

Measurement and analysis of AC induced corrosion

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1. Some short history on AC corrosion

Dévy [1] clearly showed that, under AC influence, there may be a significant corrosion even under cathodic protection. For example with a CP current of 5 A/m² (or 0.5 mA/cm²) and 50 A/m² AC, corrosion is 0.5 mm/y (figure 1).

Such AC rms current densities are quite common. Field measurements often show AC current densities of 50-100 A/m² and more.

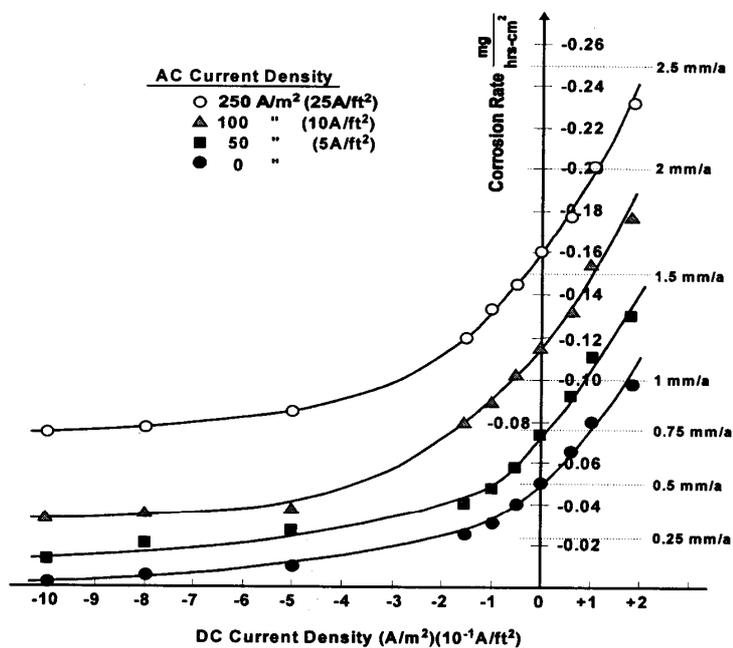


Figure 3-2 - Corrosion Rate of Iron vs. AC and DC Current Densities in 5% KCl Solution
(redrawn from Dévy et al, p.65)

Figure 1: Dévy 1967 work on AC induced corrosion (steel in 5% KCl) [1]

2. Current or potentials ?

The results of Dévy are reported in terms of current. Let us not repeat a famous mistake from the years 1940's: at that time, CP was more and more widely used and the big question was: "how much current do we need to protect our pipes ?". Everybody reported different values, depending on their experience in various types of soils. This big debate was at the origin of the creation of the famous NACE organisation in the USA. Until it became clear, in the late forties or in the fifties, that the occurrence or absence of corrosion was more a question of electrode potential than of current density.

3. Measuring potentials correctly

So, our approach has always been to measure and interpret electrode potentials. Of course, the potential must be measured correctly and we all know the importance of ohmic drop errors. The position of the reference electrode, the resistivity of the soil and the geometry of the coating defects have an influence on the importance of this ohmic drop error.

One example from the field : in a soil of 400.000 ohm.cm resistivity, a potential measured on the ground level of -4.3 VCuSO₄, corresponds to a potential measured with a reference electrode placed as close a possible from the pipe (with its coating) of -0.74 VCuSO₄ and to a potential measured with a switch-off method (which we consider as the true potential) of -0.54 VCuSO₄ [2]. This shows that correction of the ohmic drop error is essential if we wish to interpret the potentials correctly.

4. Probes and coupons

From a quick analysis of literature, we selected 1 ms as the time for measurement after switch-off. This delay could certainly be more rigorously adapted to the various types of soils. More data on this would be welcome.

To use a switch-off method, a separate probe or coupon is needed. Such a probe is represented in figure 2: the probe is designed to be cheap and is intended to be buried in the same soil as the pipe and to remain connected to the pipe at all time (except during the measurements). In this way, the calcareous deposits formed under CP will be present also on the probe. The reference electrode is removable and can be verified between measuring campaigns. The probes come with various exposed areas (for example 0.1 cm², 1 cm² and 10 cm²).

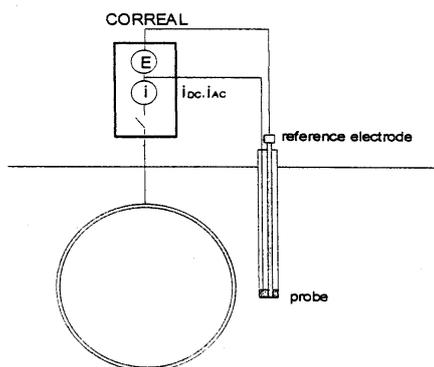


Figure 2: Probe for switch-off measurement of the electrode potential

The probes simulate correctly open defects, but it is clear that porosity defects, fine scratches or coating disbonding may require additional approaches.

