

Field and Laboratory Detection of AC Corrosion Using High-Sensitive ER-Technology

L. Vendelbo Nielsen

VNI – C/O Technical University of Denmark

Abstract

This paper states that high sensitivity ER sensors can be applied with great success and as a necessary tool in AC corrosion detection. The effect of the coating defect size (and geometry) is observed in both ohmic spread resistance and polarisation behaviour (diffusion and charge transfer kinetics). Spread resistance is entirely in control of the density of the AC current. In turn, for certain AC polarisation behaviour, AC current density conducts the peak values in off-potential and corrosion behaviour. The coating defect size accordingly becomes a very important parameter when designing coupons in general and ER sensors in particular.

Keywords

Cathodic protection, pipeline, AC induced corrosion, Monitoring, ER-probe

Introduction

Cathodic polarisation is usually applied on pipelines to provide cathodic protection (CP) against corrosion. Evaluation of the proper functioning of the CP system is usually based on potential measurements. In the specific case of CP of coating defects in buried pipelines influenced by induced AC current, the CP evaluation becomes complicated, and the usual potential criteria are no longer necessarily valid. Parameters like AC current density or anodic peak values of the true (IR-free) potential can be applied [1,2] but they provide no measure of the corrosion conditions.

Measurements relating to AC conditions are performed on coupons electrically connected to the pipe. In Denmark, the connection of high sensitivity electrical resistance (ER) sensors for evaluation of CP and corrosion rate measurements has become usual practise, particularly when studying risks of AC corrosion.

The principle of connecting coupons or sensors to the pipeline requires considerations on how these sensors should be designed in order to represent pipeline – or worst case – conditions.

The electrical equivalent diagram of pipeline with superimposed AC may be sketched as in figure 1. The electrochemical conditions as well as the CP rectifier produce electromotive forces. E_{01} and E_{02} denote equilibrium potentials relating to those electrochemical processes that are active at a coating defect (these e.g. may constitute ferrous corrosion and hydrogen production). $VB1$ and $VB2$ are components analogous to diodes and represent (Volmer-Butler) activation kinetics of involved processes. Warburg impedance component (W) is coupled to indicate influence of diffusion limitation. R_S denotes the ohmic resistance from pipe to remote earth (also known as spread resistance), and C denotes interfacial capacitance. The AC generator refers to AC on pipe due to induction from a paralleled high-voltage power line.

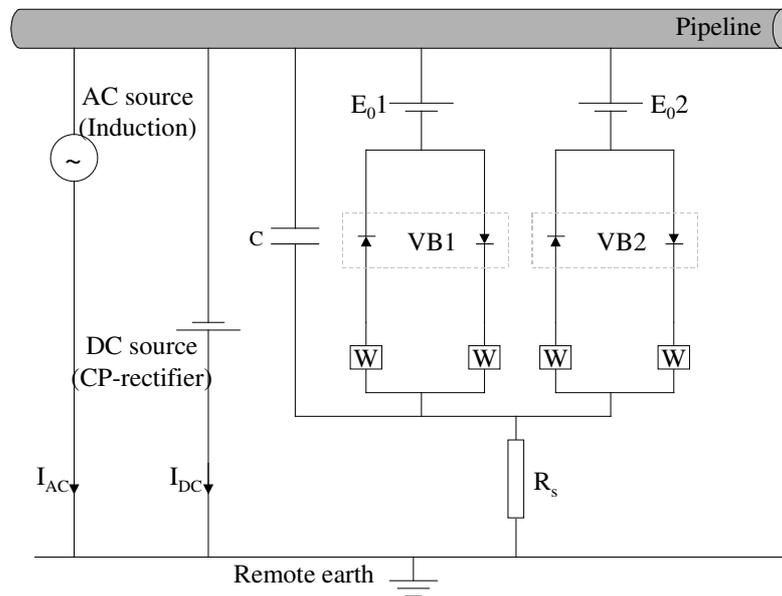


Fig. 1. Equivalent circuit diagram for pipeline CP-system with superimposed AC. [3]

This paper demonstrates simple correlations between

- coating defect size and magnitude of the ohmic spread resistance,
- ohmic spread resistance and the magnitude of the AC current density,
- AC current density and the oscillation in IR-free off-potential, E_{off} .

