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The Effect of Superimposed Alternating Current on Hydrogen Absorption by Cathodically Polarised Steel Exposed in a Non-Scaling Artificial Soil Solution

Lars Vendelbo Nielsen
lvn@ipt.dtu.dk

Abstract

The effect of AC current superimposed onto a DC charging current on the hydrogen absorption of steel has been investigated in an artificial soil solution. The hydrogen absorption was detected by the Devanathan principle. The AC and DC current was applied using two galvanostats, one feeding DC current, the other feeding AC current to the membrane. DC currents in the range 0.2 to 10 A/m^2 each superimposed by AC currents in the range $0 - 300$ A/m^2 were applied. The hydrogen permeation at each DC current level was quite constant regardless of the AC charging conditions – in average about one tenth of the produced hydrogen was absorbed by the steel. However, the superimposed AC-current caused a depolarisation of the cathodic behaviour of the electrode in the sense that around a decade higher DC current was needed to maintain a certain DC potential when comparing the pure DC condition with the highest level of superimposed AC (300 A/m^2). Due to this depolarisation phenomenon, the hydrogen absorption at constant DC potential was increased by approximately a decade or more when comparing the pure DC condition with the highest level of superimposed AC.

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Introduction

The displacement in the cathodic direction of the potential of a cathodically protected pipeline may cause reduction of hydrogen ions or water molecules if the potential is more cathodic than the hydrogen equilibrium potential. The hydrogen evolution reaction mechanism may follow the Volmer-Tafel mechanism or the Volmer-Heyrovsky mechanism.[1]

In both mechanisms, the hydrogen ion is discharged at the steel surface by receipt of an electron, then adsorbed to the surface (according to the Volmer discharge reaction):

$$H^+ + e^- \rightarrow H_{ads} \tag{1}$$

According to the Volmer-Tafel reaction scheme, the adsorbed hydrogen atom then diffuses along the surface of the steel until another adsorbed hydrogen atom is met. The collision between two adsorbed hydrogen atoms leads to a production of a hydrogen molecule due to the Tafel recombination reaction:

$$H_{ads} + H_{ads} \rightarrow H_2 \tag{2}$$

Alternatively, according to the Volmer-Heyrovsky mechanism, a hydrogen ion is discharged directly at an adsorbed hydrogen atom thus producing a hydrogen molecule:

$$H^+ + H_{ads} + e^- \rightarrow H_2 \tag{3}$$

In competition with production of hydrogen molecule ((2) and (3)), the adsorbed hydrogen atoms rather easily absorbs into the steel microstructure:

$$H_{ads} \rightarrow H_{abs} \tag{4}$$

whereby the risk of any kind of hydrogen-related stress corrosion cracking arises.[2,3]

The hydrogen atoms adsorbed at the steel surface may result from either a direct discharge of the hydrogen ion (acid solution (1)) or by reduction of water (alkaline solution):

$$H_2O + e- \rightarrow H_{ads} + OH^- \tag{5}$$

Figure 1 represents in a schematic way the above reaction sequences.

The purpose of the present study was to provide experimental data showing the effect of AC on the hydrogen uptake by cathodically polarised steel, i.e. to give some verification of whether one should be concerned with AC in respect to increased hydrogen absorption and consequently increased risk of hydrogen-related stress corrosion cracking.
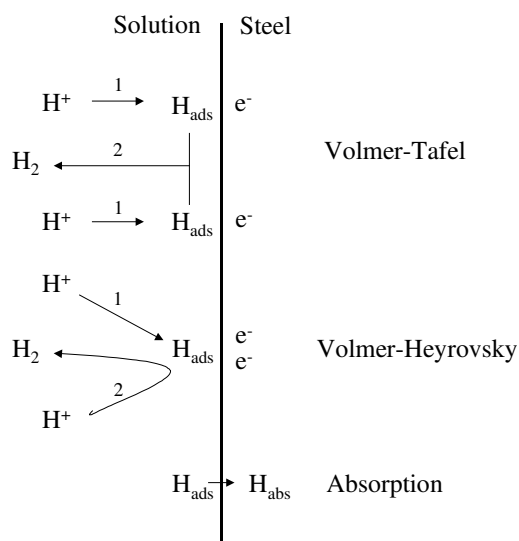
Figure 1. Schematic illustration of the hydrogen evolution reaction and the competing hydrogen absorption reaction.

