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The Inhibitive Effect of Carbon Containing Corrosion Products Inside Corrosion Pits on the Repassivation of Carbon Steels

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The effect of carbon containing corrosion products within corrosion pits on the repassivation of pits has been studied on 20# and 45# carbon steels in sodium chloride and sodium hydroxide / nitrate / nitrite solutions. Anodic polarisation tests have been carried out in an attempt to cause pitting corrosion and then measure the repassivation potential. The presence of corrosion products within pits has been demonstrated via EDX. Pits in 0.1 M $NaNO_2$ solutions with different concentrations of NaCl (20 mM, 40 mM, 0.1 M and 0.2 M) have been found to repassivate at different potentials. The repassivation potential of 45# carbon steel is lower than that of 20# when carbon containing corrosion products are detected within corrosion pits, but the difference is negligible when the products are not detected. The presence and absence of carbon containing corrosion products is found to depend on the concentration of chloride. The difference on the repassivation potentials has been ascribed to the inhibitive effect of corrosion products on metal ion diffusion, which may maintain aggressive solution within pits and inhibit repassivation at a low dissolution rate. It has also been found that pits cannot repassivate in NaOH and NaCl solutions, while pitting corrosion cannot take place in $NaNO_3$ and NaCl solutions.

Keywords: pitting corrosion, repassivation, corrosion products, carbon

1. INTRODUCTION

Since nuclear power is used widely, the nuclear waste disposal has become an increasingly important issue all over the world. Permanent (deep geological) disposal of liquid radioactive waste requires complicated procedures and controversial international protocol [1], so the management of interim storage of the liquid waste is currently applied. Carbon steel is an appropriate material for the tanks for temporary storage of high-level liquid radioactive waste [2]. However, localised corrosion has been reported on carbon steel tanks for the liquid waste, including pitting corrosion [2] and stress corrosion cracking [3].

Since nitrate, nitrite, hydroxide and chloride ions are the main anions of high-level liquid radioactive waste [4-6], pitting corrosion of carbon steel in solutions containing chloride/hydroxide/nitrate/nitrite has been studied to understand the corrosion behaviours in high-level liquid radioactive waste [7-10]. The author has also carried out a study on pitting corrosion of iron in chloride and nitrate mixed solutions, and Fe_3C has been detected in pit solutions (appeared as black within an iron artificial pit) via synchrotron XRD and Raman spectroscopy in both pure chloride solutions and chloride nitrate mixed solutions under certain circumstances [11].

Solid carbon/carbides within local corrosion sites, appeared as black in colour, have also been reported in previous work, e.g. inside corrosion pits [12, 13] and cracks [14]. Furthermore, solid products on exposed steel surfaces have been found to inhibit the diffusion of metal ions and/or decrease dissolution rate under various conditions [12, 15-18]. Flis [12] and Zhang [19] have suggested that solid corrosion products in a local corrosion site may lead to the limitation of mass transport, promoting local acidification and attack. However, this effect has not yet been studied further and demonstrated electrochemically.

In this study, the effect of carbon containing corrosion products within corrosion pits has been investigated on 20# and 45# carbon steels. Anodic polarisation tests have been carried out on both carbon steels in NaCl with NaOH or $NaNO_3$ or $NaNO_2$ solutions in an attempt to cause pitting corrosion and then measure the repassivation potential of pits, thus to study the effect of possible corrosion products within a pit on pitting corrosion. The pit morphology has been studied via SEM, and the elemental analysis of possible corrosion products within a pit has been carried out via EDX.

2. EXPERIMENTAL METHODS

The samples were 20# and 45# carbon steel (Chinese National Standard code GB699-1999) with different carbon contents but very similar contents for other impurities. The chemical specifications of the samples are listed in Table 1. Carbon content of 45# carbon steel is more than twice that of 20#. The size of the sample surface is 1×1 cm^2.

The electrochemical tests were carried out with a Gamry Potentiostat (IFC1000-07199). All potential values were with respect to SCE in this work, and the counter electrode was a platinum mesh (surface area ~7 cm^2). Electrolytes used in this work were 0.01 M NaCl + 0.01 M NaOH (pH=12.1), 0.01 M NaCl + 3 mM NaOH (pH=11.7), 1 M $NaNO_3$ with no NaCl or 0.1 mM NaCl or 1 mM NaCl (pH values for the three solutions were all 6.3), 0.1 M $NaNO_2$ with 20 mM or 40 mM or 0.1 M or 0.2 M NaCl (the pH values were 6.3, 6.5, 6.5 and 6.6, respectively), which were all prepared with deionised water (resistivity ~18 MΩ·cm). All chemicals were provided by Sinopharm Chemical Reagent Co., Ltd. The pH values of all the solutions in this work were measured with a pH meter (PHS-3C, INESA Electron Co., Ltd). The pH of each solution was measured for three times, and the results agreed well with each other. The solution volume for each electrochemical test was 300 ml.

The sample was mounted in acrylic resin with an exposed area of 1×1 cm^2 and ground with 240, 600 and 1000 grit SiC papers successively. The fresh sample surface was immersed in electrolyte for 1 hour right after grinding and cleaning with deionised water and ethanol (then dried with a clean hair dryer), and the OCP was stable after 1 hour. Then a potential cyclic sweep started from -50 mV vs. OCP to a voltage where the current density just exceeded 0.1 mA/cm^2, and the potential sweep reversed to the original OCP value. Sweep rate was 1 mV/s. The temperature in the laboratory was kept at ~20 °C.

The surface morphology and the elemental composition were investigated on a Hitachi S-3400N SEM (accelerating voltage 15 kV, beam current ~60 μA; EDX acquisition time 100 s) after electrochemical measurements. The carbon steel samples were cleaned with deionised water and ethanol, and then dried with a clean hair dryer quickly before SEM measurements.