The importance of the above correlations is briefly discussed in relation to examples of AC influenced polarisation curves in which instant rate of corrosion was established using ER sensors.

Experimental

AC influenced polarisation curves were produced in a traditional 3-electrode electrochemical cell in which an high-sensitive electrical resistance (ER) sensor (3x30 mm, 25 μm thick sensing element) was used as working electrode, a platinum mesh used as counter electrode and calomel SCE as reference. The set-up is illustrated in figure 2. A Ramlog Correal recorder from a.b.i data was inserted in the working electrode circuit for measurement of true (IR-free) potentials (E_{off}).

The high-sensitive ER concept has been described in further detail elsewhere [4-6]. The circuitry (fig. 3) allows for measurement of resistance of exposed element C, reference element R, as well as differential resistance C-R. The differential resistance measurement in combination with asymmetrical excitation to give zero adjustment provides a high-resolution measurement $< 0.1 \mu\Omega$. Instant corrosion rate can be detected within minutes.

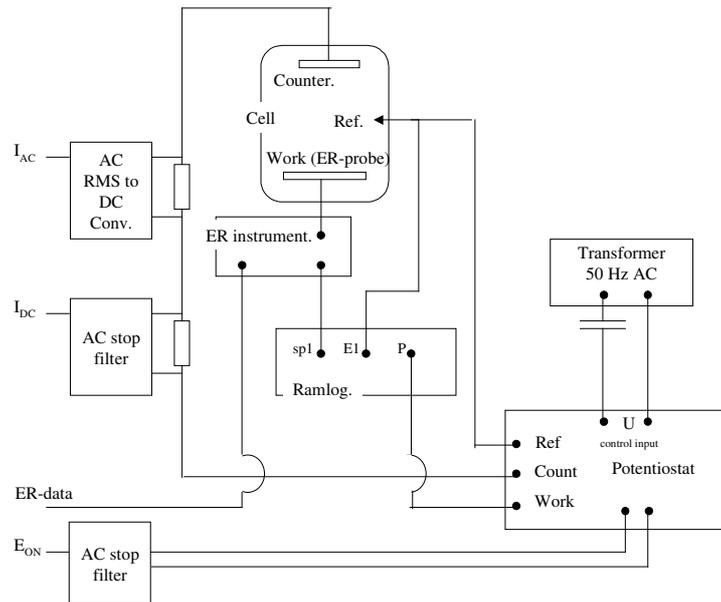


Fig. 2. Experimental set-up for laboratory AC corrosion studies.

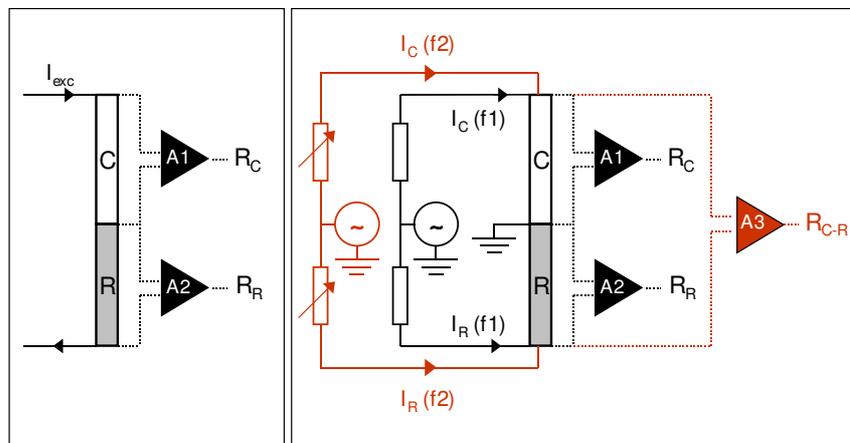


Fig. 3. Circuitry for high-sensitive ER concept (right) versus traditional concept (left).