Experimental

The amount of hydrogen absorption was detected by the well-known Devanathan principle.[4]

The principle is based on establishment of a well defined concentration gradient of absorbed hydrogen across a steel-membrane (thickness L) placed in between two electrochemical 3-electrode cells.

In one of the cells (charging cell) the membrane is cathodically charged giving rise to a certain level of hydrogen evolution and absorption (processes (1) – (5)). In the other electrochemical cell (sensor cell) a potential is established on the membrane, which favours oxidation of hydrogen. A hydrogen concentration gradient is established across the membrane, and consequently the absorbed hydrogen atoms diffuse across the membrane and are re-oxidised at the exit side in the sensor cell via processes opposite to those occurring at the entry side of the membrane in the charging cell (figure 2).

Provided that the exit side of the membrane is properly passivated, the current flowing in the sensor cell is a measure of the flux of hydrogen atoms according to the equation:

$$i_{ox} = F \cdot j_H \qquad (6)$$

where i_{ox} is the re-oxidation current, j_H is the flux of exiting hydrogen and F is Faraday's number.

The Effect of Superimposed Alternating Current on Hydrogen Absorption by Cathodically Polarised Steel Exposed in a Non-Scaling Artificial Soil Solution.

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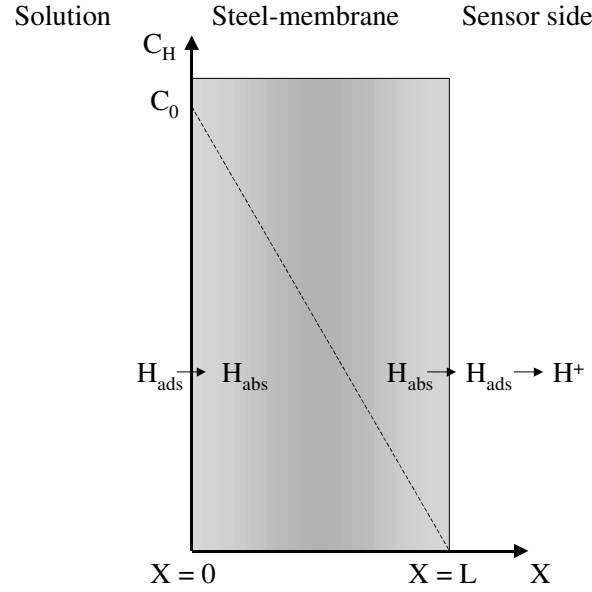Solution   Steel-membrane   Sensor side

Figure 2. Hydrogen diffusion through a steel membrane quantified by re-oxidation at sensor (exit) side of membrane.

In a steady state condition, Fick's first law of diffusion describes the hydrogen permeation flux:

$$j_H = -D \cdot \frac{dC_H}{dx} \qquad (7)$$

where dC_H/dx is the established hydrogen concentration gradient and D is the diffusion coefficient for hydrogen in the steel.

If the exiting hydrogen atoms are re-oxidised sufficiently fast at the exit side of the membrane, the concentration of absorbed hydrogen existing just beneath the exit surface approaches zero, and the re-oxidation current can be related to the concentration of absorbed hydrogen existing just beneath the entry surface C_0 by:

$$i_{ox} = F \cdot D \cdot \frac{C_0}{L} \qquad (8)$$

where L is the thickness of the membrane.