Table 1. Chemical specifications of carbon steel sample 20# and 45# (provided by the vendor)

Constituent	20# (wt.%)	45# (wt.%)
Carbon	0.19	0.45
Silicon	0.25	0.28
Manganese	0.59	0.62
Phosphorus	0.035	0.035
Sulphur	0.035	0.040
Chromium	0.25	0.25

3. RESULTS AND DISCUSSION

To measure the pitting potential and repassivation potential of carbon steel, there has to be a passive region in the anodic branch of a polarisation curve. It has been found that carbon steel cannot passivate in pure NaCl solutions, even at a concentration of 1 mM at open circuit, for which rust was visible on metal surface after 20 min immersion. Therefore, inhibitive ions have to be added to obtain a passive region during anodic polarisation. Hydroxide, nitrite and nitrate have all been reported as inhibitive ions for pitting corrosion of iron-alloys [20-23], so the three ions have been added into NaCl solutions respectively in this study.

3.1. NaOH and NaCl

20# carbon steel was immersed in 0.01 M NaOH and 0.01 M NaCl for 1 h before polarisation, and the OCP started at around -0.58 V_{SCE} in the beginning and stabilised at around -0.47 V_{SCE} after 2500 s (the OCP value changed by less than 10 mV in 1000 s, see Figure 1a). Since the sample was immersed in the solution right after grinding and cleaning, the growth of a stable passive film in the solution would take some time, resulting in an increase of OCP before stabilisation. Figure 1b shows the polarisation curve after 1 hour immersion, which presented a corrosion potential value (E_{corr}) very similar to the OCP value in the end of 1 hour immersion. There was a passive region on the anodic branch, and current started to increase rapidly at 0.65 V_{SCE}. However, after reaching 0.1 mA/cm^2, current density dropped with the reversing potential and levelled off at a lower value than the original passive current density, indicating that the passive film became thicker during backward sweep [24], and pitting corrosion did not take place. The test was aborted. The increase of current after 0.65 V_{SCE} may be ascribed to the oxygen evolution reaction.

Since the steel was passive in 0.01 M NaOH and 0.01 M NaCl, a lower concentration of hydroxide has to be used. Figure 2a shows the OCP data of 20# and 45# carbon steels in 3 mM NaOH and 0.01 M NaCl during 1 hour immersion, which increased and stabilised in a similar way to Figure 1a. Figure 2b shows cyclic polarisation curves of both steels after 1 hour immersion. The measured OCP values in the end of immersion were very similar to the corrosion potentials (E_{corr}) presented on the two polarisation curves, respectively. The passive current density was at ~10^{-2} mA/cm^2, and the current density started to increase rapidly at 20 mV_{SCE} and 180 mV_{SCE} for 45# and 20# steels, respectively. After reaching 0.1 mA/cm^2, there appeared a hysteresis loop, i.e. the current density did not decrease with reversing potential and follow the previous current-voltage relationship, instead, the current density increased with the reversing potential for a period of time before decreasing, indicating the occurrence of pitting corrosion [24].

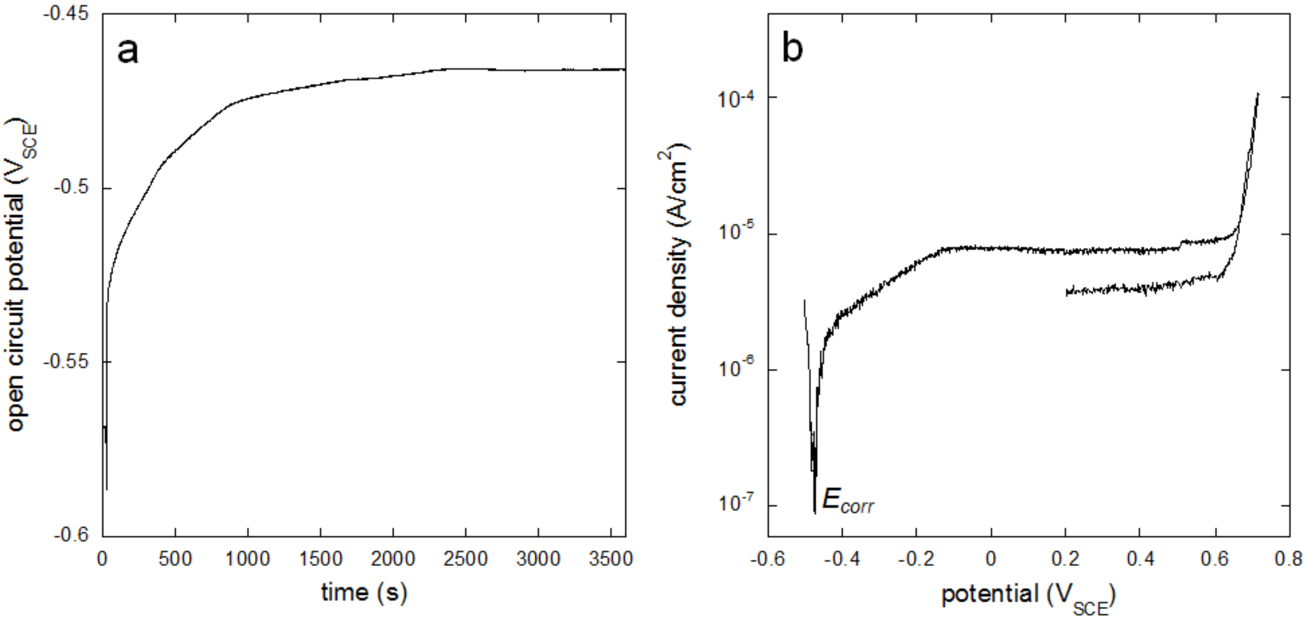

Figure 1. (a). A measurement of open circuit potential of 20# carbon steel in 0.01 M NaOH and 0.01 M NaCl for 1 hour. (b). A cyclic polarisation curve of 20# carbon steel in 0.01 M NaOH and 0.01 M NaCl after 1 hour OCP measurement, potential started from -50 mV vs. OCP and reversed when current density exceeded 0.1 mA/cm^2, sweep rate 1 mV/s.

