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Published

2013

Conference Title

Annual Conference of the Australasian Corrosion Association 2013: Corrosion and Prevention 2013

Version

Version of Record (VoR)

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PASSIVATION OF IRON IN PH BUFFERED SOLUTIONS WITH AND WITHOUT CHLORIDE IONS

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SUMMARY: Interaction with the chloride ions can significantly cripple the service life of steel structures. It is therefore necessary to understand the impact of chloride ions on the kinetics of iron passivation. In order to firstly estimate the pH-potential region for iron passivation, potentiodynamic polarisation tests were carried out in borate buffer solutions at different pH. The optimum condition to achieve passivation was subsequently found to be in a solution having pH 9 with the electrode potential in the range 0.5 to 0.8 V_{SCE}. The influence of chloride ions on iron passivation was then studied under these conditions by performing chronoamperometry. These experiments were carried out in different solutions at pH 9 with/without borate buffer, both in the presence and absence of chloride ions. In general, passivity, which is manifested by the drop of the chronoamperometric currents from millamperes to few microamperes, was immediately achieved in chloride-free borate solutions (in a few seconds). In non-borate solutions with chlorides, passivity was not achieved even after many hours of chronoamperometry. In borate buffered solutions with the chlorides added, the chronoamperometric currents dropped to a few 100s of microamperes with time, implying that a less protective passive film forms on steel. These results have been discussed in the context of passivity breakdown in the presence of chlorides and local acidification.

Keywords: Iron, Borate buffer, Passivity and Passivity Break down

1. INTRODUCTION

The passive state of iron was explained by Michael Faraday and, thus passivity is known to be caused by the formation of an oxidized species on a metal surface under the narrow conditions of potential and pH. The literature concerned with the growth and nature of the passive film (1, 2) formed by potentiodynamic polarisation of iron in alkaline solutions is extensive. With a few exceptions, a broad consensus has emerged from the many studies on iron (3-7) and a variety of steels using a number of techniques, namely that the composition of the passive film is complex and inhomogeneous. Several workers have concluded that the film consists of two layers. These are considered to comprise of a continuous inner layer with a spinel structure (8, 9) composed of a cubic oxide which adheres to the metal surface, being either magnetite (Fe₃O₄) or both maghemite (γ -Fe₂O₃) and magnetite (8, 10), a Fe(II)/Fe(III) oxide (11) or a solid solution of intermediate composition (12) and an outer layer that is more loosely bound and composed of either Fe(OH)₂ and FeOOH, a hydrated Fe(III) hydroxide or Fe₂O₃·H₂O (8-11). The passive film is thus composed by an inner compact layer which is anhydrous oxide acting as a barrier layer only few nm thick (the so-called natural passive film) and an outer hydroxide layer that grows on top, which is porous layer and very thick when compared to the inner layer (13). Iron suffers passivity breakdown in the presence of chloride and sulphate ions (14, 15). Alvarez and Galvele have shown that the passive film formed on steel becomes unstable due to the depletion of the hydroxyl ions at the metal-solution interface (16). Galvele (17, 18) postulated that localised acidification at the metal-metal oxide-solution interface results in passivity breakdown, whilst Sergi et al (19) reported that passivity breakdown was more due to the variations in pH compared to variations in chloride concentration. Augustynski

and co workers (20) attributed passivity breakdown to the depassivation effect of anions in solutions, whereby anions which have ability to form more soluble salts with iron will tend to readily breakdown the passive film. Passivity breakdown may take place due to an accumulation of chloride ions at the metal-solution interface (19, 21). In the current work, the pH-potential region to achieve iron passivation is being studied, and this information has then been used to study the impact of the chloride ions and local acidification (using buffered/non-buffered solutions) on the kinetics of iron passivation.

2. EXPERIMENTAL DETAILS

2.1 Materials preparation

To perform experiments, HA1 steel plates (99.8% Iron) were used. The steel samples were cut into square sheets of 25mm and polished to 2000 grit (SiC grit paper) followed by diamond polishing from 9 to 1 micron. All chemicals used in the experiments were of analytical purity. Sodium chloride (NaCl) solution of concentration 0.1 M was prepared, and the pH was adjusted with appropriate additions of diluted H₂SO₄ and NaOH solutions. The borate buffer was prepared with 0.3 M boric acid and 0.15 M disodium tetra borate. The specifics of these experiments will be discussed in the next section.