Until steady state is reached, a rising permeation transient is observed (figure 3), from which the diffusion coefficient can be calculated using characteristic time constants for break-through time of hydrogen (τ_B) and the time-lag (τ_{lag}) until 0.67 times steady state diffusion is reached. Recognising this, the oxidation current (or permeation current, i_p) measured in the sensor cell is a measure of the hydrogen concentration C_0

established in the steel membrane at a certain level of charging, thus a measure (ranking) of the risk of hydrogen-related cracking in steel.
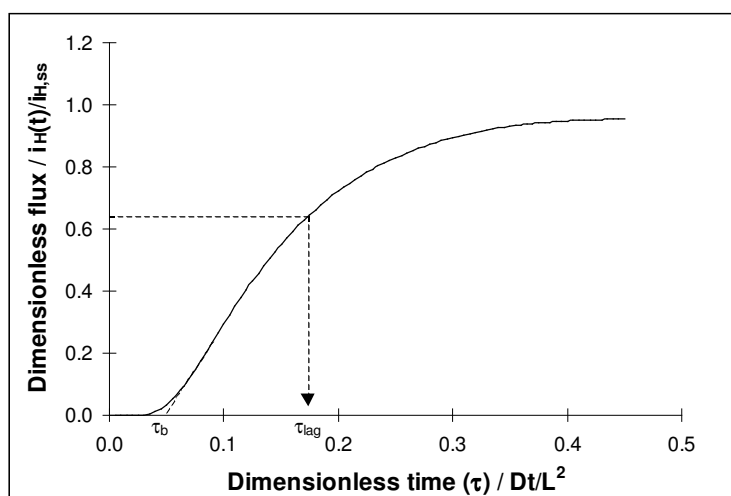

Figure 3. Rising hydrogen permeation transient (dimensionless parameters).

In the present study, a 100-µm thick steel membrane was placed in between the two cells. The active area of the membrane was adjusted by coating to be 1 cm^2. The exit side of the membrane facing the sensor cell was coated by palladium, which catalyses the oxidation of hydrogen, using a procedure described elsewhere.[2]

The sensor cell was filled with filled with 0.1 N NaOH-solution (pH = 13) purged with nitrogen, and the membrane was held at a potential of +200 mV SCE for 24 hours to ensure proper passivation of the membrane. The resulting background current reached after 24 hours was 50 – 100 nA.

The charging cell was then filled with artificial soil solution with chemical composition according to table 1. This solution is known not to develop cathodic scaling (i.e. a constant spread resistance is maintained) under cathodic charging.[5]

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 1. Chemical composition of the artificial soil solution used for the hydrogen permeation studies. Initial pH = 8.2, initial conductivity = 2530 µS/cm.

Charging of the membrane was made by means of a DC and an AC galvanostat both made by connecting the working- and reference electrode terminals via variable resistors (figure 4). 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 (20mF) capacitor in the counter electrode circuit. The

charging conditions were monitored by a Ramlog correal recorder that picked up average ON-potential, instant OFF-potential and instant current every 10 minutes. The permeation current density was sampled by a datalogger every 10 minutes from the potentiostat coupled to the sensor cell. Additionally, the quantities of relevance (AC- and DC charging currents, membrane potential and AC voltage) were followed frequently by a fluke type multimeter. The overall electric circuit is sketched in figure 4.
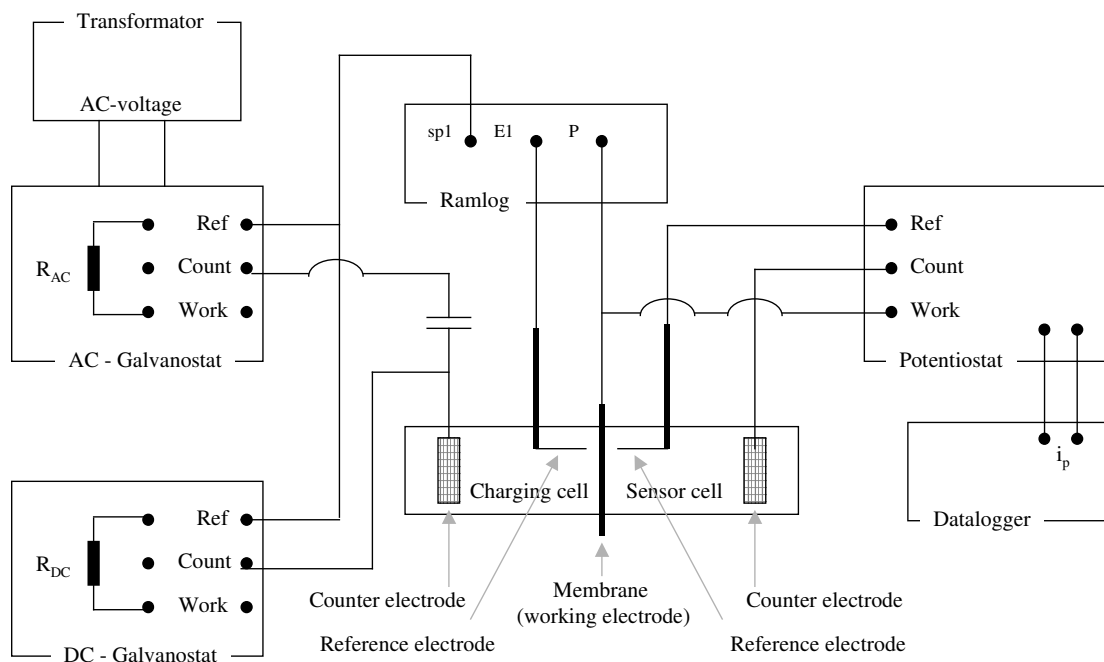