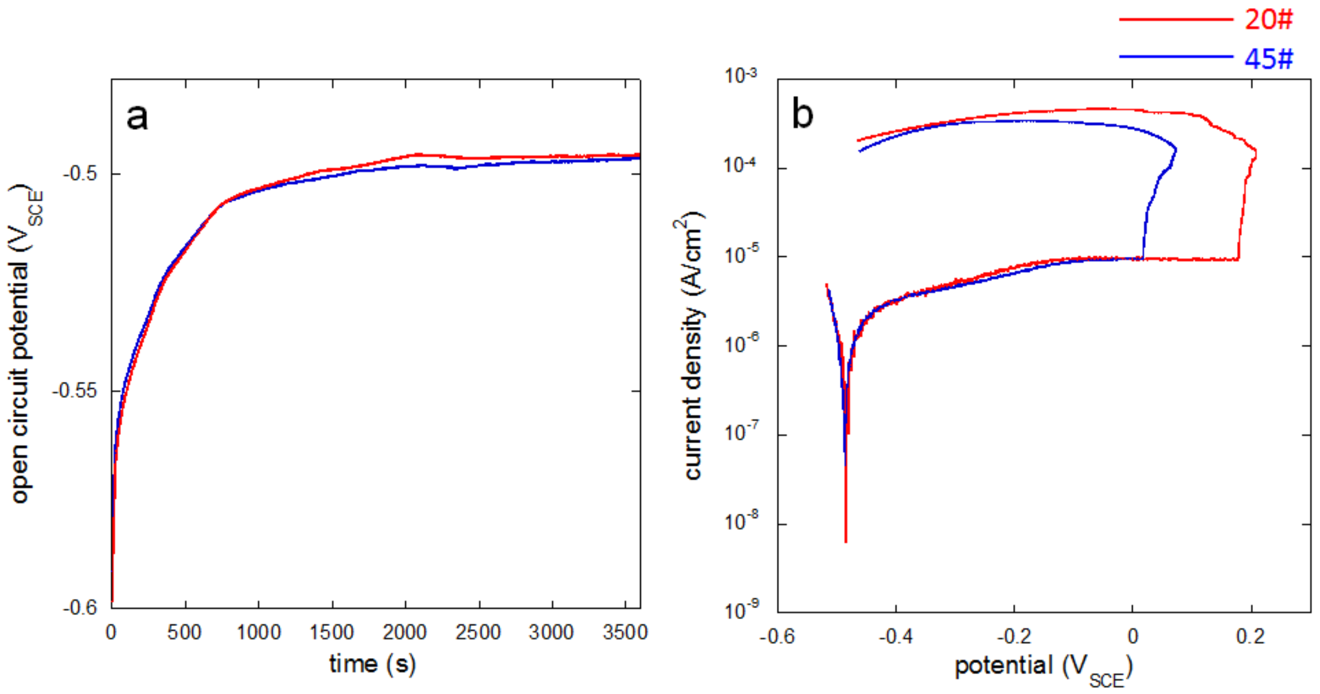

Figure 2. (a) Measurements of open circuit potentials of 20# and 45# carbon steels in 3 mM NaOH and 0.01 M NaCl solution for 1 hour. (b). Cyclic polarisation curves of 20# and 45# carbon steels in 3 mM NaOH and 0.01 M NaCl after 1 hour OCP measurements, potential started from -50 mV vs. OCP and reversed when current density exceeded 0.1 mA/cm^2, sweep rate 1 mV/s.

However, during the backward sweep, both steels did not repassivate, and the current density was always above 0.1 mA/cm^2. Since a large amount of ferrous ions diffused out from a growing pit, hydroxide ions outside the pit were consumed quickly, producing ferrous hydroxide and resulting in a drop of pH value around the growing pit, which may suppress repassivation. The existence of a critical pH has been reported by Galvele [25]. A small amount of dark products could be observed to be floating in the electrolyte near the metal surface after the test, which could be ferrous hydroxide and/or ferric hydroxide.

3.2. NaNO$_3$ and NaCl

The dissolution of carbon steel samples in NaNO$_3$ and NaCl has also been studied. Rust were visible on the surface of carbon steels after immersion for 20 min at open circuit in 0.1 M NaNO$_3$ with trace NaCl solutions, and OCP kept decreasing without being stable, so more concentrated nitrate solutions were used. Figure 3a shows the OCP data of 20# steel in 1 M NaNO$_3$ with no NaCl and 0.1 mM NaCl and 1 mM NaCl solutions during 1 hour immersion, which increased slightly and then stabilised (the OCP value changed by less than 10 mV in 1000 s). The polarisation curves after 1 hour OCP measurements in the three solutions are presented in Figure 3b (sweep rate 1 mV/s). The measured OCP values in the end of immersion were very similar to the corrosion potentials (E_{corr}) presented on the three polarisation curves, respectively. The current density increased directly to more than 1 mA/cm^2 without a passive region on the polarisation curve. Therefore, nitrate promoted general corrosion of carbon steel (consistent with Ma [26]), so the presence of chloride ions did not induce pitting corrosion.