2.2. Electrochemical Tests

The electrochemical experiments namely open circuit potential (OCP) measurements, cyclic potentiodynamic polarisation and chronoamperometry (CA) experiments, were carried out using a VMP3 potentiostat. This instrument is controlled using the software EC lab v10.32. The electrochemical cell used to test the steel samples was the Princeton Applied Research (PAR) Flat cell. The reference and counter electrodes used were saturated calomel electrode (SCE) and a titanium electrode respectively. In one set of experiments the iron samples were potentiodynamically polarised in 0.1 M NaCl of different pH under aerated conditions and also some chronoamperometry studies were performed using borate buffer (pH 9) with and without ramping the potential. In the cyclic potentiodynamic polarisation, the potential scan was carried out from $-0.5 V_{OCP}$ to $1 V_{OCP}$ using a scan rate of 0.167 mV/sec. For the CA studies, the potential was ramped from OCP to 0.7 V at a scan rate of 0.5 mV/sec and then held at 0.7 V for 24 hours to form a passive layer over steel. Direct potential hold at 0.7 V was also applied without ramping the potential. In both the experiments the exposed area of the samples was 1 cm².

3. RESULTS

3.1 Passive Regime of iron

The potentiodynamic polarisation curves of steel in aerated 0.1 M NaCl solution with pH 9, 10 and 11 are shown in Figure 1. The steady-state currents corresponding to passivation of the metal are not seen in these polarisation curves. This implies that steel may not readily passivate in chloride containing solutions even at slightly alkaline pH. The average values of the corrosion current (i_{corr}) and corrosion potential (E_{corr}) for each pH were determined from the polarisation curves. When pH increases from 9 to 11, E_{corr} increases steadily to more noble values and i_{corr} decreases as shown in Table 1.

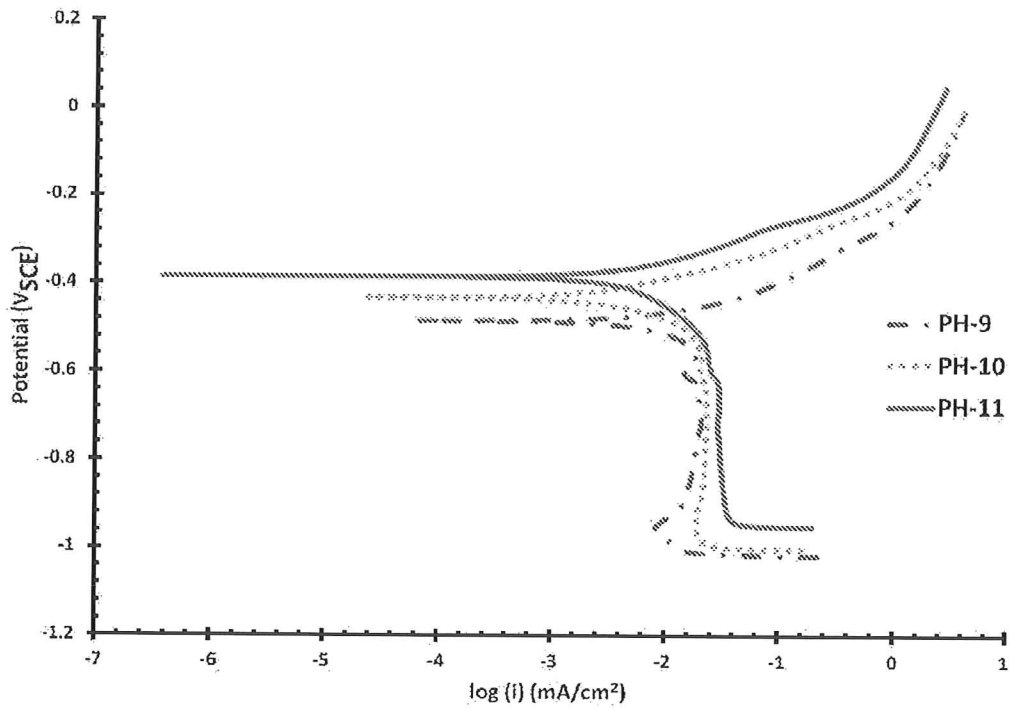


Figure 1: Polarisation curves of steel in aerated 0.1 M NaCl solution with pH 9, 10 and 11.