Figure 4. Electric diagram used for charging the membrane and for measuring the resulting hydrogen permeation current.

Initial permeation experiments showed that with the applied membrane thickness (100-µm), a steady state permeation current was reached after 4-5 hours, and on this basis, each individual charging condition was maintained for at least this amount of time. The experimental series comprised a DC-load of 0.20, 0.50, 1.00, 2. 00, 5.00, and 10.00 A/m^2 superimposed by 0, 10, 30, 100, and 300 A/m^2 AC current (RMS) – in all 30 different charging conditions.

Results and Discussion

The resulting steady state hydrogen permeation levels represented by the hydrogen permeation current densities are shown in table 2 as a function of the AC- and DC charging currents. The data are graphically presented in figure 5.

I_{DC} (A/m^2)	I_{AC} (A/m^2)				
	0	10	30	100	300
0.20	0.025	0.023	0.025	0.035	0.030
0.50	0.045	0.045	0.060	0.075	0.040
1.00	0.135	0.150	0.090	0.085	0.085
2.00	0.075	0.080	0.075	0.085	0.075
5.00	0.180	0.190	0.165	0.145	0.185
10.00	0.600	0.500	0.530	0.450	0.560

Table 2. Permeation current density (A/m^2) as a function of AC and DC current density.
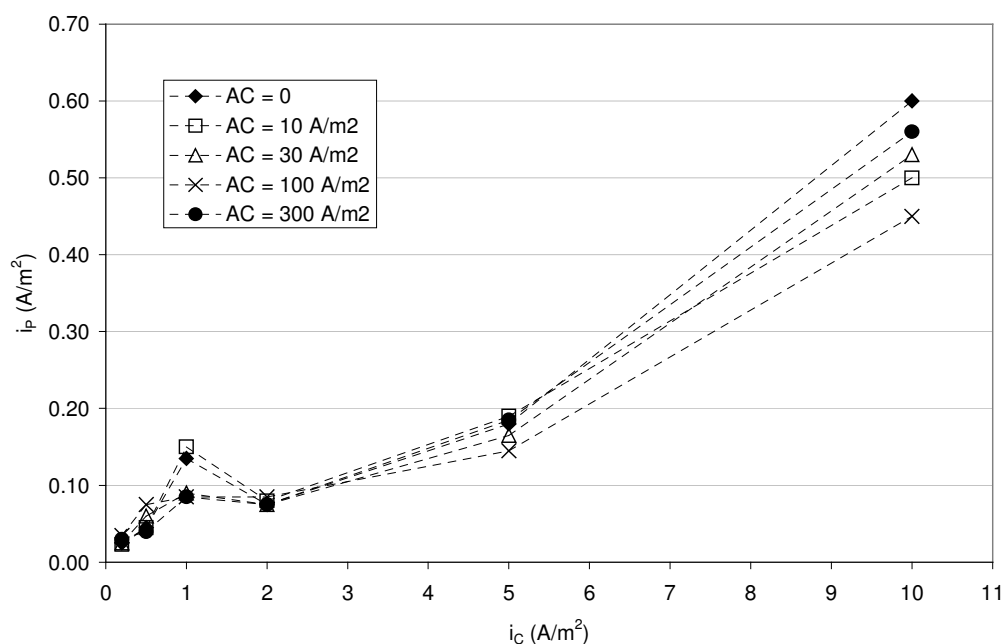

Figure 5. Graphical presentation of the hydrogen permeation current density as a function of the DC current density at the different superimposed AC-currents.