Using this experimental set-up, the AC infected polarisation curves were established in aqueous solution of $0.1\text{M NaHCO}_3 + 0.1\text{M Na}_3\text{PO}_4$ (pH 9.15). AC voltage 0, 1, and 3V, with E_{ON} offset $-200, -400, -600, -800, -900, -1000, -1100, -1200$ and (in 3V AC case also) -1400 mV (SCE) were maintained in separate experiments for one hour. The corrosion rate (ER-data) and corresponding values of peak potentials (OFF condition) and DC current density were picked-up by datalogger/Ramlog (fig. 1).

The reported studies on effect of coating defect size on ohmic spread resistance and on correlation between ohmic spread resistance and AC current density were based on measurements performed in field. Among several test sites, two sites (test site 1 at which no AC corrosion occurs on ER-probes, and test site 2 at which severe AC-corrosion was detected on ER-probes) have been selected for direct comparison. Selected characteristics from the sites are shown in table 1.

Quantity	Site 1 (non-corrosive)	Site 2 (corrosive)
pH	7.4	4.7
Conductivity $\mu\text{S}/\text{cm}$	320	225
Alkalinity mmol/L	2	≈ 0
Acidity mmol/kg	16	164
CaCO ₃ %	9.3	0
Total C %	2.6	0.3
Ca mmol/kg	658	36
Mg mmol/kg	14	2
Na mmol/kg	1	3
K mmol/kg	2	1

Table 1. Test site description – selected quantities.

Alkalinity was determined by addition of 0.1M HCl to pH 3.5 in extract of distilled water after 1 week of equilibrating. Acidity was determined by adding different concentrations of NaOH solution into soil samples and determining pH in extract after equilibration. Acidity was defined as the amount of NaOH (mmol/kg) added to produce pH 10. The difference in acidity is remarkable, and - in particular - the lack of CaCO₃ and earth alkaline cations (Ca, Mg) at test site 2.

Four different probes were prepared for each site. First probe having rectangular coating defect (size 1x6 mm, area 0.06 cm²), second probe having circular coating defect (size Ø6mm, area 0.28 cm²), third probe having rectangular coating defect (size 6x12 mm, area 0.72 cm²), and the fourth probe having rectangular coating defect (size 6x60 mm, area 3.6 cm²). Ohmic spread resistance was measured against a large electrode placed in remote earth by a Saturn Geo earth tester. AC current density was measured as voltage across 10 Ω series resistor.

The effect of AC current density on off-potential oscillation is illustrated by results obtained in laboratory using soil from test site 2 enriched by distilled water. A set-up similar to the set-up illustrated in fig. 2 was employed. Fixed DC offset (-1000 mV SCE) was superimposed by 0, 1.5, 3.5 and 7.5 V AC. 5 working electrodes (ordinary coupons) with different coating defect areas and shapes (1x10mm rectangular, 3x30 mm rectangular, Ø2.5mm, Ø5.0mm, Ø10.0mm) were coupled in parallel.

Results

Figure 4 shows the AC influenced polarisation curves. Left graph is the usual polarisation curve (E vs. DC-current density) obtained with superimposed AC (0, 1 and 3V). Right graph is the corrosion rate plotted against off-potential oscillation (1 and 3V AC).

