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## AC Induced Passivity Breakdown in NaHCO<sub>3</sub>/Na<sub>3</sub>PO<sub>4</sub>-Solution

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### **Keywords:**

*AC induced passivity breakdown, polarisation scans, IR-free peak potentials, corrosion rate, ER-technique*

### **Abstract**

The AC corrosion behaviour of steel has been investigated in a non-scaling bicarbonate-phosphate system at pH 9.15. The investigation included corrosion rate measurements using the ER-technique during a DC polarisation scan as well as during a scan in which the DC was superimposed by 300 A/m<sup>2</sup> 50 Hz AC. In addition, fixed conditions of DC (-850 mV SCE) superimposed by 300 A/m<sup>2</sup> and 400 A/m<sup>2</sup> were maintained for prolonged periods (18 hours) during which the corrosion rate was measured. Further, the corrosion rate was measured during a period of 10 hours where the steel was kept close to its OCP (-300 mV SCE) and superimposed by 300 A/m<sup>2</sup>. The DC scan showed a passive/immune condition for the steel and no corrosion was detected during this scan. The DC scan with superimposed AC showed a depolarisation in the DC behaviour. The corrosion rate measurements during the DC/AC scan revealed a peak in corrosion rate when the OFF potential oscillated around -850 mV SCE. In the cathodic scan, a maximum corrosion rate of 0.2 mm/year was detected, and when the scan was reversed, a maximum corrosion rate of 0.8 mm/year was detected in the same potential region. The above observations confirm data presented by Pourbaix et al, showing that when the OFF-potential oscillates around the borderline between passivity (in the DC case) and immunity corrosion occurs due to a destabilisation of the passive film formation. These observations were confirmed by experiments at fixed conditions.

## Introduction

Previous papers<sup>1-4</sup> have shown that AC influenced corrosion can be produced in near-neutral artificial soil solutions under cathodic polarisation. It has been shown that the anodic dissolution reaction strongly depolarises (activates) under AC influence, and that this may produce corrosion even under CP. In case earth alkaline cations are present in the environment, the spread resistance of the steel increases throughout time and decreases the AC current at fixed AC voltage. The corrosion rate decreases accordingly in this case. If earth alkaline cations are not present, the spread resistance is more stable, and the AC current can be maintained. In this case, the AC influenced corrosion rate may decay under cathodic polarisation, e.g. due to a decreasing depolarising effect of the AC throughout time.

This paper deals with investigations in a solution in which the steel is passive in the DC case, but activates when superimposed by 50 Hz AC. The solution employed was a non-scaling bicarbonate-phosphate system, that has been shown by Pourbaix et al<sup>6</sup> to provoke this unpleasant behaviour.

The non-scaling nature (absence of earth alkaline cations) made the system well suited for polarisation scans with superimposed AC, since a fixed AC voltage creates a constant AC current density (as demonstrated in paper 7 of the present report<sup>2</sup>). Accordingly, the investigations presented here involve corrosion rate measurements by the ER-technique during such scans as well as during prolonged exposure at three fixed AC/DC conditions.

## Experimental

The chemical composition of the solution employed in the studies is listed in table 1.

Component	Mg/L	Mol/L
$\text{NaHCO}_3$	8400	0.10
$\text{Na}_3\text{PO}_4$	1640	0.01

*Table 1. Chemical composition of the solution (pH 9.15, conductivity 11120  $\mu\text{S}/\text{cm}$ ).*

The experimental set-up used in the investigations is illustrated in figure 1.

Electrochemical three-electrode arrangements were established in 2-liter glass vessels each equipped with a 2-cm<sup>2</sup> ER-probe as working electrode, a large (500 cm<sup>2</sup>) titanium-mesh as counter electrode, and a saturated calomel electrode (SCE, +0.242 V vs. SHE) as reference electrode.