Table 1: E_{corr} and i_{corr} values for the pH range (9-11).

pH	E_{corr} (V_{SCE})	i_{corr} ($\mu\text{A}/\text{cm}^2$)
11	-0.38	5.6
10	-0.42	6.0
9	-0.48	10.58

Figure 2, shows the Polarisation curves of steel in aerated 0.1 M NaCl solution having a pH 9 and in the borate buffer solution without chloride. The E_{corr} of steel in the buffered solution ($-0.2V_{\text{SCE}}$) is more anodic when compared to the chloride solution ($-0.5 V_{\text{SCE}}$) and the i_{corr} is two orders of magnitude lower than that in the chloride solution. Steady state passive currents corresponding to the passivation of the metal are seen in the potential range 0.5 to about 0.8 V_{SCE} in the borate buffered solution. There is a slight increase in the anodic currents from 0 to 0.5 V_{SCE} , however on further anodic polarisation past 0.5 V_{SCE} the currents are stable and in the microampere range. Thus the passive regime of steel (pH-potential region) is in a solution having a pH 9 with the electrode potential range being close to 0.5 to 0.8 V_{SCE} .

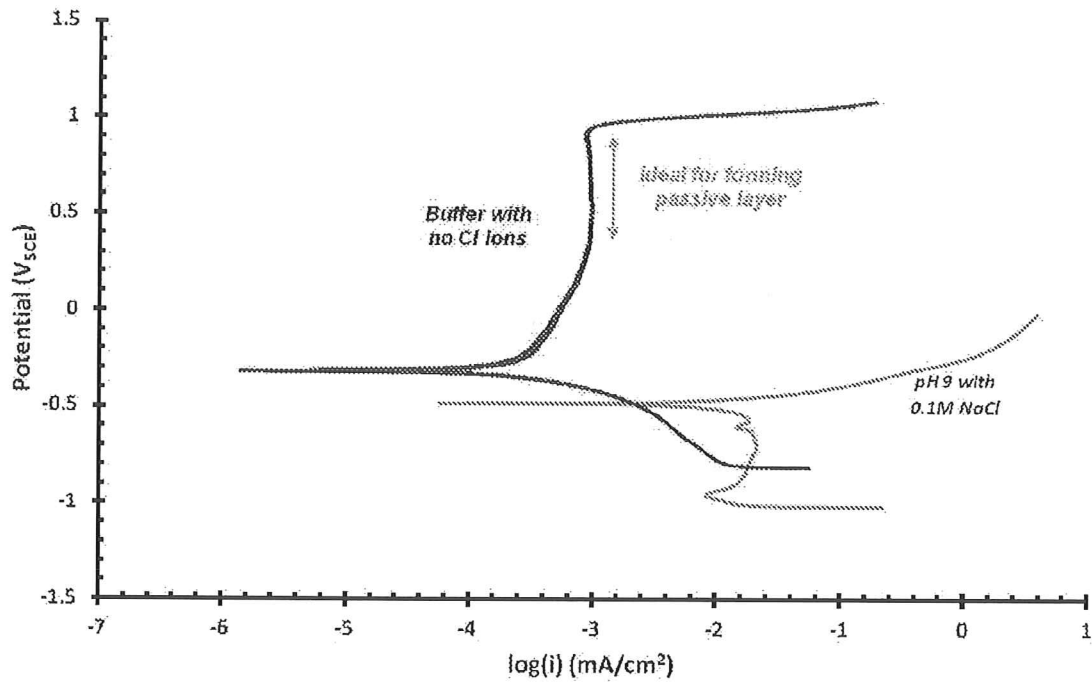
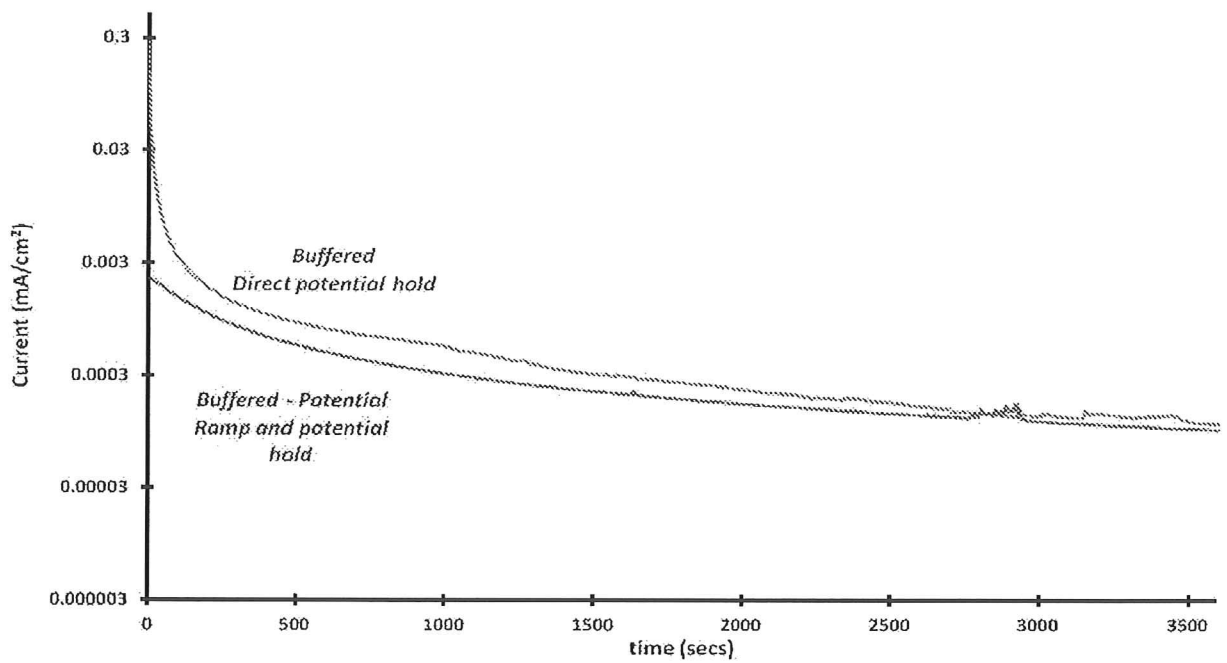
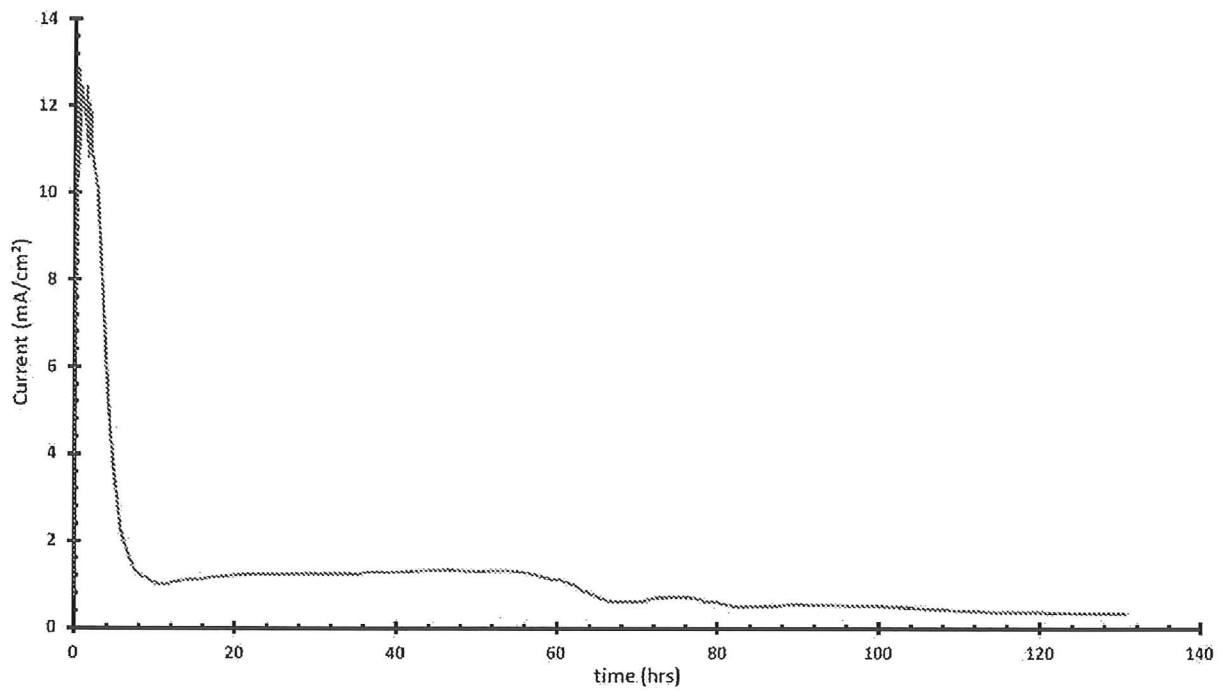