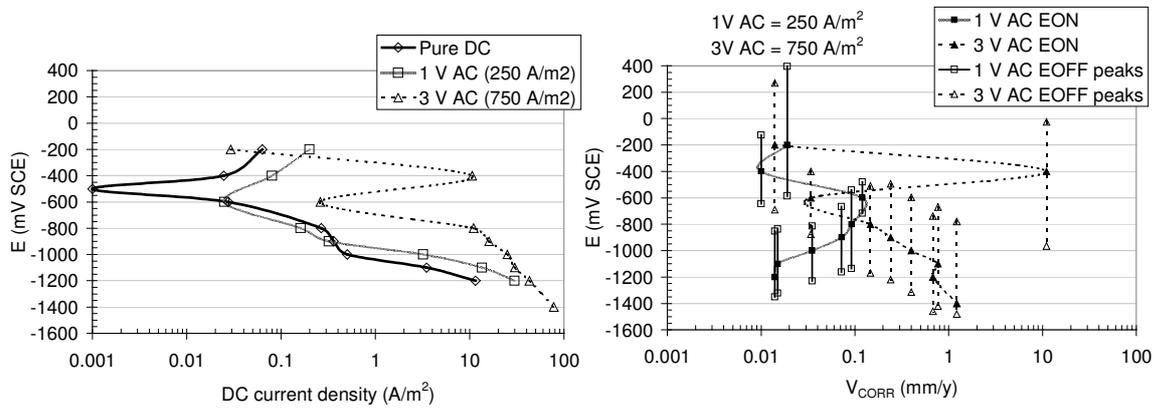


Fig. 4. Polarisation curves under influence of AC. Left is the usual E vs. DC current density, right is the corrosion rate against off-peak potentials.

Figure 5 shows the dependency of ohmic spread resistance on coating defect size (left), and the right graph shows correlation between measured ohmic spread resistance (y-axis) and AC voltage divided by AC current density (x-axis).

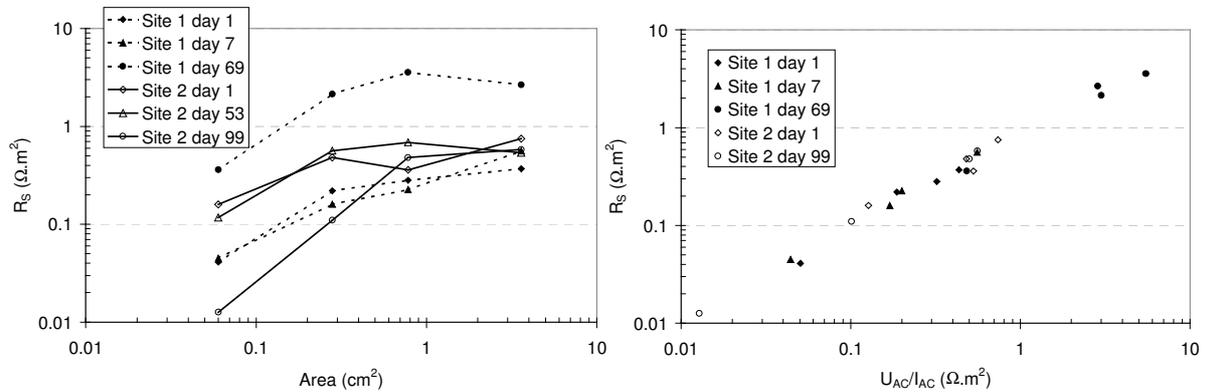


Fig. 5. Left: Dependency of ohmic spread resistance on coating defect size. Right: Correlation between measured ohmic spread resistance and AC voltage divided by AC current density.

Figure 6 shows the development in the effect of AC current density on off-potential oscillation throughout exposure time for coupon placed at site 1 (left), and ditto for coupons of different areas exposed in soil from site 2 (all measurements performed after some 90 days of exposure).

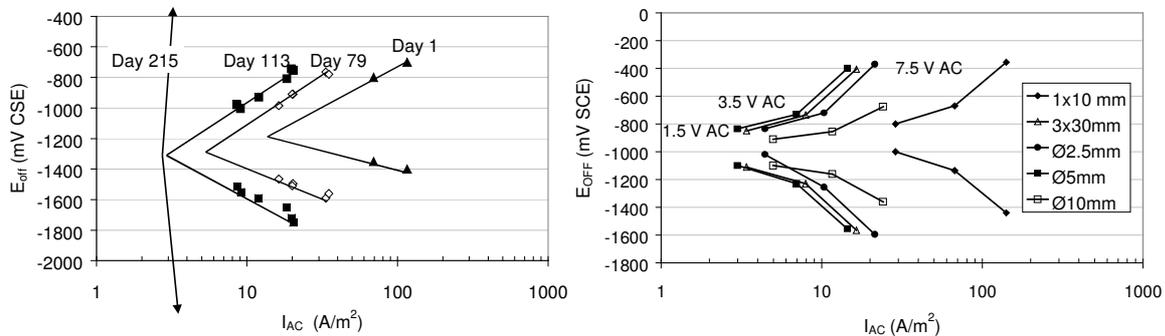


Fig. 6. Development in the effect of AC current density on off-potential oscillation throughout exposure time for coupon placed at site 1 (left), and ditto for coupons of different areas exposed in soil from site 2 (all measurements performed after some 90 days of exposure).