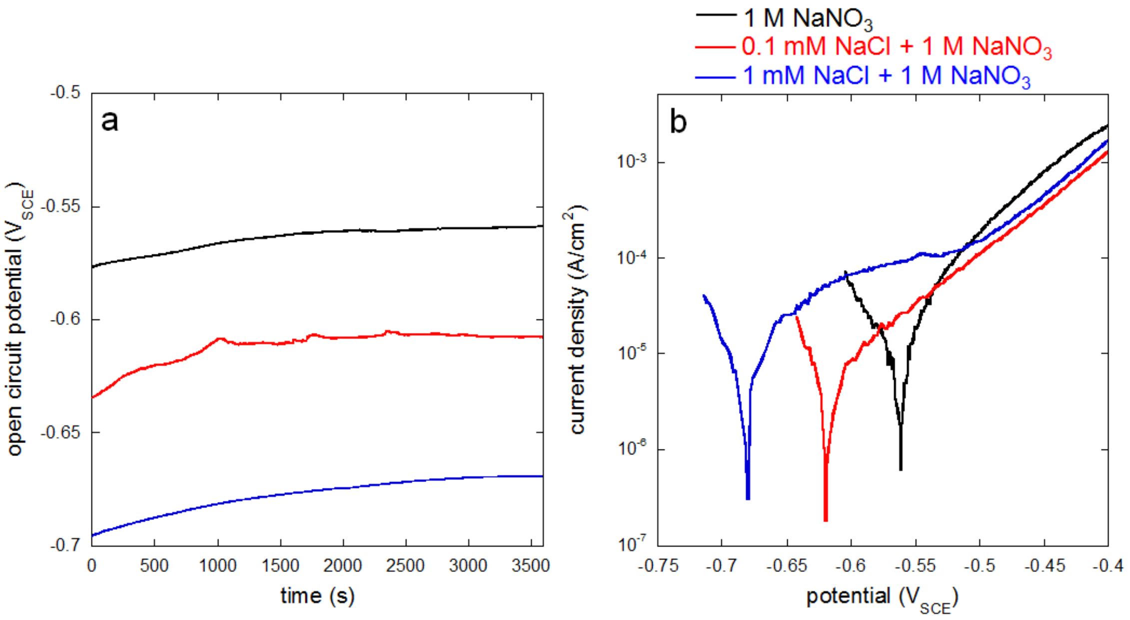

Figure 3. (a). Measurements of open circuit potentials of 20# carbon steels in 1 M $NaNO_3$ with no NaCl and 0.1 mM NaCl and 1 mM NaCl solutions for 1 hour. (b). Polarisation curves of 20# carbon steels in 1 M $NaNO_3$ with no NaCl, 0.1 mM NaCl and 1 mM NaCl solutions after 1 hour immersion, potential started from -50 mV vs. OCP, sweep rate 1 mV/s.

3.3. $NaNO_2$ and NaCl

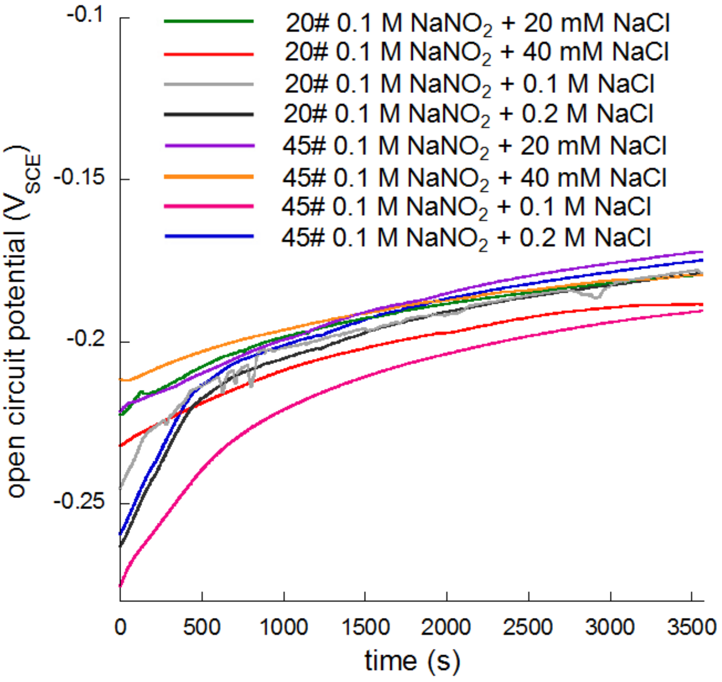

Figure 4. Measurements of open circuit potentials of 20# and 45# carbon steels in 0.1 M $NaNO_2$ with 20 mM, 40 mM, 0.1 M and 0.2 M NaCl for 1 hour, respectively

