June 2004

Effects of 50 Hz AC on the DC Polarisation Behaviour of Steel Exposed in Artificial Soil Solutions

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Abstract

Two parallel experiments in slightly different electrolytes were conducted involving samples of steel acting as working electrodes in conventional electrochemical 3-electrode arrangements. By making a galvanostatic control of the DC- and AC current flowing to the electrodes and simultaneously measuring the electrode DC potentials, a picture of the effect of AC on the DC polarisation behaviour of the steel samples.

The experimental results indicate a quite strong effect of AC on the DC polarisation behaviour. In both environments, the anodic behaviour depolarises by approximately one decade of current, whereas the cathodic behaviour depolarises by approximately ½ decade of current. In other words, an increased activation of the electrode kinetics is observed. In one of the environments, a shift in the cathodic direction of the OCP (which in this case is rather the potential of zero DC current) is observed due to this.

The reason for this may be some rectifying effect of the AC, which can be generically described by describing the DC current at any OFF-potential employed throughout time during one cycle of AC by the traditional Butler-Volmer equation and making an integration of this equation with respect to time.

Introduction

It has been a general observation in practice that the current demand for cathodically protected pipelines increases when the pipeline is subjected to AC.[1]

This paper seeks to verify this experience by describing the results from very simple laboratory experiments where steel samples have been exposed in two different solutions. By controlling the level of DC- and AC current flowing to the samples, the effects of AC on the DC polarisation behaviour have been established by measuring the DC potentials in a range of DC- and AC current load.

Experimental

Two parallel experiments were conducted in identical electrochemical three-electrode arrangements in 2-liter glass vessels each equipped with a 1-cm^2 steel sample as working electrode, a large (500 cm^2) titanium-mesh as counter electrode, and a saturated calomel electrode (SCE, +0.242 V vs. SHE) as reference electrode.

One experiment was conducted in a solution with chemical composition according to table 1. This solution is denoted "scaling solution", since it has previously been used as a solution forming cathodic scaling when the steel working electrode was cathodically polarised for an extended period of time,[2] however, the present experiment extended over just a few hours, and no scaling was expected.

Component	Concentration (mg/L)	Concentration (mol/L)
$MgSO_4, 7H_2O$	617	$2.5 \cdot 10^{-3}$
$CaSO_4, 2H_2O$	430	$2.5 \cdot 10^{-3}$
$NaHCO_3$	210	$2.5 \cdot 10^{-3}$
$CaCl_2$	554	$5.0 \cdot 10^{-3}$

Table 1. Chemical composition of the scaling solution. Initial pH = 7.8, initial conductivity = 1900 μS/cm.

The other experiment was conducted in a solution with chemical composition according to table 2.

Component	Concentration (mg/L)	Concentration (mol/L)
Na_2SO_4	710	$5.0 \cdot 10^{-3}$
$NaHCO_3$	210	$2.5 \cdot 10^{-3}$
$NaCl$	585	$1.0 \cdot 10^{-2}$

Table 2. Chemical composition of the non-scaling artificial soil solution. pH = 8.2, conductivity = 2530 μS/cm.

This solution is identical to the scaling solution with respect to concentration of anions, however, earth-alkaline cat-ions (Mg, Ca) were replaced by Na instead. The solution is denoted "non-scaling solution", since it has previously been used as a solution that does not form scaling under cathodic charging.[2]

Both solutions were purged with nitrogen gas throughout the test period.