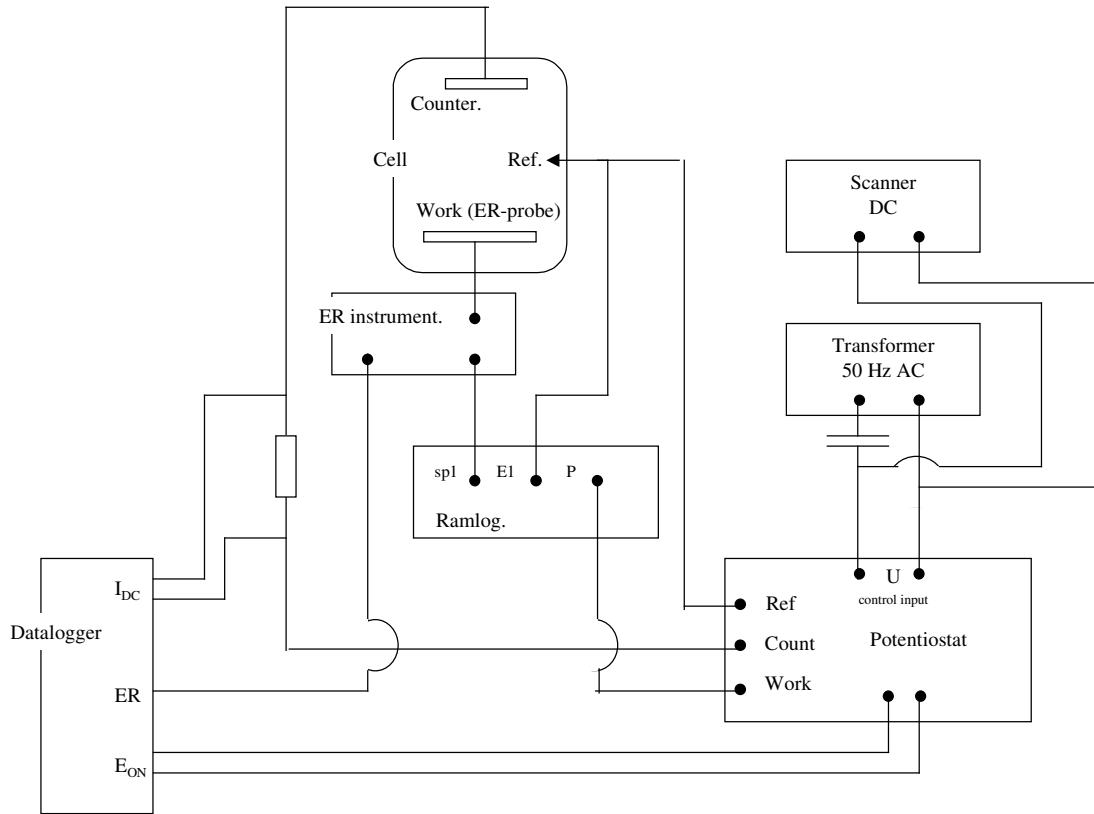


Figure 1. Electric diagram used for the potentiostatic AC- and DC-charging of the ER-probe.

The ER-probes were prepared from 25  $\mu\text{m}$  thick steel foils. As described elsewhere<sup>7,8</sup> the sensitivity of the ER-instrument is below 0.1  $\mu\Omega$  allowing for real time logging of the corrosion rate of the probe according to the algorithm:

$$V_{\text{corr}} = \frac{dR}{dt} \cdot \frac{\rho}{R^2} \cdot \frac{L}{W} \quad (1)$$

in which  $R$  is probe resistance,  $\rho$  is specific material resistivity,  $L$  is probe length and  $W$  is probe width.

A Wenking type potentiostat was fed with AC from a transformer and a DC scanner was coupled to control the DC potential during scans. Ramlog Correal recorders picked up the average ON-potentials, the instant IR-free OFF potentials and the instant current. A datalogger picked up the signals from the ER-instrument as well as the ON potential controlled by the potentiostat (and the DC scanner). In addition, the DC current flowing to the cell was recorded by the datalogger as the voltage across a 10  $\Omega$  resistor inserted in the counter electrode circuit.

The following experiments were made in this investigation:

1. The probe was left under open circuit conditions for 1 hour to make sure that the open circuit potential (OCP) indicated passive behaviour. After this, a slow (30 mV/hour) DC scan was made from the rather anodic OCP (-300 mV SCE) in the cathodic direction. During the scan, the corrosion rate was monitored by the ER-technique.
2. The probe was fixed for some 10 hours at the passive OCP (-300 mV SCE) as DC offset, superimposed by the 300 A/m<sup>2</sup> AC, and the corrosion rate monitored.
3. The probe was left at its OCP for one hour, then scanned in the cathodic direction, however, this time with 300 A/m<sup>2</sup> superimposed AC. At -1100 mV SCE, the scan was reversed and continued in the anodic direction. Corrosion rate was monitored.
4. The probe was fixed at the -850 mV SCE DC offset and superimposed by 300 A/m<sup>2</sup> AC, and the corrosion rate monitored for some 18 hours. The same experiment was made, however with 400 A/m<sup>2</sup> superimposed AC.

The applied AC current was dosed simply by adjusting the transformer to give a voltage producing the desired AC current. The constant spread resistance meant that no adjustments of the AC voltage were necessary during the experiments. The maintenance of a constant AC current was checked frequently by a fluke multimeter (measuring the AC voltage across the 10 $\Omega$  resistor inserted in the counter electrode circuit).

## Results and discussion

The spread resistance calculated as in paper 7<sup>2</sup> and justified in paper 4<sup>5</sup> was constantly around 0.0040  $\Omega\cdot\text{m}^2$  in this environment. The OCP of the coupon stabilised around -300 mV SCE during the one hour at open circuit conditions.

