperature (Figure 15c), the duration of the current transient as indicated by the green box was around 30 s, and the decreased current resumed to the baseline before the other transient began. In comparison, for the gas phase (Figure 15a,b), increased current was not able to return to the original value before the other increasing event occur. This pattern could be related to the propagation of the pit, resulting in larger pit depths [35]. Accordingly, it is expected that the steel samples exposed to the gas phase had larger pit depths than those exposed to the liquid phase. This hypothesis was supported by the maximum pit depths values measured in the weight loss samples presented in Table 2.

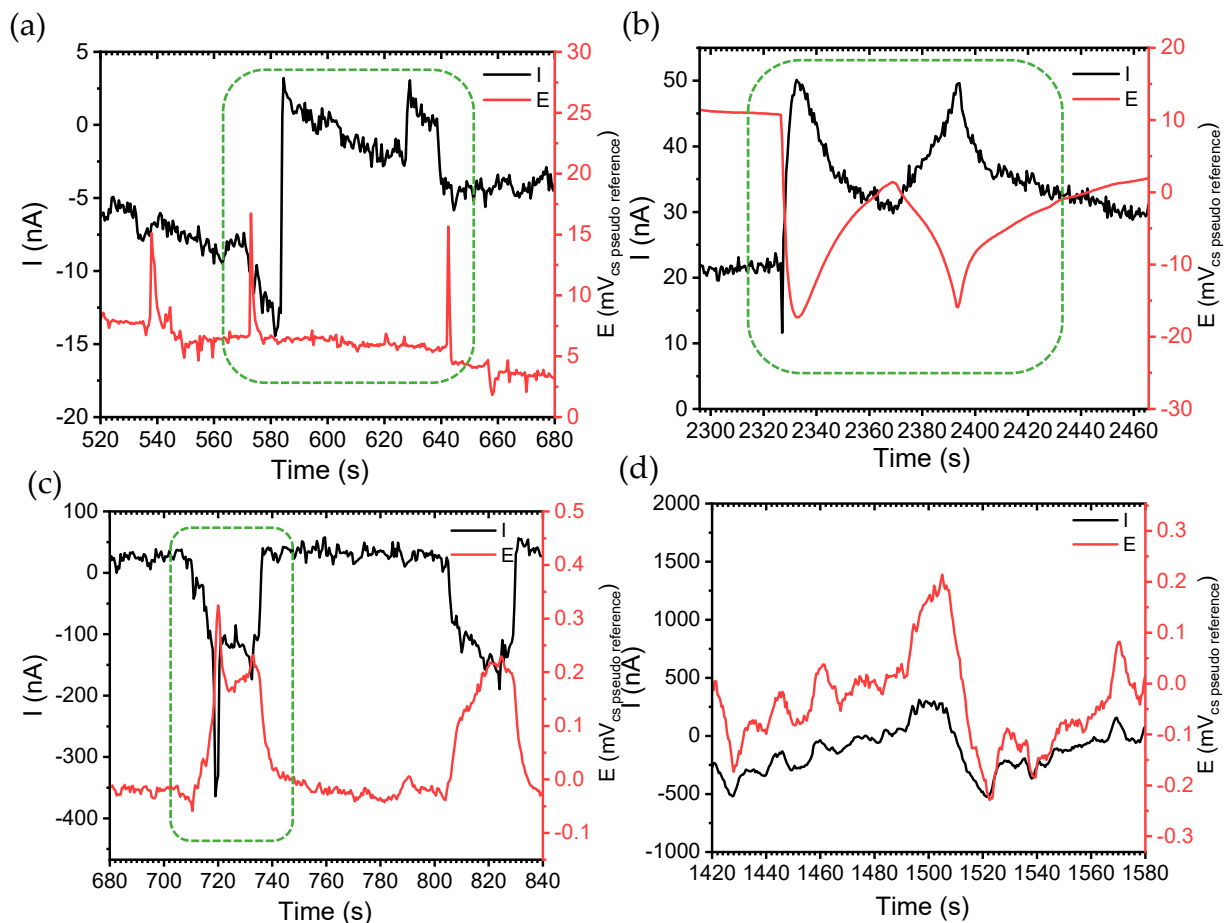


Figure 15. Details of the typical transients associated with the EN signals obtained under (a) gas phase (80 °C), (b) gas phase (25 to 80 °C), (c) liquid phase (80 °C) and (d) liquid phase (25 to 80 °C).

4. Conclusions

This study investigated the corrosion behaviours of carbon steel under close environments that were fully immersed in 3.5 wt.% NaCl solution and exposed to humid (condensation) conditions. Examination was also directed towards the effects of a constant

temperature (80 °C) and cyclic temperature (25 °C ↔ 80 °C). Based on the results, the following conclusions were drawn.

- Localised corrosion was evident on the samples in the gas phase exposed to condensing condition. However, uniform corrosion was a dominant form of corrosion on samples immersed in 3.5 wt.% NaCl.
- Thermal cycling appears to promote the formation of a protective corrosion product layer on the carbon steel surface, thus creating an effective barrier and reducing the extent of localised corrosion in the immersion condition.
- Hematite ($\alpha\text{-Fe}_2\text{O}_3$) was the dominant corrosion product in all conditions. Lepidocrocite ($\gamma\text{-FeOOH}$) was detected only on the sample immersed in 3.5 wt.% NaCl solution under thermal cycling.

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