Taken as a whole, it is observed that the steel membrane absorbs hydrogen corresponding in the order of one tenth of the DC charging current density, and that the effect of AC on the hydrogen permeation seems quite modest. The variation of the hydrogen permeation at each DC level may reflect only the degree of reproducibility in such permeation experiments.

However, the permeation levels should be viewed not only as a function of the charging current conditions but also in view of the resulting DC potential established on the entry side of the membrane. Table 3 gives the established DC-potentials as a function of the charging current densities, and figure 6 is a graphical presentation of the data.

I_{DC} (A/m^2)	I_{AC} (A/m^2)				
	0	10	30	100	300
0.20	-0.890	-0.885	-0.850	-0.820	-0.790
0.50	-0.990	-0.945	-0.940	-0.920	-0.830
1.00	-1.110	-1.080	-1.065	-1.010	-0.850
2.00	-1.335	-1.120	-1.080	-1.005	-0.960
5.00	-1.194	-1.190	-1.155	-1.140	-1.040
10.00	-1.290	-1.230	-1.215	-1.190	-1.090

Table 3. DC-potential (V SCE) as a function of AC and DC current density.
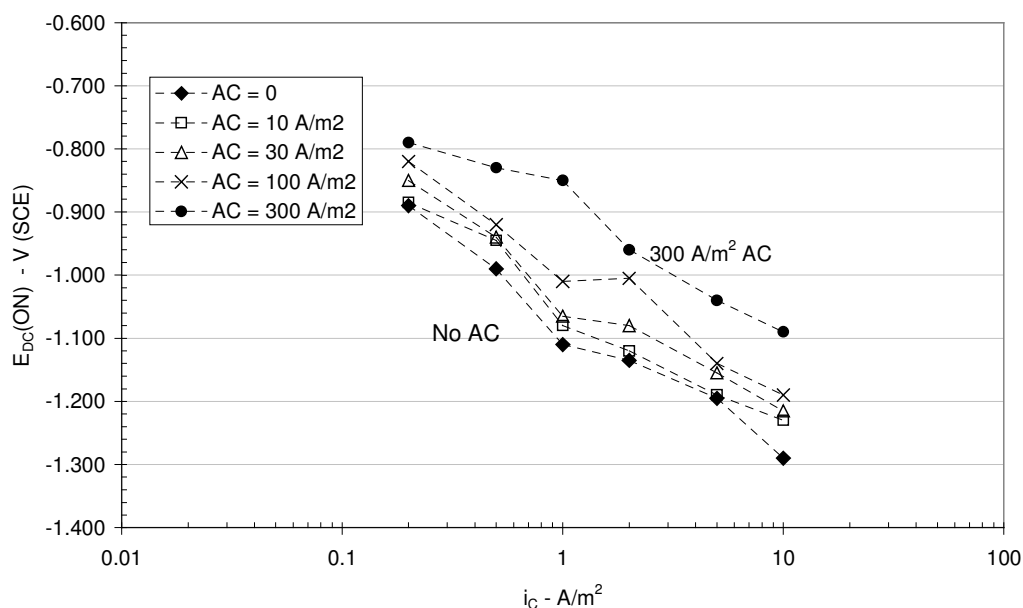

Figure 6. Graphical presentation of the cathodic polarisation behaviour of the membrane in terms of the steady state DC potential as a function of the steady state DC charging current density at the various levels of AC.