Figure 2: Polarisation curves of steel in aerated 0.1 M NaCl solution with pH 9 and pH 9 Buffer solutions.

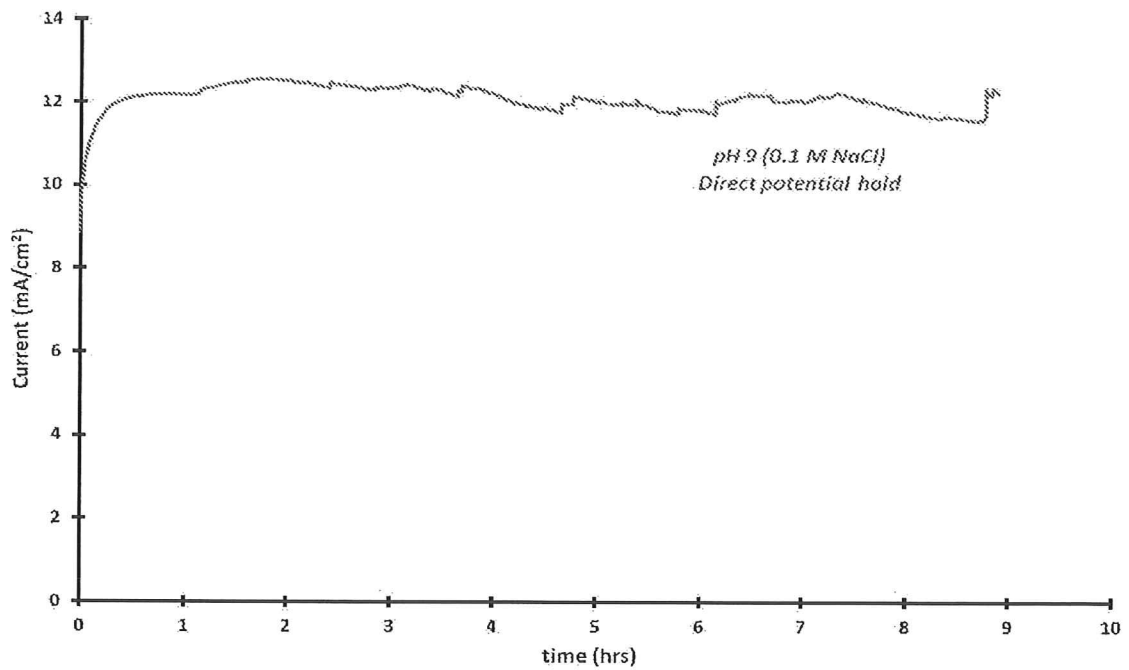
3.2 Influence of chloride on iron in the presence and absence of buffered solutions