Figure 2 shows the polarisation curve resulting from the DC scan. The current was cathodic in the entire range from the OCP and downward. Diffusion controlled behaviour corresponding the oxygen reduction is observed in the potential region approximately -500 to -800 mV SCE, where after the hydrogen evolution reaction takes over and dominates at lower potentials. No corrosion could be detected during this scan.

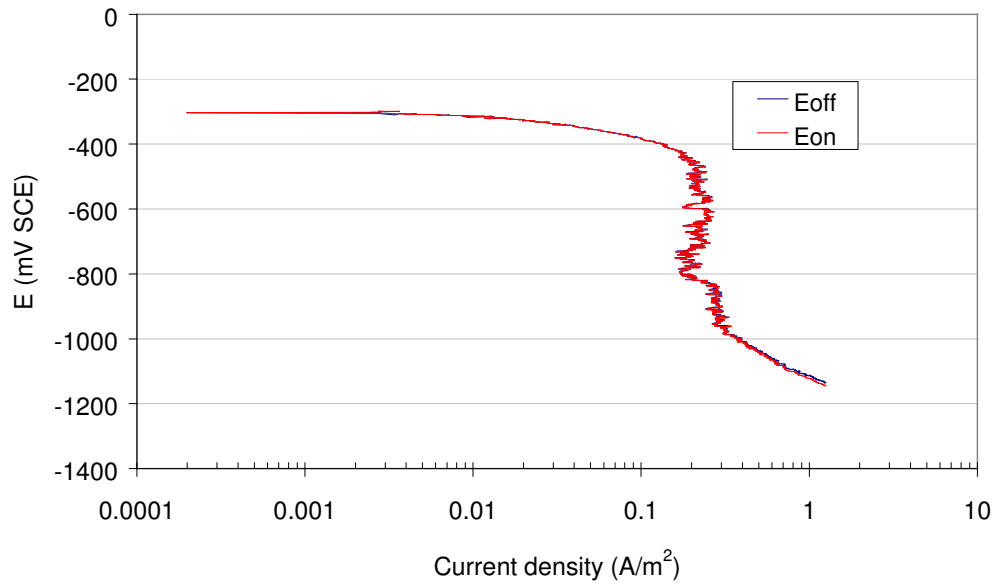


Figure 2. DC scan – no corrosion detected throughout the scan.

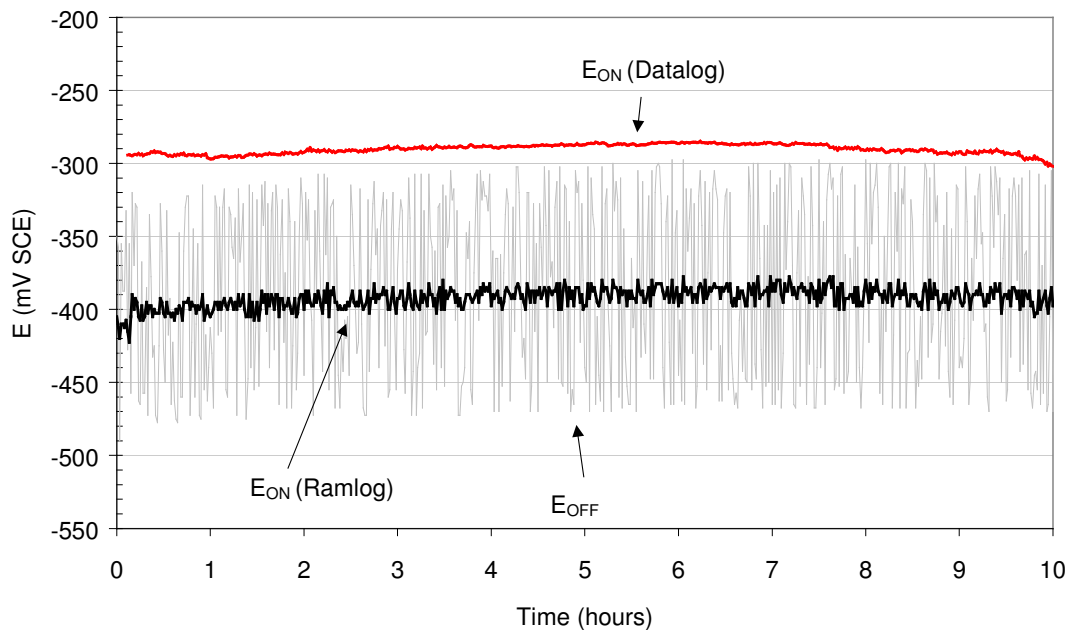


Figure 3.  $E_{\text{ON}}$  and  $E_{\text{OFF}}$  during the period of fixed DC offset (-300 mV SCE) superimposed by  $300 \text{ A/m}^2$  AC.