Figure 6 in particular demonstrates that the superimposed AC depolarises the cathode by up to one decade, i.e. the DC current level necessary for maintaining a certain DC potential increases by approximately a factor 10 when comparing the pure DC condition with the DC superimposed by 300 A/m^2 AC. This effect of the AC has been demonstrated previously[5] in the same solution as used here. Since the hydrogen absorption level was quite unaffected when described as a function of the DC current

level, it follows that when describing the hydrogen permeation level as a function of the cathode potential, a quite large effect (up to a factor 10 increase) of the AC is observed (figure 7).
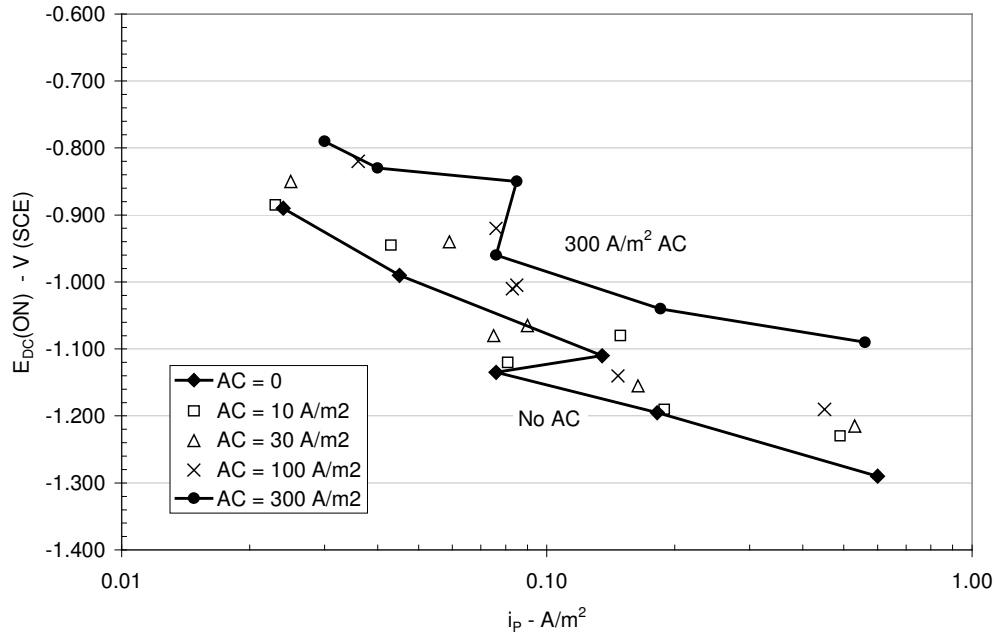

Figure 7. Hydrogen permeation in relation to the DC cathode potential.

Since criteria for proper cathodic protection of pipelines are typically based on the pipeline potential, a fair conclusion to the above would be that the hydrogen absorption at constant DC protection potential is in fact increased by superimposed AC. In figure 7, the DC potential is represented by the uncompensated ON-potential. In order to eliminate any doubts that the observed effects of AC on the hydrogen absorption can be attributed to any misinterpretation relating to the iR-drops, the cathode potential can be cleaned from iR-drops according to the relation:

$$E_{OFF} = E_{ON} - i \cdot R_S \tag{9}$$

where R_S is the spread resistance of the electrode. As justified elsewhere,[6] the spread resistance can be assessed from the Ramlog recordings using the equation:

$$R_S = \frac{U_{AC,ON,RMS} - U_{AC,OFF,RMS}}{i_{AC,RMS}} \tag{10}$$

where $U_{AC,ON,RMS}$ is the total AC voltage supplied to the membrane in order to establish the particular levels of AC current ($i_{AC,RMS}$), and $U_{AC,OFF,RMS}$ is the corresponding variation of the OFF-potentials established from the Ramlog recordings. Figure 8 shows the difference between "ON"- and "OFF" AC voltage as a function of the AC current density, the slope of which gives an average spread resistance of 0.0125 $\Omega.m^2$ in this electrode system.