The conditions under which steel undergoes passivation as described in the previous section, is at pH 9 and in the electrode potential range of 0.5 to 0.8 V_{SCE} . The influence of chloride ions on the kinetics of iron passivation has been studied using chronoamperometry when steel is subject to these passivating conditions. Figure 3 & 4, shows the chronoamperometry curves on the steel samples held at a potential of 0.7 V_{SCE} in both chloride and chloride-free borate buffered solutions. In chloride containing solutions (Figure 3) there is a rapid drop of currents after about 10 hours of chronoamperometry; however after 80 hours the chronoamperometric currents drop to a few 100s of microamperes, suggesting that a passive film may have formed on the steel (22). In chloride free solution (Figure 4) there was a sudden drop of the chronoamperometric currents to a few microamperes ($0.2 \mu A/cm^2$) implying that a passive film may spontaneously form on the surface.

When the experimental conditions are slightly altered, wherein, the steel sample is first subject to a potential ramp prior to chronoamperometry, the initial current (recorded during the first few seconds of chronoamperometry) is $0.0023 mA/cm^2$ which is significantly lower than that when steel is directly held at 0.7 V_{SCE} (without a potential ramp). In the case of Potential ramp followed by potential hold in buffered solution, the thickness of the oxide layer was found to be 1.32 micron whereas in the buffered solution for direct potential hold it was 4.28 micron. This was characterized by FIB-SEM and the data was not presented due to page limitations. From FIB-SEM analysis it was evident that a compact layer with few nanometres can be formed by applying direct potential holds or potential ramp followed by a potential hold under borate buffer. This was in good agreement with our CA tests as shown in figure 4. For the buffered chloride solution, the outer layer was very thick and it was not possible to analyse the inner compact layer due to the instrument limitation. If an inner layer exists then this layer must allow some transport of Fe ions through itself to the solution therefore it could precipitate and form a very thick outer layer. In the case of the borate buffer, the inner layer was very compact and restricts the migration of Fe ions. So the outer layer was not very thick and it was possible to analyse the inner layer by using FIB-SEM.



In chloride solutions in the absence of borate buffer, the chronoamperometric currents are high in the range of 10 mA/cm² (Figure 5). The currents in this case do not drop as in the case where borate buffer was present in the solution (Figure 3). This suggests that in the absence of borate buffer and presence of the chloride ions a passive film may not form upon steel. In the presence of the borate buffer, in spite of the chlorides being present in solution, a slightly protective passive film may form after prolonged exposure.



In these set of experiments, chlorides are added into the solution after chronoamperometry in the borate buffer solution for a fixed period. The passive film forms on steel during the initial chronoamperometry and the subsequent addition of chlorides serves to evaluate the influence of chlorides on the kinetics of iron passivation. Figure 6, shows the Chronoamperometry for steel in pH 9 buffered solutions with the chlorides (0.1 M NaCl) being added after 10 minutes. With the addition of 0.1 M chloride to the buffered solution, as shown in figure 6 & 7, the currents increased sharply and took 70 hours to re-stabilize. In contrast, after 10 hours the currents stabilised when the chloride was present from the start, thus it seems some degree of passivation can occur even if Cl^- are present but when Cl^- are added to an already passivated sample the breakdown of this passive layer occurs almost instantaneously and repair takes longer compared to the solution where chloride was present from the start. The spikes in the chronoamperometric currents may be due to some metastable pitting combined with stable pitting. This aspect is not yet clarified and will be explored in detail in the future research.