Figure 3 shows the Ramlog data ( $E_{\text{ON}}/E_{\text{OFF}}$ ) resulting from experiment involving a constant DC offset of -300 mV SCE (a potential close to the OCP of the system) superimposed by  $300 \text{ A/m}^2$  AC current. The ON potential recorded by the datalogger is shown as well. The OFF-potential is observed to oscillate between approximately -300 mV and -470 mV SCE. The average ON-potential measured by the Ramlog shows a fairly constant value of -400 mV SCE, and compared with the potential recorded by the datalogger, which was around -300 mV SCE, some discrepancy

between the ON-potentials is observed for some reason. This may have to do with the way the Ramlog records the ON-potential as an average of 300 measurements made within 20 ms. Again, no corrosion was detected in this experiment.

Figure 4 shows the average ON-potential (Ramlog), ON-potential (datalogger), and OFF-potential (Ramlog) resulting from the slow AC ( $300 \text{ A/m}^2$ ) superimposed DC scan.

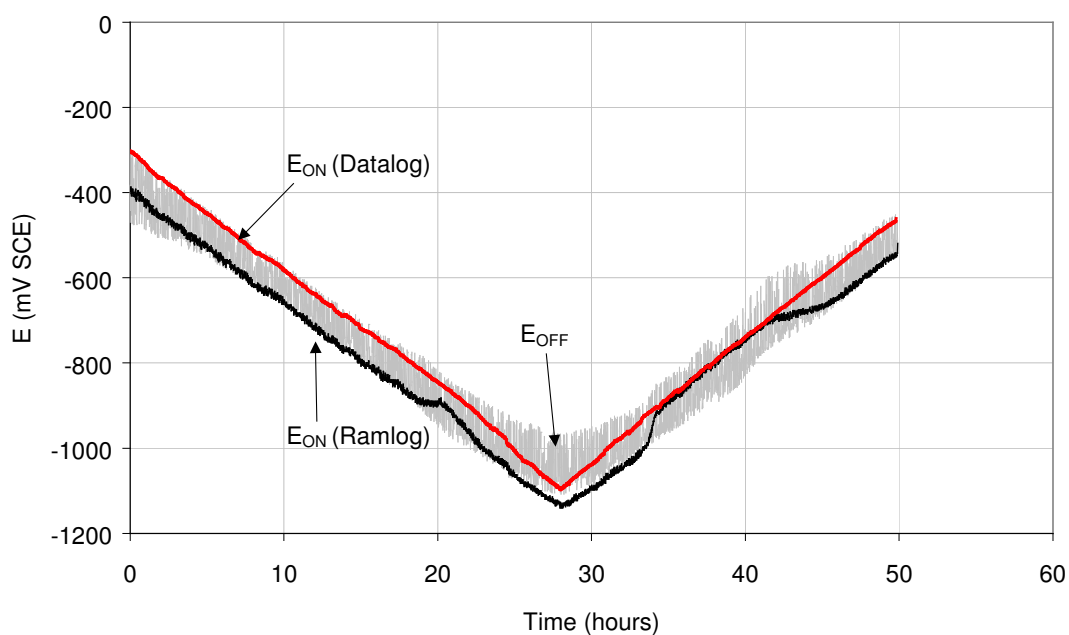


Figure 4. Average ON-potential (Ramlog), ON-potential (datalogger), and OFF-potential (Ramlog) resulting from the slow AC ( $300 \text{ A/m}^2$ ) superimposed DC scan.

Figure 5 compares the DC polarisation behaviour in the pure DC scan with the DC polarisation behaviour when superimposed by  $300 \text{ A/m}^2$  AC. As observed in numerous other cases,<sup>2,4</sup> the DC polarisation behaviour depolarises significantly when superimposed by the AC.