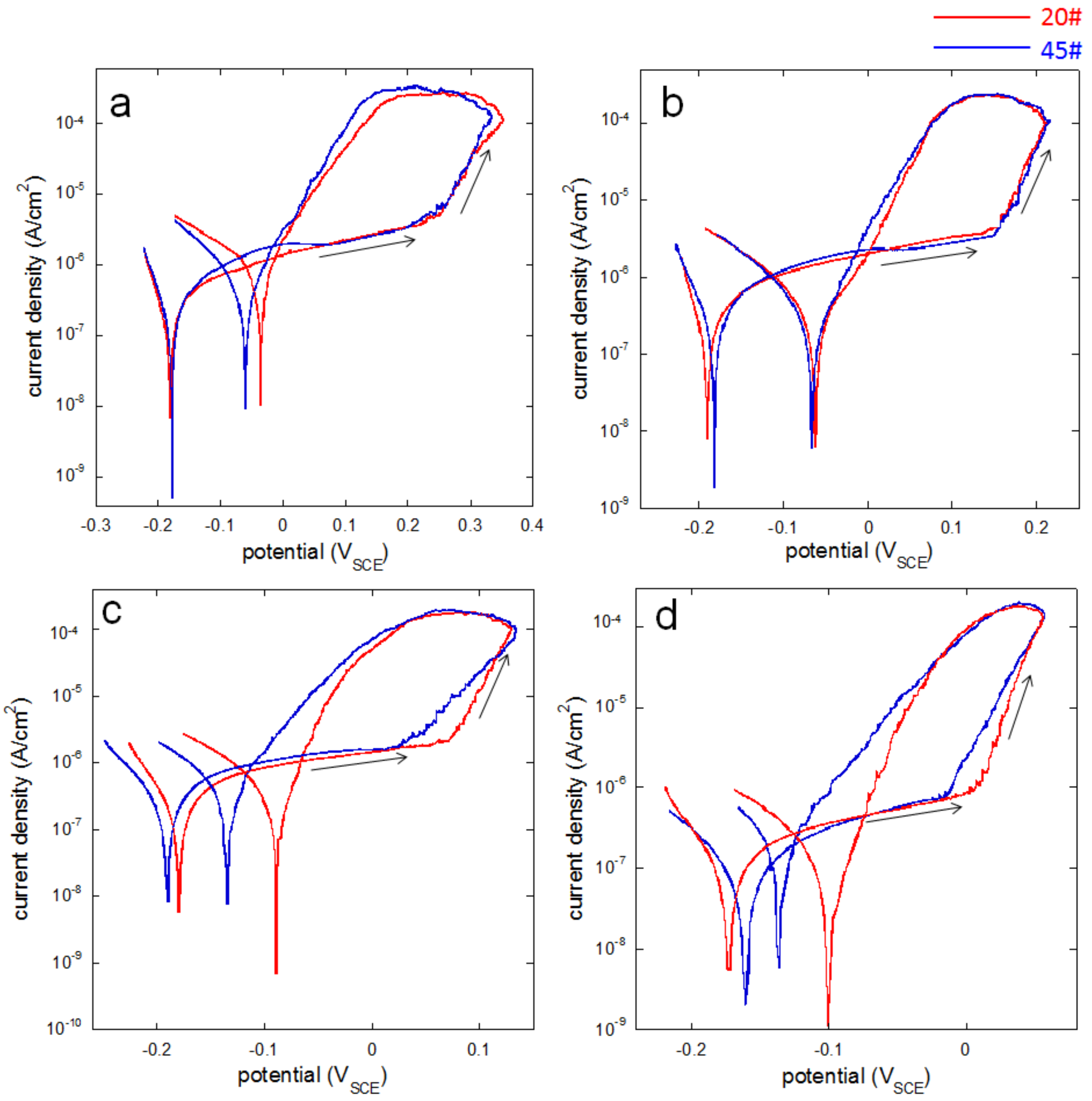

Figure 5. Cyclic polarisation curves of 20# and 45# carbon steels in 0.1 M $NaNO_2$ and (a) 20 mM NaCl, (b) 40 mM NaCl, (c) 0.1 M NaCl and (d) 0.2 M NaCl, potential started from -50 mV vs. OCP and reversed when current density exceeded 0.1 mA/cm^2, sweep rate 1 mV/s. The arrows in each diagram represent the direction of potential sweep.

Since the pits on carbon steel in NaOH and NaCl did not repassivate, and general corrosion instead of pitting corrosion took place in $NaNO_3$ and NaCl, the repassivation behaviour of corrosion pits could not be studied.

Nitrite ions have been reported to passivate pure iron [22], so the pitting and repassivation of carbon steel in $NaNO_2$ and NaCl solutions have been studied in this section, and the effect of hydroxide ions can be removed. The pitting potential (E_p) is the potential value at which stable pits start to grow, and the repassivation potential (E_{rp}) is the potential (after reversal of potential sweep) below which the already growing pits are repassivated and the growth is stopped [27]. The E_p and E_{rp} have also been interpreted by a schematic polarisation curve [27]. Simply speaking, on the forward sweep, potential reaches E_p when current starts to increase rapidly; after potential sweep is reversed, potential reaches E_{rp} when the current decreases to the previous passive current value.

Table 2. Weight of dissolved metal of 20# and 45# carbon steels in 0.1 M $NaNO_2$ solutions with different concentrations of NaCl from the onset of pitting corrosion to repassivation according to the polarisation curves in Figure 5 and Equation 1.

Solution	Metal loss of 20# (μg)	Metal loss of 45# (μg)
0.1 M $NaNO_2$ and 20 mM NaCl	16.0	16.2
0.1 M $NaNO_2$ and 40 mM NaCl	7.1	7.4
0.1 M $NaNO_2$ and 0.1 M NaCl	6.2	7.1
0.1 M $NaNO_2$ and 0.2 M NaCl	3.8	4.5

Figure 4 shows the OCP data of 20# and 45# carbon steels during 1 hour immersion in 0.1 M $NaNO_2$ with different concentrations of NaCl. It can be seen that the OCP of each condition increased in the beginning of immersion and tended to stabilise (the OCP value changed by less than 10 mV in 1000 s) in the end.