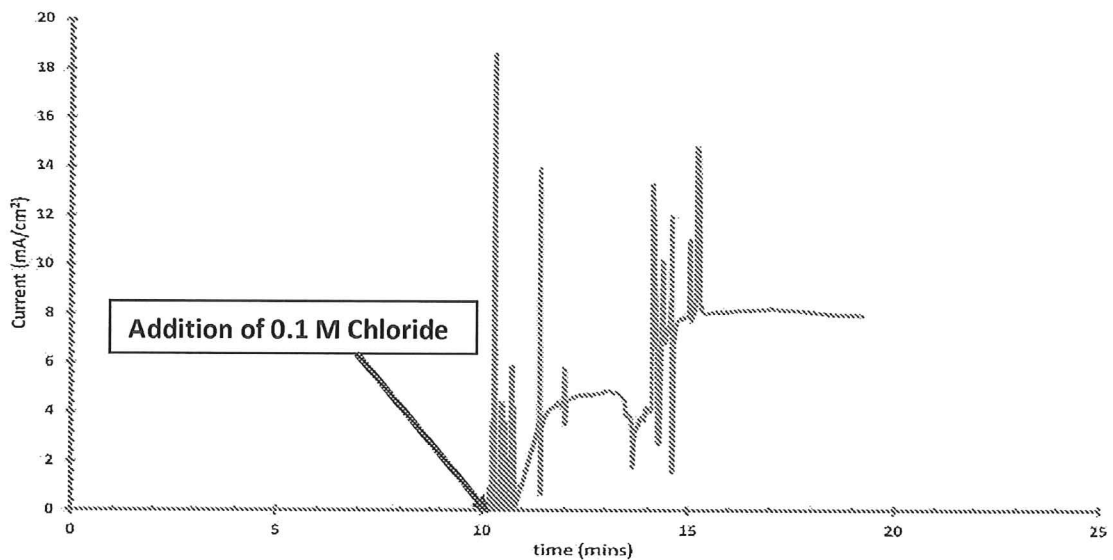
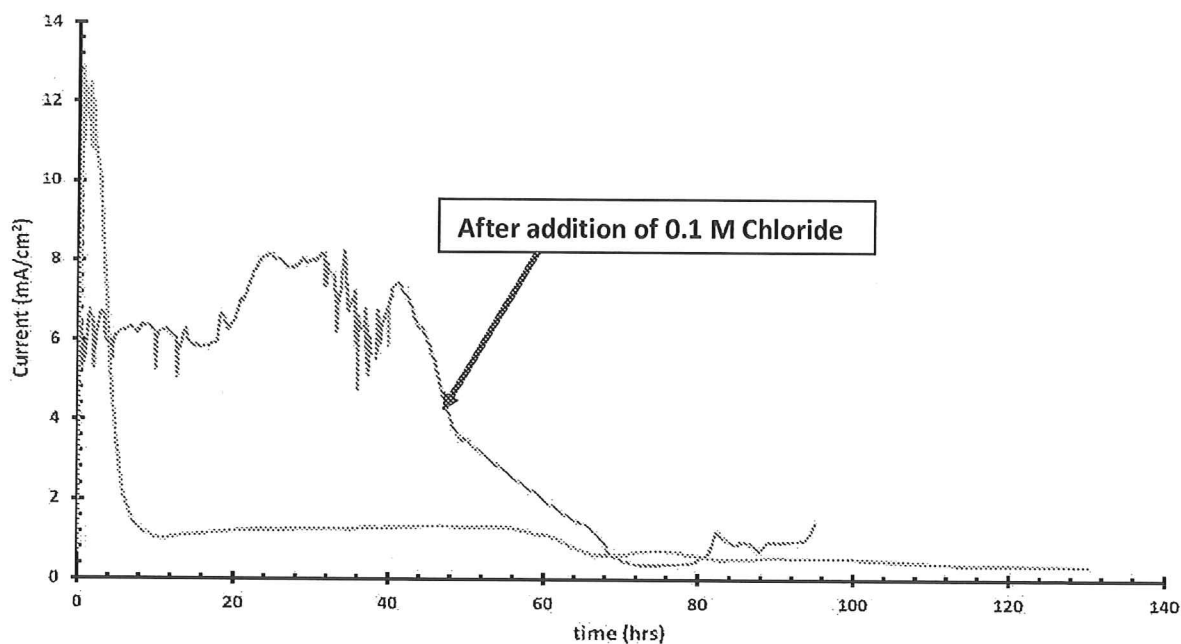