The Effect of Superimposed Alternating Current on Hydrogen Absorption by Cathodically Polarised Steel Exposed in a Non-Scaling Artificial Soil Solution.
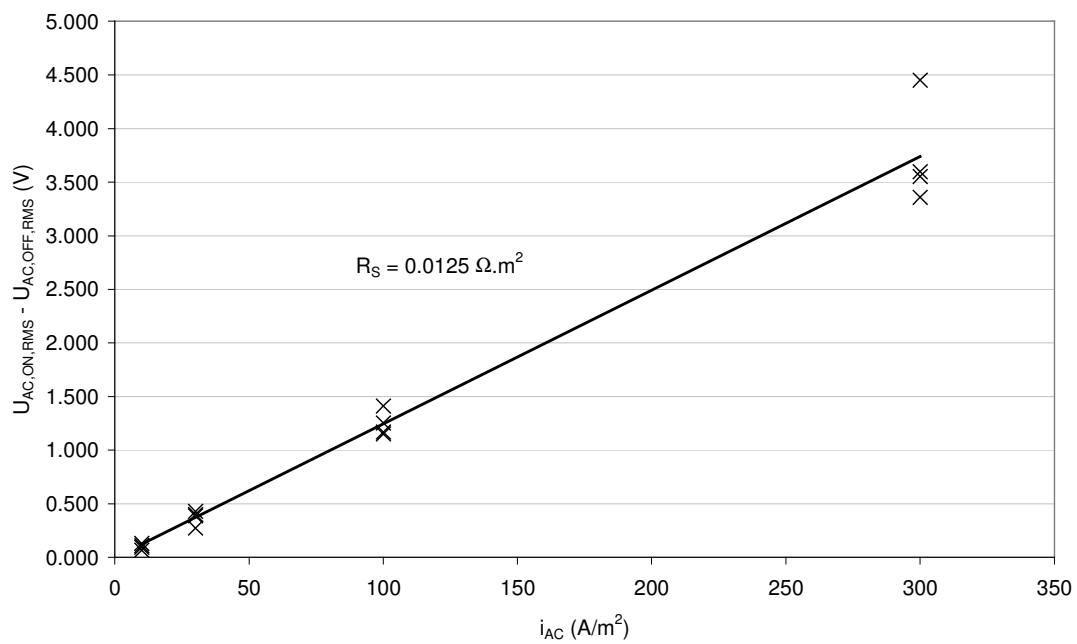
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Figure 8. Difference between "ON"- and "OFF" AC voltage as a function of the AC current density.

Using the individually calculated spread resistances, the DC "OFF" potential can be calculated according to equation (9), and iR-corrected versions of figures 6 and 7 can be derived, which has been shown in figures 9 and 10.
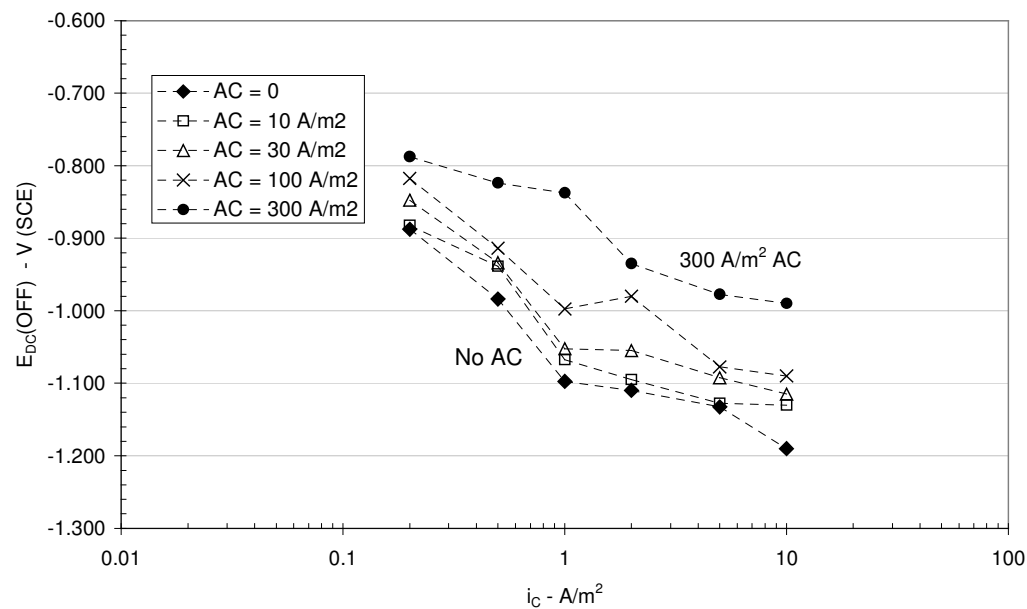

Figure 9. iR-corrected polarisation behaviour.