Figure 5 shows polarisation curves of 20# and 45# carbon steel samples in various concentrations of $NaNO_2$ and NaCl mixed solutions after 1 hour immersion, and the OCP value in the end of each immersion test shown in Figure 4 was similar to the corrosion potential (E_{corr}) presented on each polarisation curve in the corresponding solution. Figure 5a shows the polarisation curve of 20# and 45# carbon steel in 0.1 M $NaNO_2$ and 20 mM NaCl, and it can be seen that the differences on pitting potential and repassivation potential were negligible for both steels. When the concentration of chloride increased to 40 mM, the pitting potential and repassivation potential were still similar. When the concentration of chloride increased to 0.1 M and 0.2 M, the pitting potential and repassivation potential of 45# steel were both noticeably lower than that of 20# (see Figure 5c and d). In addition, from the curves in Figure5a to d, the weight of dissolved metal from the onset of stable pitting to repassivation can be calculated via the passed charge from the pitting potential to the repassivation potential (according to Equation 1),

$$m = QM/nF \tag{1}$$

where m is mass, Q is charge, M is molar mass, n is the average valence of metal ions (2 in this work), F is the Faraday’s constant (96500 C/mol). The calculated weight of dissolved metal is listed in Table 2 for both 20# and 45# carbon steels in 0.1 M $NaNO_2$ solutions with different concentrations of NaCl. It can be seen that the weight of disslved metal for 45# is similar to 20# in 20 mM NaCl, but became 18.4% greater than 20# in 0.2 M NaCl.

Table 3. The pitting potential (E_p) of 20# and 45# carbon steels in 0.1 M $NaNO_2$ with different concentrations of NaCl

Solution	**E_p of 20# (mV_{SCE})**	**E_p of 45# (mV_{SCE})**
0.1 M $NaNO_2$ and 20 mM NaCl	253±8	250±10
0.1 M $NaNO_2$ and 40 mM NaCl	152±11	148±7
0.1 M $NaNO_2$ and 0.1 M NaCl	70±10	35±8
0.1 M $NaNO_2$ and 0.2 M NaCl	10±8	-15±9

Table 4. The repassivation potential (E_{rp}) of 20# and 45# carbon steels in 0.1 M $NaNO_2$ with different concentrations of NaCl

Solution	**E_{rp} of 20# (mV_{SCE})**	**E_{rp} of 45# (mV_{SCE})**
0.1 M $NaNO_2$ and 20 mM NaCl	0±7	2±5
0.1 M $NaNO_2$ and 40 mM NaCl	0±4	-4±5
0.1 M $NaNO_2$ and 0.1 M NaCl	-60±5	-109±10
0.1 M $NaNO_2$ and 0.2 M NaCl	-77±9	-116±7

The anodic polarisation tests shown in Figure 5 were carried out four times for each concentration and each carbon steel sample. The results of the pitting potential and repassivation potential are listed in Table 3 and Table 4, respectively.

The effect of carbon content on the pitting potential of carbon steels in around 0.5 M NaCl (pH 8 to 9) has been reported previously [28], and it has been found that the pitting potential was lower for the steel with higher carbon content, which might be ascribed to the impurities or inclusions related to carbon. In this study, however, the difference on pitting potential was negligible for 20# and 45# carbon steels when the chloride concentration was 20 mM and 40 mM, and became obvious when the chloride concentration increased to 0.1 M and 0.2 M. It seems that the dependence of pitting potential on carbon content may be sensitive to chloride concentration. This was not studied intensively in the current work because it was not a key point for this study.

The morphology and possible corrosion products within pits have been studied using SEM and EDX. It can be seen from Figure 6 that the dissolved area in 20 mM NaCl was the largest, and decreased with increasing chloride concentration, which is consistent with the calculation of weight loss (see Table 2). EDX measurements were carried out on the dissolved areas. Since the morphology and EDX results of the pits in 20 mM NaCl and 40 mM NaCl are very similar, the results of the pit in 40 mM NaCl were not included the following discussion.

The dissolved areas were covered with a large amount of oxides according to EDX results (not shown), although the measurements in the SEM were all carried out less than 0.5 hour after electrochemical measurements, so the formation of oxides seems very quick and non-avoidable. Therefore, the elemental contents were measured on certain areas where the pit interiors could be observed (see the red boxes shown in Figure 6a to f).

Iron, carbon, oxide and silicon were detected within pits. The carbon contents within pits in different solutions are compared in Figure 7a. Although the use of EDX for accurate measurement of carbon levels is not practical, it can be applied for the comparison on carbon levels [11]. It was found that the carbon content was very low in 20 mM NaCl and noticeably higher in 0.1 M and 0.2 M NaCl, which indicates that carbon/carbides may be dissolved in 20 mM NaCl, but left within pits when chloride concentration was 0.1 M and 0.2 M.