Charging of the working electrodes were made by means of a DC and an AC galvanostat both made by connecting the working- and reference electrode terminals via variable resistors (figure 1). The AC galvanostat was fed by AC-voltage from a transformer. The AC- and DC currents were separated (ensuring no leak of DC through the AC galvanostat) by inserting a large (20 mF) capacitor. The charging conditions were measured by Fluke multimeters M1 and M2 inserted as shown in the circuit for measurements of current and potential conditions respectively.
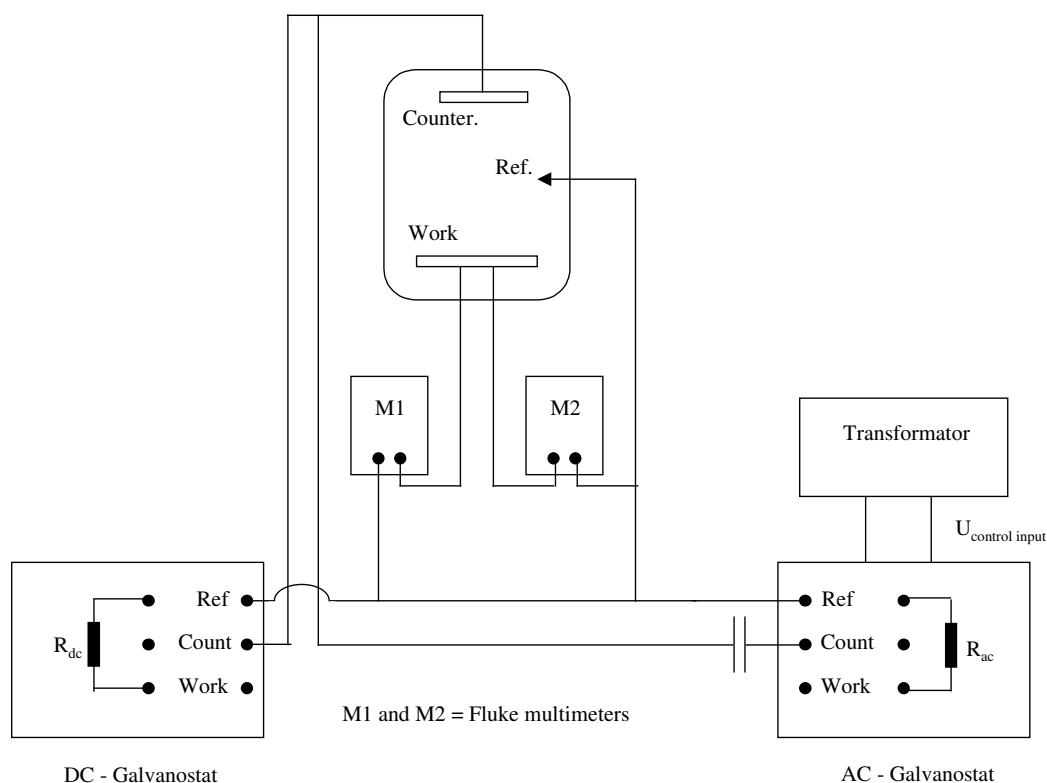

Figure 1. Electric diagram used for the galvanostatic AC- and DC-charging of the charging the membrane and for measuring the resulting hydrogen permeation current.

At onset of the tests, the working electrodes were allowed to rest at open circuit potential for one hour under nitrogen purging. After this, cathodic DC currents of 0.01 A/m^2 were imposed on the electrodes, and the DC potentials read by the multimeter M2. Then AC currents of density 10 A/m^2 were superimposed onto the DC currents, the cell allowed to stabilise for another 5 minutes and then the DC-potentials were read again. The tests continued in such manner, superimposing AC current of 30, 100,

and 300 A/m^2 onto the DC current. For each condition, the DC potentials were read after 5 minutes of stabilisation. In all, cathodic DC currents of 0.01, 0.03, 0.1, 0.3, 1.0, 3.0, and 10.0 A/m^2 were applied, all successively superimposed by AC currents of 0, 10, 30, and 100 A/m^2. Upon finishing the cathodic DC series, the analogue anodic conditions were brought about, thus in all creating a picture of the DC-polarisation behaviour of the electrodes when increasingly superimposed by AC.

Results and discussion

Figures 2 and 3 show the DC polarisation behaviour in the scaling- and the non-scaling environment respectively.