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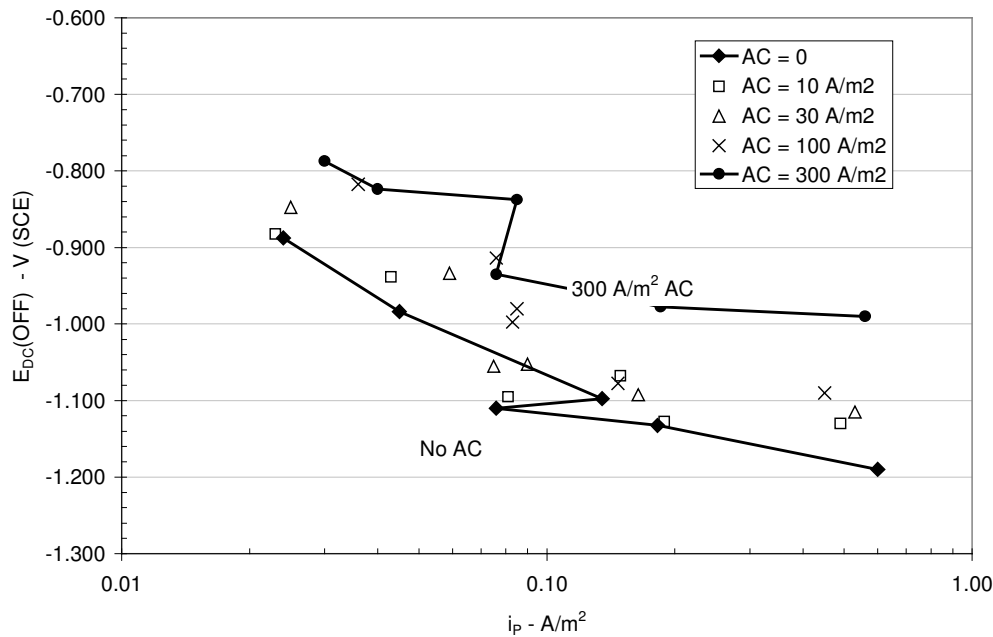
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Figure 10. Hydrogen permeation versus iR corrected DC potential.

As observed from these figures (9 and 10), the iR-correction does not interfere with the general conclusion that due to a depolarisation of the cathode behaviour of the electrode system caused by superimposed AC, the hydrogen absorption – being fairly constant at constant DC current levels – increases significantly at constant DC potential with increasing superimposed AC current. In the ranges of superimposed AC current applied in this study (0-300 A/m2), the increase is about a decade.

Conclusions

* The effect of AC current superimposed onto DC charging current on the hydrogen absorption of steel has been investigated in an artificial soil solution. The hydrogen absorption was detected by the Devanathan principle by which a steel membrane (in this case 100 mm thick) was charged on one side and the resulting hydrogen permeation detected by oxidation of the exiting hydrogen on the opposite side of the membrane. The AC and DC current was applied using two galvanostats, one feeding DC current, the other feeding AC current to the membrane. DC currents in the range 0.2 to 10 A/m^2 each superimposed by AC currents in the range 0 – 300 A/m^2 were applied.

* The hydrogen permeation at each DC current level was quite constant regardless of the AC charging conditions – in average about one tenth of the produced hydrogen was absorbed by the steel.

* The superimposed AC-current caused a depolarisation of the cathodic behaviour of the electrode in the sense that around a decade higher DC current was needed to

maintain a certain DC potential when comparing the pure DC condition with the highest level of superimposed AC (300 A/m^2).

- Due to this depolarisation phenomenon, the hydrogen absorption at constant DC potential was increased by approximately a decade or more when comparing the pure DC condition with the highest level of superimposed AC.

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