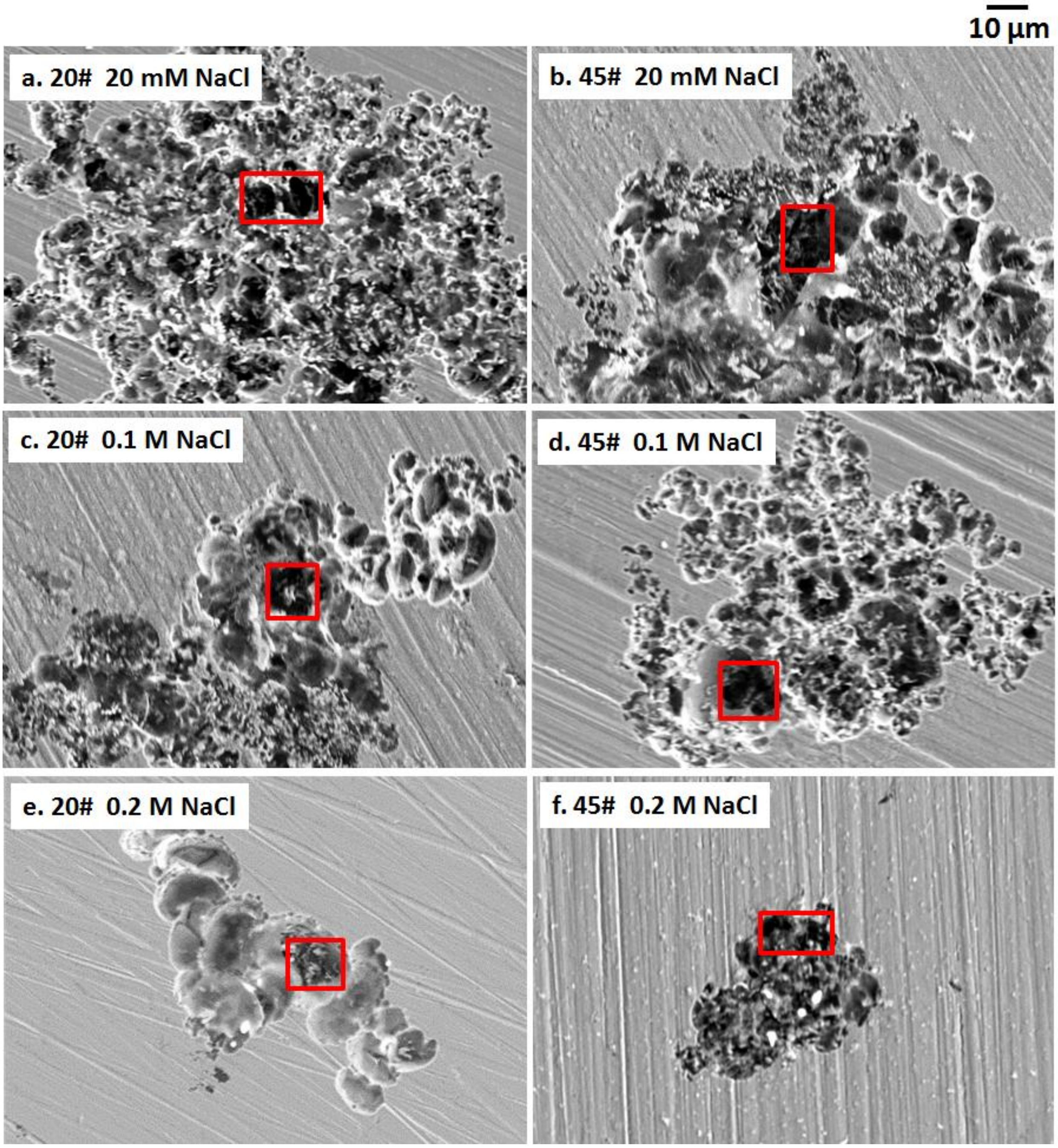

Figure 6. SEM images of pits on 20# and 45# carbon steels after dissolution in 0.1 M $NaNO_2$ and 20 mM NaCl (a and b), 0.1 M $NaNO_2$ and 0.1 M NaCl (c and d) and 0.1 M $NaNO_2$ and 0.2 M NaCl (e and f). The red boxes in the images represent the areas where EDX measurements were carried out.

The presence or absence of carbon can be ascribed to the potential dependence of carbon/carbides dissolution, which has been reported in a previous study of the author, where an E-pH diagram of Fe_3C was constructed [11]. The dissolution of carbon/carbides is a kinetic process, and the dissolution rate would increase with increasing potential. In 0.1 M $NaNO_2$ and 20 mM NaCl, the pitting potentials of both steels were about 250 mV_{SCE}, while in 0.1 M $NaNO_2$ and 0.2 M NaCl, the pitting potentials decreased to 5 mV_{SCE} and -15 mV_{SCE} for 20# and 45# carbon steels, respectively. When the pitting potential was low (e.g. in 0.2 M NaCl), pitting corrosion started at a low potential value, so carbon/carbides dissolve relatively slowly and may be left in the dissolving pit. On the contrary, when the pitting potential is high (e.g. in 20 mM NaCl), the dissolution rate of carbon/carbides is high enough to be comparable with iron, so the content of carbon left in the pit was negligible.

The element silicon was at 2.8% to 4.1% (atomic%) for all the pits in different solutions (see Figure 7b), but this difference on silicon cannot be related to the identical or different repassivation potentials in 0.1 M $NaNO_2$ with different concentrations of NaCl as shown in Figure 5. The element oxide was at 19.5% to 23.0% (atomic%) for all pits in different solutions, which was believed to be ascribed to the oxides formed after electrochemical tests, so it cannot affect the repassivation potential.