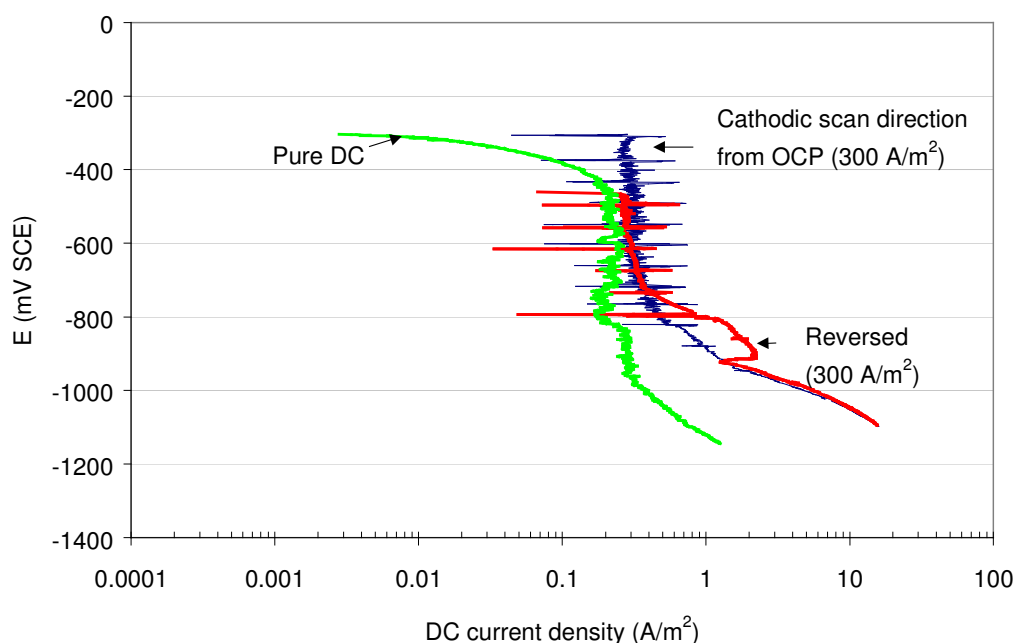


Figure 5. Comparison of the DC polarisation behaviour experienced in the pure DC scan compared with the AC ( $300 \text{ A/m}^2$ ) superimposed DC scan.

Figures 6 and 7 show the corrosion rate measured during the cathodic scan (figure 6) and the reversed scan (figure 7). In both cases, the corrosion rates have been presented versus the peaks in between which the OFF potentials oscillate. A very interesting observation here is the appearance of high corrosion rates in the region around  $-850 \text{ mV SCE}$ . At lower potentials, the corrosion rate decreases due to usual thermodynamical stability of the Fe. At higher potentials, the corrosion rate decreases due to formation and stabilisation of passive ferrous hydroxides or oxides. In the intermediate region, the potential oscillates between the immune region and the region favouring passivity, but apparently the passivation process under these circumstances becomes inhibited or destabilised as also suggested by Pourbaix et al.<sup>6</sup> The passive film is probably reduced at cathodic peaks and/or it fails to form during the anodic peaks (kinetic problem).

It is further observed that when coming from the passive region (i.e. when scanning in the cathodic direction), the maximum corrosion rate ( $0.2 \text{ mm/year}$ ) is lower than when coming from the cathodic direction ( $0.8 \text{ mm/year}$ ). The difference between these two situations is that when coming from the anodic region, a stable passive film is formed in advance, whereas this passive film is absent when coming from the cathodic region.

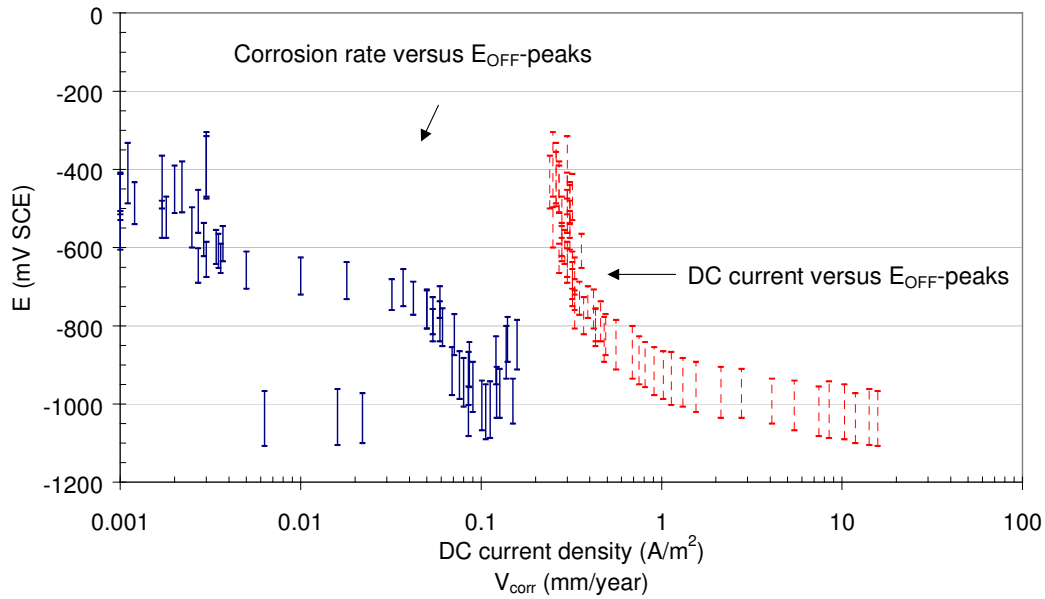


Figure 6. DC polarisation behaviour and measured corrosion rate during the cathodic scan ( $300 \text{ A/m}^2$  AC superimposed).