Discussion

From figure 4 is evident that superimposed AC not only causes a depolarisation of the electrochemical kinetics (left) but also may have tremendous effect on corrosion rate. The electrolyte investigated in figure 4 is usually passivating; i.e. no corrosion is detected by the ER sensor under pure DC conditions. Superimposing 3 V AC is observed to give a peak in corrosion when on-potential is controlled to -400 mV. In this condition, the off-potential is oscillating between 0 and -1000 mV SCE which obviously destabilises the passive film. In the cathodic region, superimposing 1V AC creates a maximum in corrosion rate around on-potential -600 to -800 mV, whereas 3V AC gives highest corrosion rate (in excess of 1 mm/y) in the most cathodic region -1400 mV, at which off-potential oscillates between -800 and -1450 mV SCE. For 1V AC, this off-potential oscillation gives corrosion rate about 2 decades lower. Recording only off-potential oscillation obviously gives no reliable measure of the corrosion conditions, but in combination with ER sensors, a complete AC interfered polarisation behaviour can be obtained.

Figure 5 (left) describes firstly the effect of coating defect area on ohmic spread resistance (increases with increasing area), and secondly that in the corrosive sediment, the spread resistance tends to decrease throughout time, whereas in the non-corrosive sediment, the spread resistance tends to decrease throughout time. The increase in the corrosive sediment (site 2, table 1) is believed to be due to ferrous ions released by corrosion contributing to increase the near-surface conductivity. In the non-corrosive site 1, precipitation of earth alkaline insoluble species (Ca(OH)_2 CaCO_3 etc.) decreases near-surface conductivity (in agreement with work by Stalder et al [1], and in agreement with soil characteristics in table 1).

Figure 5 (right) describes how spread resistance almost entirely controls the level of AC current density for a given AC voltage. In relation to the equivalent diagram in figure 1, this is obtained since the impedance of the short circuiting interfacial capacitor is close to zero at 50 Hz.

Figure 6 shows how the term *AC polarisation* behaviour can be defined. In a certain environment, at a certain time, at a certain coupon, a certain density of AC current causes an off-potential oscillation. Increasing this AC current density will increase the off-potential oscillation.

It seems that a correlation exists between peak values in off-potential and the density of AC current. In the non-corrosive sediment (left) this AC polarisation behaviour changes throughout time (as does the spread resistance), and eventually, only a very small current density causes a very large oscillation in off-potential. This situation may be interpreted as an AC passive condition and defined in the case where the kinetics of the electrochemical processes has become too slow to keep up with the AC frequency (in this case 50 Hz). In general, the geometry and size of the coating defect (figure 6 – right) also influence the AC polarisation behaviour very heavily.

Conclusions

In relation to the equivalent circuit in figure 1, the effect of the coating defect size (and geometry) is observed in both ohmic spread resistance and polarisation behaviour (diffusion and charge transfer kinetics and undoubtedly also in interfacial capacitance). Since spread resistance is entirely in control of the density of the AC current, and since AC current density for a certain AC polarisation behaviour conducts the peak values in off-potential, the coating defect size becomes a very important parameter when designing coupons in general and ER sensors in particular.

Acknowledgements

Studies on AC corrosion sponsored by DONG-Natural gas – field measurements performed in collaboration with P. Cohn (DONG), soil analysis performed by H. Breuning-Madsen (Institute of Geography, University of Copenhagen), ER-Technology designed by K. Vendelbo Nielsen and sponsored by VN-Instrument.

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