Figure 6: Chronoamperometry for steel in pH 9 buffered solutions for 10 minutes and then the addition of 0.1 M chloride to the buffered solution



buffered solutions with 0.1M chloride

4. DISCUSSION

Passivity breakdown has been historically attributed to result from either local acidification (due to metal hydrolysis) or due to the presence of chlorides (18). In the current work, the borate buffer was used to neutralise the local acidification, enabling a study of both chlorides and local acidification on the kinetics of iron passivation. In a borate buffered solution (without chlorides) steel spontaneously undergoes passivation (refer Figure 4) with extremely low passive currents of the order 0.2 to 0.3 $\mu\text{A}/\text{cm}^2$ (21). This is an ideal scenario where both local acidification and chloride attack may not be present in the system resulting in the formation of a highly protective passive film on the surface. In a chloride containing borate buffer solution, there is a drop in the chronoamperometric currents recorded on steel with time, however the currents are still in the range 100-200 $\mu\text{A}/\text{cm}^2$ (Figure 4) implying that a passive film may form on steel but it may not be highly protective (23). In this scenario, wherein local acidification is hindered but chloride attack is possible so a passive film may form on the metal, but is not highly protective. The addition of chlorides may destabilise a pre-existing passive film however after prolonged periods of exposure repassivation may take place, and the passive film may be redeveloped on the surface (Figure 6-7). In the absence of the borate buffer solution with chloride ions present, both local acidification and chloride attack take place and the chronoamperometric currents are significantly high during the experiment (Figure 5). In this case a passive film does not form on steel due to the combined effect of detrimental factors like local acidification and chloride attack. Therefore the solution chemistry has an influence on passive oxides formed during the potential hold experiments but it was not fully understood (24).

5. CONCLUSIONS

In borate buffered solutions, iron passivation is manifested at pH 9 and the electrode potential range 0.5 to 0.8 V_{SCE} . Local acidification (due to metal hydrolysis) and presence of chloride ions are the two historically well known factors inducing the passivity breakdown of iron. Since local acidification may take place in unbuffered solutions, borate buffered solutions have been used in the current work to keep the solution pH constant. In chloride-free pH buffered solutions, passivity is spontaneously achieved (as inferred from chronoamperometry). In unbuffered chloride solutions, the chronoamperometric currents are very high revealing that the combination of local acidification and chloride ions is detrimental towards passivation. In borate buffered solutions containing chloride ions, chronoamperometric currents drop with time to a few 100s of microamperes, implying that a less protective passive film may form on the surface. Addition of chloride, to the solution under passive conditions leads to the rapid destruction of the passive layer on steel although repassivation appears to be possible at longer times. On the other hand, if a passive layer is formed in a buffered chloride solution, the chloride appears to have a less detrimental affect and passivation occurs more rapidly. In the broader

perspective, strategies to counterbalance the two detrimental factors namely local acidification and chlorides may serve to develop more protective passive films on steel.

6. ACKNOWLEDGEMENTS

Sebastian Thomas is thanked for his assistance in modifying this manuscript.

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8. AUTHOR DETAILS



I. Bosco graduated as a Mechanical Engineer from Anna University in Tamilnadu, India. He is currently undertaking his PhD under the supervision of Maria Forsyth and Ivan Cole. For his undergraduate project, he studied the corrosion of aluminium alloy 5083 using electrochemical techniques. His PhD project attempts to develop strategies on self repairing oxides to protect steel system from corrosion.



Dr I. Cole is a Chief Research Scientist at CSIRO and was previously the Deputy Chief of the CMSE division. His depth of expertise in material science and mathematical modelling allowed him to work in areas such as manufacturing and aerospace alloy corrosion protection. He was awarded the Silver Medal, BAE Systems Chairman's Award for Innovation and the Guy Benough Award throughout the course of his career. He remains at CSIRO, offering his skill and knowledge to colleagues and students.



Professor M. Forsyth is the Associate Director of ARC Centre of Excellence for Electromaterials Science. Her research is directed towards development and understanding of charge transport at metal/electrolyte interfaces and within electrolyte materials. These include a wide range of ionic liquids, polymer electrolytes and plastic crystals. Using this understanding, her team collaborates very productively with colleagues within academia, CSIRO, DSTO as well as industry to design new materials and processes to control and optimise these phenomena in two key areas - corrosion and electrochemical devices.