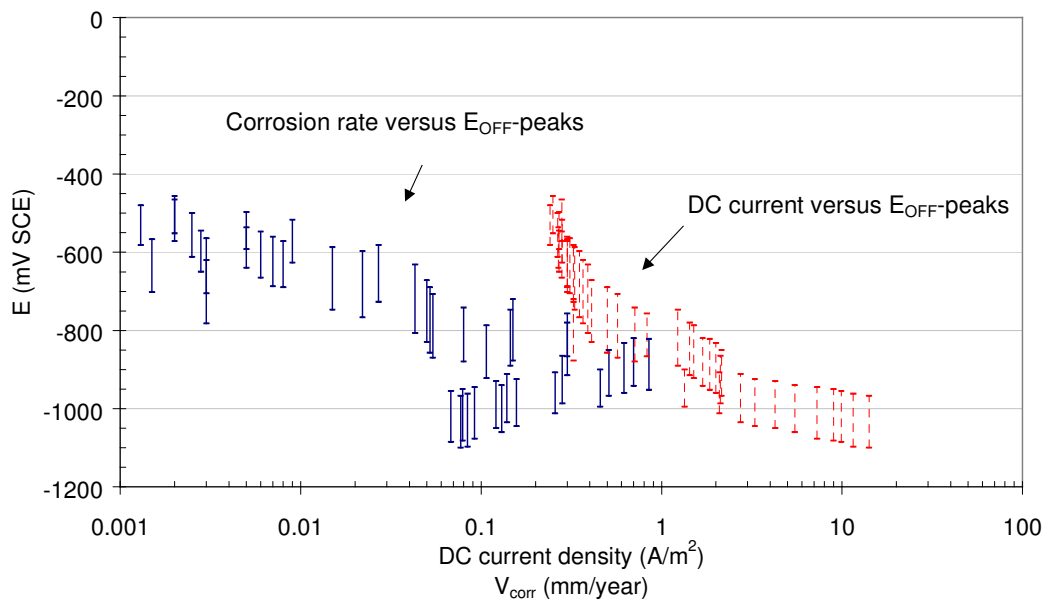


Figure 7. DC polarisation behaviour and measured corrosion rate during the reversed scan ( $300 \text{ A/m}^2$  AC superimposed).

In order to test whether the high corrosion rate (or corrosion as such) can be maintained for extended period of time during fixed conditions, two experiments were conducted in which the DC potential was fixed at  $-850 \text{ mV SCE}$ . In the first of these experiments, this offset condition was superimposed by  $300 \text{ A/m}^2$  AC. In the second experiment, the AC current was increased to  $400 \text{ A/m}^2$ . Both experiments were run overnight for about 18 hours.



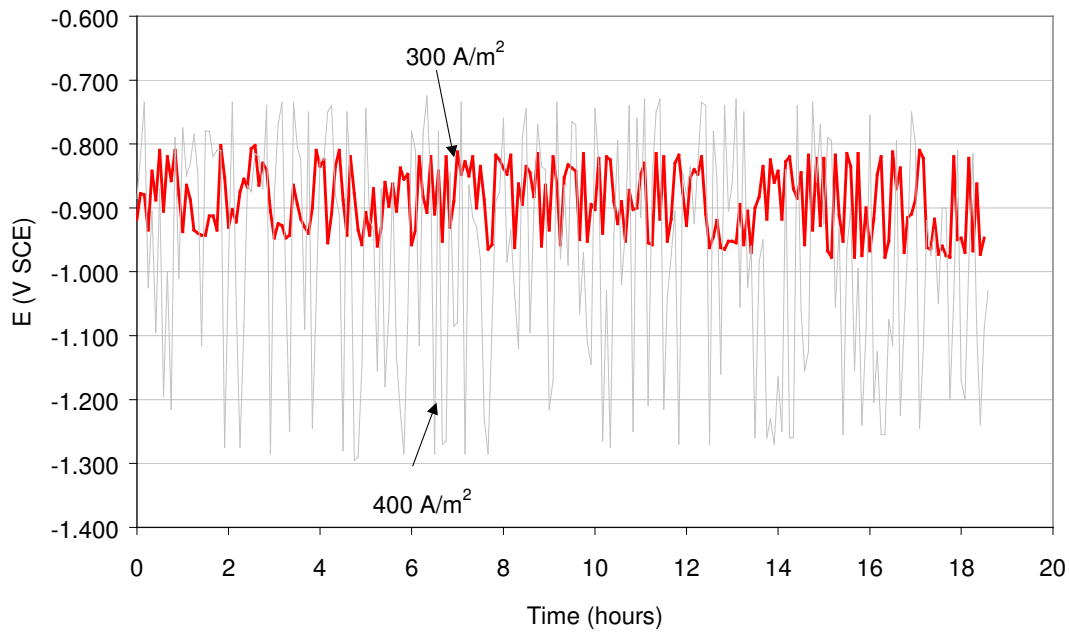


Figure 8. The OFF-potential oscillation at  $-850 \text{ mV (ON)}$  DC offset superimposed by  $300$  and  $400 \text{ A/m}^2$  AC.

Figure 8 shows the oscillation of the OFF potentials measured throughout time in the two experiments, and figure 9 shows the fitted corrosion rate in the two cases.