The switch-off operations are performed by the instrument (Correal or a computer inserted in the connection of the probe). The whole system is designed to be used without any difficulty in the field.

5. True potentials : Correal

Since 1998 the Correal system is available to measure the true peak potentials under AC influence. "True" means with a correction for the ohmic drop error. "Peak" means the maximum and minimum true potentials along an AC period.

An example of recording from the field with the Correal equipment is shown in figure 3 : the maxima and minima of the curves are the maximum and minimum peak true potentials under AC.

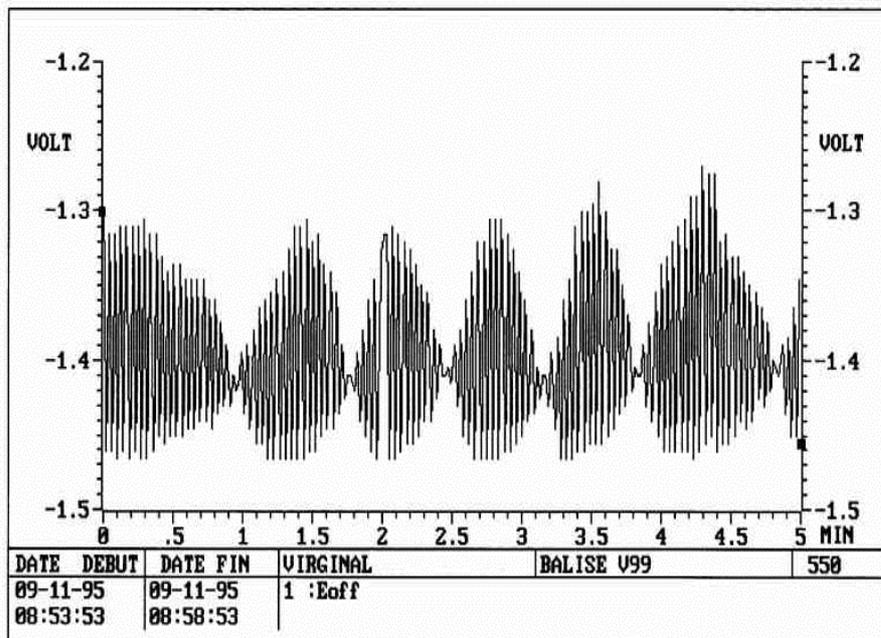


Figure 3: Example of Correal recording of true peak potentials under AC influence

6. True potentials and current density : Correac

In 2000, the system was completely revisited to allow to measure simultaneously the true potentials and the current density all along the AC period. The switch-off operation is repeated at slightly shifted instants of successive AC periods and the current density is measured just before these switch-offs. In this way, the result is an instantaneous true potential versus instantaneous current density curve. It is in fact a polarisation curve plotted along a 50 Hz period. It shows the various reactions taking place during a 50 Hz period.

Examples are shown in figure 4. Several well known reactions can be recognised:

- hydrogen evolution in the lower part of curve a,
- corrosion or oxide formation and reduction on curve b
- passivation by Fe₂O₃ on curve d

- oxygen evolution on curve e.

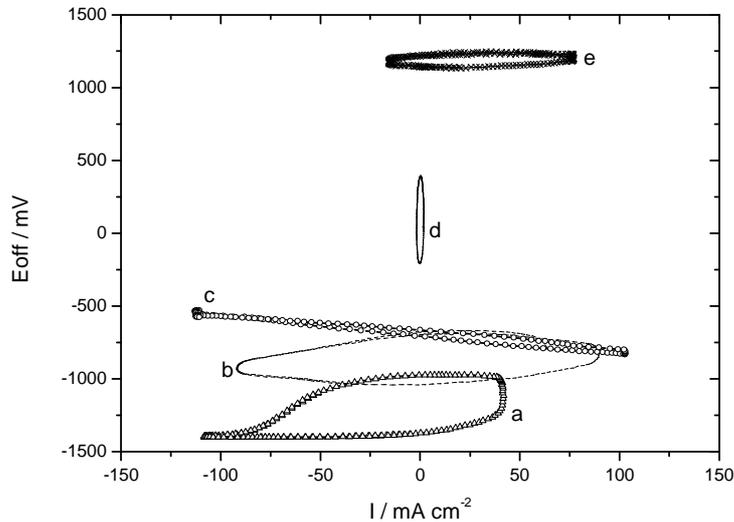


Figure 4: Lissajous E-i curves obtained in different potential ranges under 50 Hz AC on C-steel in NaHCO₃ 0.1 M + Na₂CO₃ 0.1 M solution at pH 10.

The comprehensive interpretation of these curves is not always that simple because capacitive currents can flow through oxide layers or through double layer capacitance, because some reactions or reaction intermediate steps are rapid and reversible. On the contrary, some other phenomena are slow (diffusion for example) and do not show well under a 50 Hz scan.

For these reasons, it would be hazardous at this time to convert current densities into corrosion rate. However, these curves help to identify the types of reactions resulting from AC influence.