As observed, these experimental results indicate a quite strong effect of AC on the DC polarisation behaviour. In both environments, the anodic behaviour depolarises by approximately one decade of current, whereas the cathodic behaviour depolarises by approximately ½ decade of current. In the non-scaling environment, a shift in the cathodic direction of the OCP (which in this case is rather the potential of zero DC current) is observed.
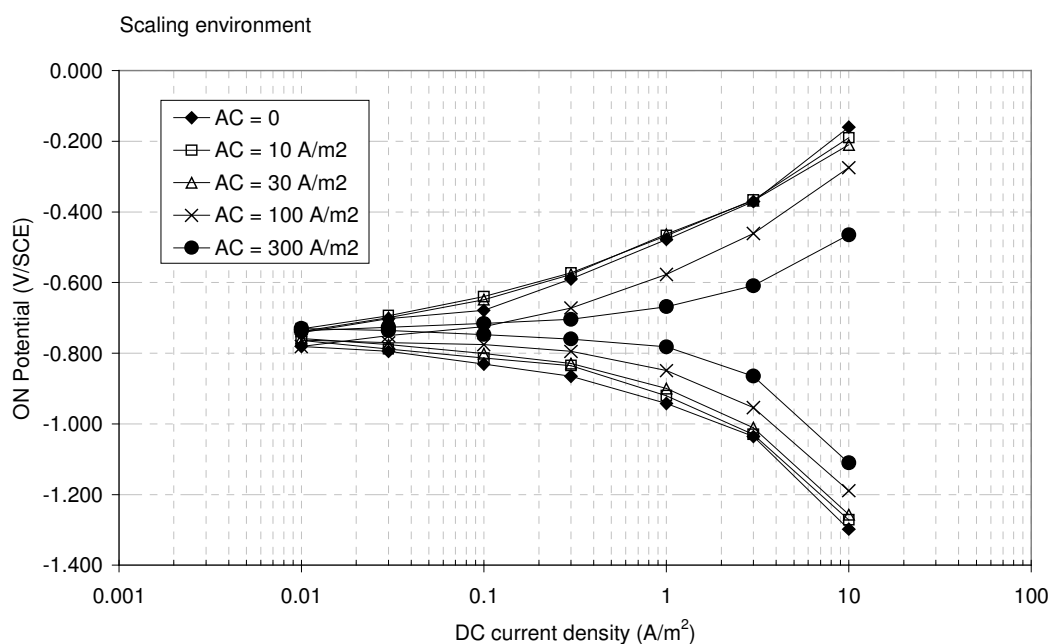

Figure 2. DC polarisation behaviour of the electrode exposed in the scaling environment – effect of AC current.
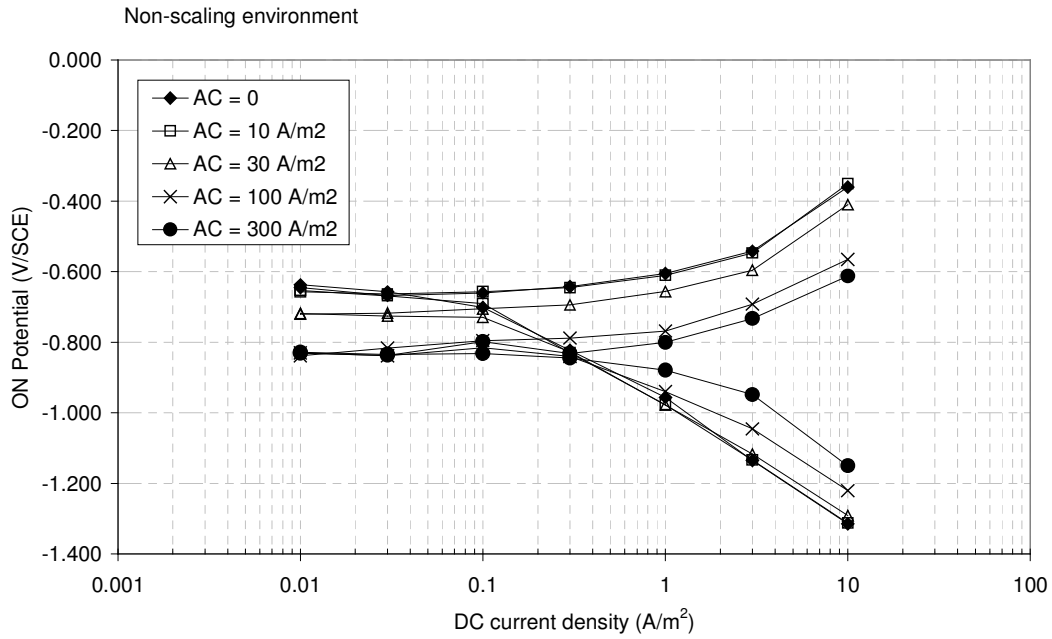
Figure 3. DC polarisation behaviour of the electrode exposed in the non-scaling environment – effect of AC current.