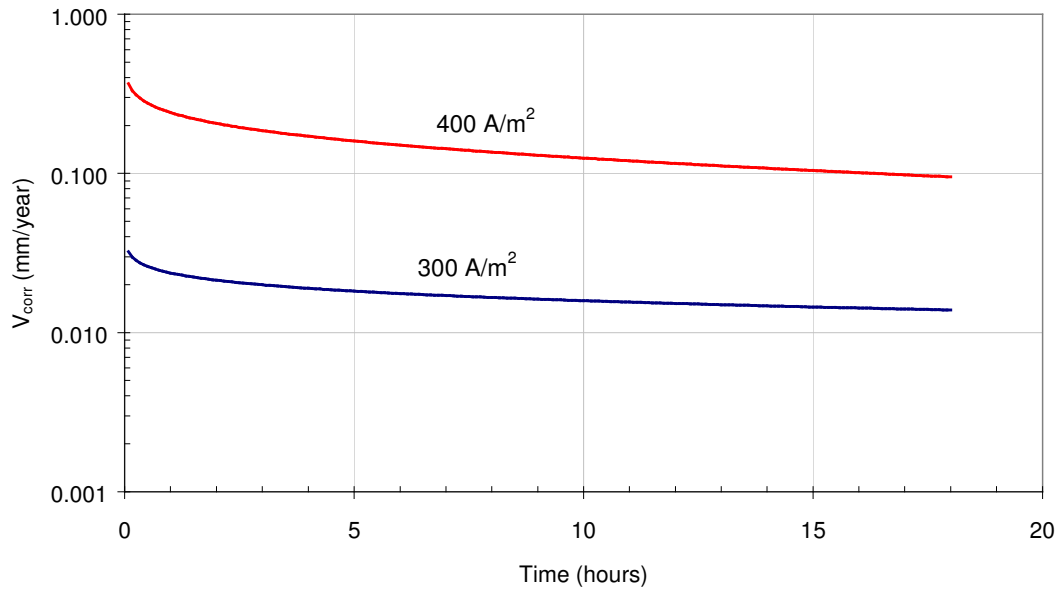


Figure 9. Corrosion rate profiles in the fixed experiments ( $-850 \text{ mV SCE} + 300/400 \text{ A/m}^2$  AC current).

As observed from figure 8, there seems to be quite a difference in the obtained peak potentials (outlined in table 2), and from figure 9 is observed that this large difference

in peak potentials gives almost a decade in difference in corrosion rate. In both cases, the initial corrosion rate is quite larger than the corrosion rate after 18 hours (values shown in table 2). Although a constant steady state corrosion rate was not achieved during the experimental periods, it seems that the curves show an asymptotic behaviour. However, further experiments involving longer time of exposure under the fixed AC/DC conditions is recommended. Also, it is recommended that this electrolyte system is investigated more closely as a whole. The quite dramatic broadening of the region in which the OFF potential oscillates when changing the AC load from 300 to 400  $\text{A/m}^2$  should be investigated further by establishing a range of different AC loads. The DC offset potential is naturally playing a key role as well in determining the potential oscillation.

No.	$E_{\text{ON}}$ mV SCE	$E_{\text{OFF}} (\text{max})$ mV SCE	$E_{\text{OFF}} (\text{min})$ mV SCE	$I_{\text{AC}}$ $\text{A/m}^2$	$V_{\text{corr}}$ mm/year
1	-300	-300	-475	300	0
2	-850	-800	-950	300	0.040 / 0.014
3	-850	-725	-1300	400	0.400 / 0.095
4*	-700	-470	-1150	686	2.080

\*: Data from Pourbaix et al.

*Table 2. Corrosion rate observations under fixed AC/DC conditions. Corrosion rate given in number 2 and 3 reflects initial and final value. Number 4 is data given by Pourbaix et al.<sup>6</sup>*

In table 2 is included data from Pourbaix et al<sup>6</sup> who investigated the exact same system, however at different AC/DC load ( $E_{\text{DC}} = -700$  mV,  $I_{\text{AC}} = 686$   $\text{A/m}^2$ ). They found a very high corrosion rate under these circumstances. The tendency from the table seems quite clear. The simultaneous condition of a cathodic peak potential favouring reduction of the passive film and an anodic peak potential ranging far into the otherwise passive region prohibits the formation of the passive film and the steel corrodes. The peak potentials outlined in table 2 are inserted into the Pourbaix diagram (figure 10) for illustration.