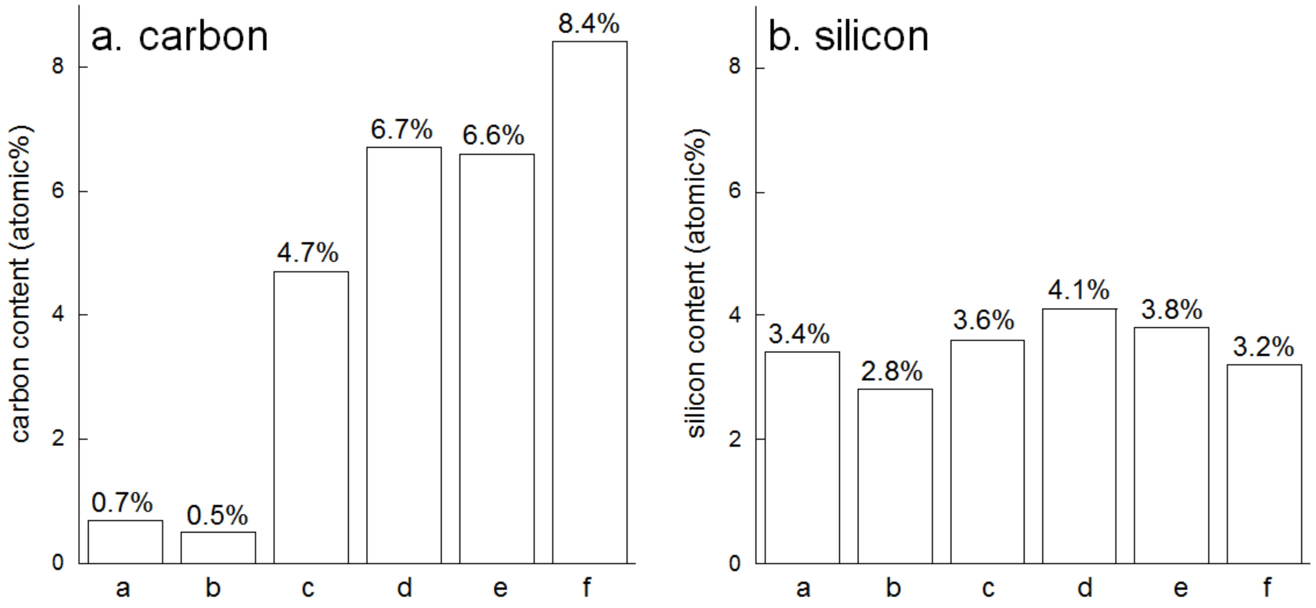

Figure 7. (a) carbon content and (b) silicon content (atomic%) within corrosion pits according to the EDX measurements carried out in the red boxes in Figure 6a to f.

Due to the presence of carbon/carbides within a pit, the escape of metal ions may be inhibited. This inhibitive effect of carbon/carbides may suppress the diffusion of metal ions. When the producing rate of metal ions is lower than the escape rate (e.g. at low overpotentials), the concentration of metal ions in a pit would decrease, but the decreasing rate is lowered in the presence than in the absence of solid products within a pit. It can be seen that carbon left in the pit was noticeably more for 45# than

20# for 0.1 M $NaNO_2$ with 0.1 M or 0.2 M NaCl (Figure 7a), because the original carbon content in 45# carbon steel is higher. Since the concentration of metal ions is critical for the maintenance of aggressive solution for pit growth [25, 29-31], more carbon/carbides is expected to be more capable of maintaining aggressive environment (i.e. concentrated metal ions) in a growing pit.

In the presence of solid carbon/carbides, metal ions could be "trapped" at the bottom of a pit, inducing increased amounts of hydrogen and chloride ions: hydrogen ions come from hydrolysis reaction of metal ions, and chloride ions are attracted by metal ions. Therefore, in the process of a potential backward sweep, the presence of more carbon/carbides within a pit may delay the repassivation, resulting in a more negative repassivation potential. It explains that the repassivation of 45# steel took place after 20# for the solution of 0.1 M $NaNO_2$ with 0.1 M or 0.2 M NaCl. Since the measured carbon content in the pit was very low in 0.1 M $NaNO_2$ and 20 mM NaCl, the difference on the repassivation potentials was negligible (see Table 4).

Frankel [32] has suggested that a "porous pit cover" favours the growth of a metastable pit after initiation, while the rupture of the cover forms openings and induces repassivation of the metastable pit. It should be ascribed to the inhibitive effect of the porous pit cover on diffusion of metal ions, whose concentration is critical for the prevention of repassivation. This is similar to the limitation of mass transport and accumulation of aggressive ions proposed by Flis [12] and Zhang [19], only except that the porous pit cover is near the outer of a metastable pit and the solid products are near the bottom of a pit.

This effect has not been demonstrated electrochemically previously, however, it should be taken into account in studies of pit stability. Otherwise, significant deviation may be induced. Solid products within a corrosion pit may extend the lifetime of a pit when dissolution rate is not high enough for dynamic pit growth, resulting in more serious attack than in the absence of solid products. Table 2 has given evidence that the metal loss from the onset of stable pitting corrosion to repassivation was obviously greater for 45# carbon steel than 20# in the solution containing 0.1 M or 0.2 M NaCl, for which carbon containing products were detected within pits.

4. CONCLUSION

Pitting corrosion occurs on carbon steel in 0.1 M $NaNO_2$ with different concentrations of NaCl (20 mM, 40 mM, 0.1 M and 0.2 M). The repassivation potentials in the solution containing 0.1 M and 0.2 M NaCl were noticeably lower for 45# steel than 20# steel, which may be ascribed to the presence of different amount of carbon/carbides within pits, inhibiting the diffusion of metal ions and maintaining the aggressive solution in growing pits. Therefore, the lifetime of a pit in the presence of more solid products is extended when compared to the condition of less solid products.

The repassivation potentials in 0.1 M $NaNO_2$ and 20 mM NaCl show negligible difference between 20# and 45# carbon steels, which is ascribed to the absence of carbon/carbides within pits. The carbon/carbides may have been dissolved with iron during pit growth.

Pitting corrosion of carbon steel was suppressed in 0.01 M NaOH and 0.01 M NaCl. However, the repassivation of corrosion pits grown in 3 mM NaOH and 0.01 M NaCl was suppressed, which may be ascribed to the consumption of hydroxide ions by dissolved metal ions around the outer of the pit, and a drop of pH prevents repassivation.

There was no passive region during the anodic polarisation of carbon steels in nitrate and chloride mixed solutions. On the contrary, nitrate ions promoted general corrosion of steels, and no pitting corrosion occurred with or without chloride.

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