DC potentials have not been corrected from IR- drops. Making such correction should be done according to the equation:

$$E_{OFF} = E_{ON} - i_{DC} \cdot R_S \qquad (1)$$

Clearly, the amount of correction (i_{DC} x R_S) would be equal for each DC current load, and accordingly, the general impression that AC depolarises the electrodes cannot be affected by the IR-correction procedure. The amount of depolarisation might even increase beyond the above mentioned figures if the correction were made.

Different explanations may exist regarding the depolarisation behaviour. The amount of faradaic charge released during one cycle of 50 Hz AC (Q_{20ms}) can be described by integrating the faradaic current over the period of AC :

$$Q_{20ms} = \int_{0}^{20\,ms} i_{DC}(t) \cdot dt \qquad (2)$$

The DC current under AC load (i_{DC}) can then be obtained by dividing charge found through equation (2) by the duration of one cycle of AC:

$$i_{DC} = \frac{Q_{20ms}}{20ms} \qquad (3)$$

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Further, at any OFF-potential corresponding time t within the interval of one AC cycle, the infinitesimal DC current $i_{DC}(t)$ is logically described according to the usual Butler-Volmer equation:

$$i_{DC}(t) = i_0 \cdot \left[\exp\left(\frac{E_{OFF}(t) - E_0}{\beta_a} \right) - \exp\left(\frac{-(E_{OFF}(t) - E_0)}{\beta_c} \right) \right] \qquad (4)$$

Combining equations (2), (3), and (4) then gives the generalised relation describing the faradaic (DC) current flowing under AC load:

$$i_{DC} = \frac{1}{t} \int^t i_0 \cdot \left[\exp\left(\frac{E_{OFF}(t) - E_0}{\beta_a} \right) - \exp\left(\frac{-(E_{OFF}(t) - E_0)}{\beta_c} \right) \right] \cdot dt \qquad (5)$$

Clearly, there seems to be no reason why the DC current resulting from this equation would equal the DC current resulting from equation (4) valid under constant E_{OFF} conditions (DC–conditions that is). This is - of course - unless the time constants of the involved processes are too high to keep up with the 50 Hz AC (but this would cause no alternation of the DC OFF potential, and in this case equations (4) and (5) are identical.

One may argue that instead of depolarising the electrode, the AC could as well (on the basis described here) be expected to polarise (i.e. decreasing the activity of) the electrode, however, the experimental data shows otherwise, and are taken as a whole as a rectifying effect of the AC.

Besides the above effect, there may be some modification by the AC of the profiles of the concentrations of the active chemical substances nearby the electrode surfaces. In turn, this would affect the equilibrium potential (E_0) according to the Nernst equation and rise a demand for further correction of equation (3), but this is beyond the scope of this simple investigation.

Conclusions

- Two parallel experiments in slightly different electrolytes were conducted involving samples of steel acting as working electrodes in conventional electrochemical 3-electrode arrangements. By making a galvanostatic control of the DC- and AC current flowing to the electrodes and simultaneously measuring the electrode DC potentials, a picture of the effect of AC on the DC polarisation behaviour of the steel samples.

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References

1. P. Cohn (DONG Natural Gas A/S) – personal information.

2. L.V. Nielsen, Comparison of EIS and Ramlog Measurements of Spread Resistance and Polarisation Impedance for Steel Exposed in Scaling and Non-Scaling Solutions at 50 Hz AC, Paper 4, this report.