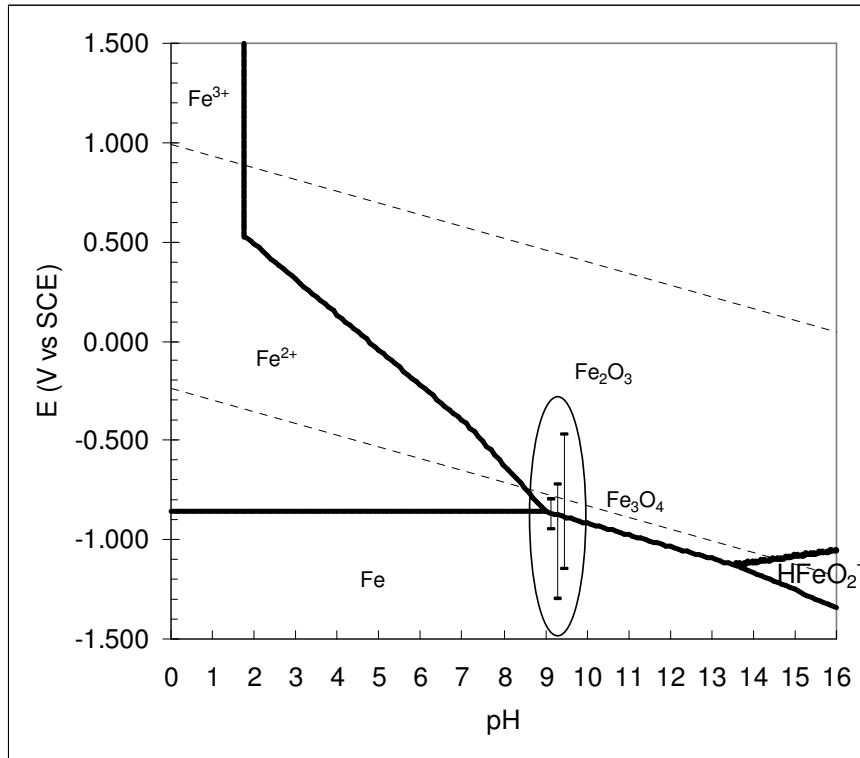
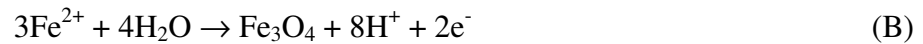


Figure 10. Pourbaix diagram showing the OFF-potential oscillation produced in the fixed AC/DC experiments as well as the potential oscillation reported by Pourbaix et al.<sup>6</sup>

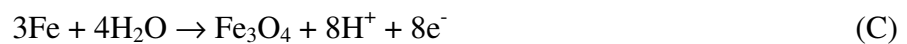
To summarise the reaction scheme, the borderline between immunity and passivity due to magnetite formation may - as a suggestion - be represented by:



followed by



In case reaction (B) is slower than reaction (A), the net result would be iron dissolution – corrosion. In other words, the total reaction:



is depressed at step (B) because magnetite formation is not achieved within a cycle of 50 Hz AC. Similar thoughts are also build into the paper of Pourbaix et al.<sup>6</sup>

## Conclusions

- The AC corrosion behaviour of steel has been investigated in a non-scaling bicarbonate-phosphate system at pH 9.15. The investigation included corrosion rate measurements using the ER-technique during a DC polarisation scan as well as during a scan in which the DC was superimposed by  $300 \text{ A/m}^2$  AC. The DC scan was run from the passive OCP ( $-300 \text{ mV SCE}$ ) in the cathodic direction. The scan involving superimposed AC was run from  $-300 \text{ mV SCE}$  in the cathodic direction to  $-1100 \text{ mV}$ , then reversed. In addition to these scans, fixed conditions of DC ( $-850 \text{ mV SCE}$ ) superimposed by  $300 \text{ A/m}^2$  and  $400 \text{ A/m}^2$  were maintained for prolonged periods (18 hours) during which the corrosion rate was measured. Further, the corrosion rate was measured during a period of 10 hours where the steel was kept close to its OCP ( $-300 \text{ mV SCE}$ ) and superimposed by  $300 \text{ A/m}^2$ .
- The DC scan showed a passive/immune condition for the steel and no corrosion was detected during this scan.
- The DC scan with superimposed AC showed a depolarisation in the DC behaviour.
- The corrosion rate measurements during the DC/AC scan revealed a peak in corrosion rate when the OFF potential oscillated around  $-850 \text{ mV SCE}$ . In the cathodic scan, a maximum corrosion rate of  $0.2 \text{ mm/year}$  was detected, and when the scan was reversed, a maximum corrosion rate of  $0.8 \text{ mm/year}$  was detected in the same potential region.
- The above observations confirm data presented by Pourbaix et al, showing that when the OFF-potential oscillates in a region defining passivity in the DC case at the anodic peak, and defining immunity in the DC case at the cathodic peak, then corrosion occurs due to a destabilisation of the passive film formation.
- It was confirmed by the fixed conditions that no corrosion occurs when the potential oscillation was kept within the passive region. It was confirmed as well that when fixing the conditions around  $-850 \text{ mV SCE}$  as the DC offset, then corrosion is maintained during prolonged exposure (however with a higher initial than “steady state” value).
- As a whole, it is confirmed that the passivity of steel can break down under AC load, and it is recommended that further investigations are carried out. These should involve longer time of exposure at fixed conditions, and investigations at higher and lower AC current densities than here applied. DC scans with a variety of superimposed AC current levels should be completed.

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