7. Corrosion risk

A very large number of measurements were made, both in the field and in the laboratory, under real or controlled conditions. The measurements were coupled with a thin foil electrical resistance system to measure cumulated corrosion rates over short durations.

In this way, a correlation could be made between the conditions of the tests (pH, soil composition, maximum and minimum true peak potentials...) and the corrosion rate. Figure 5 summarises the major results. As expected, no corrosion appears when the potential oscillates always in the immunity domain (figure 5, test 1).

On the other hand, corrosion obviously appears when the potential alternates inside the corrosion domain, be it in acidic or alkaline media (tests 2 and 3, respectively), with also a much higher corrosion rate in the former.

There is also no corrosion when the potential oscillates within a same protective ferric oxide domain (test 4), whilst some corrosion is found when the potential oscillates inside the magnetite domain (test 5), which is probably associated to a less protective layer.

An important observation is that corrosion is also observed when the potential oscillates between immunity and passivation (test 6, corrosion 0.11 mm/y). It is interesting to note that, in the absence of AC, none of the immunity or the passivation domains are detrimental at pH 10. The onset of corrosion in the presence of AC perturbation in that case is probably related to the competition between the formation and the reduction of a passive film, with a poor protective property as a result. Similarly, there is some corrosion when different oxides tend to be formed during an AC period.

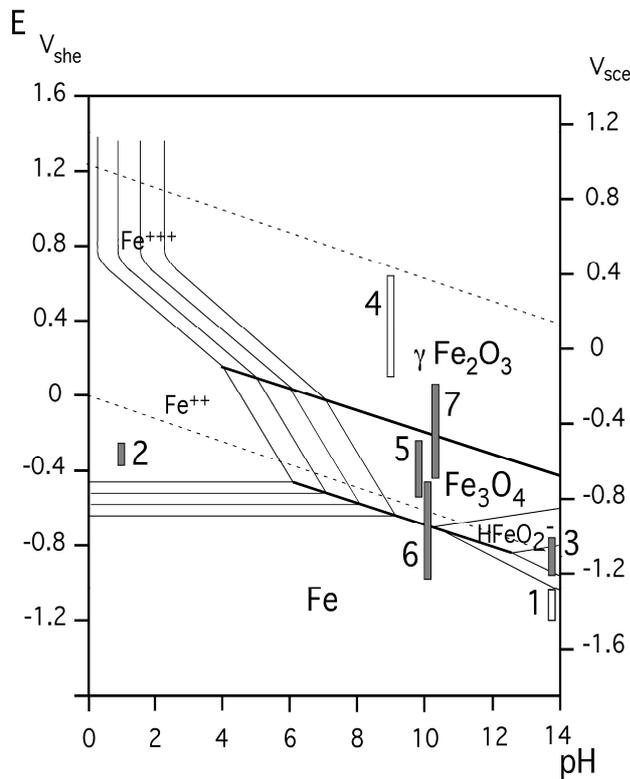


Figure 5 : pH and potential ranges of typical tests. Open bars : no corrosion (tests 1 and 4). Full bars : corrosion rates in mm/y (3.4 for test 2, 0.05 for test 3, 0.08 for test 5, 0.11 for test 6 and 0.06 for test 7).

8. Provisional recommendations

The occurrence or absence of corrosion depends more on the range of true potential covered during an AC period than on the value of the AC or DC current density. One typical and important feature of AC induced corrosion is that oscillation of the true potential between immunity and passivation may lead to some corrosion. This is an important observation because it is a common situation for structures under cathodic protection.

The safe conditions against AC induced corrosion are either such that the potential would at all times remain in the immunity domain, either that it would lead to the formation and keeping of a protective ferric oxide.

The risks of hydrogen embrittlement in the former case, and the uncertainties on the protective quality of oxide films in the latter make cathodic protection difficult for buried pipelines influenced by AC. AC mitigation, where needed, is probably a better strategy.

Another difficulty is that the critical potentials mentioned above (immunity, passivation...) depend on the pH at the metal/electrolyte interface. Until now, this pH is difficult to measure. The true potential at which hydrogen evolution shows a fast hydrogen evolution is an indirect indication of the pH at the interface. E-i curves plotted under AC influence may help to evaluate the pH and, therefore, the immunity potential in field conditions.

The AC or DC current value is not the determining factor for corrosion or no-corrosion. Instead, the range of electrode potential covered during the AC periods is more important. These potentials can easily be measured in the field in every specific situation and should be measured and reported. Rather than general guidelines based on the importance of AC and on the level of CP, direct field measurements will provide more safety.

References:

1. J.Dévay, T.Takacs, S.S.Abd El-Rehim. Electrolytic AC corrosion of iron. *Acta Chimica*, 52, 1967, 63-68
2. L. Van Hemelrijck, A.Pourbaix, J.Kissel, Ph.Carpentiers. la mesure du potentiel "vrai" en protection cathodique. *Rapports Techniques Cebelcor RT.295* (1988). See www.cebelcor.org.