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DETECTION OF AC CORROSION

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ABSTRACT

In the last years, Cebelcor and Distrigas have been actively engaged in the detection of AC corrosion. The result is a system that measures the true potential (with a switch-off method on a coupon) at many instants of the AC period. At the same time, the current density and the phase angle between the current and the electrode potential are measured. This system (CORREAC) provides useful informations about the instantaneous and local effects of induced AC currents. The details of the method, the equipment, the results of a field survey, the interpretation of the data, the identification of conditions for AC corrosion and some specific features of AC corrosion of passive metals are presented.

Keywords: AC corrosion, passivation, cathodic protection, monitoring, impedance, IR-free potential

RESUME

Ces dernières années, Cebelcor et Distrigaz se sont activement engagées dans la détection de la corrosion par les courants alternatifs et ont mis au point un système qui permet de mesurer le potentiel réel (grâce à une méthode de déconnexion de coupon) à de nombreux moments de la période de courants alternatifs. Parallèlement, la densité de courant et l'angle de phase entre le courant et le potentiel de l'électrode sont également mesurés. Ce système, appelé CORREAC, fournit des informations utiles quant aux impacts instantanés et locaux des courants alternatifs induits. Ce document présente les détails de la méthode, l'équipement, les résultats d'une étude sur le terrain, l'interprétation des données, l'identification des conditions donnant lieu à

la corrosion par les courants alternatifs et quelques caractéristiques spécifiques de la corrosion des métaux passifs par les courants alternatifs.

Mots clés : corrosion par courant alternatif, passivation, protection cathodique, monitoring, impédance, potentiel sans interférence extérieure

ZUSAMMENFASSUNG

Die letzten Jahre haben sich Cebelcor und Distrigas aktiv auf die Erfassung der Wechselstromkorrosion eingelassen. Beide Gesellschaften haben ein System zur Messung des Realpotentiales (über eine Ausschaltmethode auf einem Coupon) an zahlreichen Augenblicken der Wechselstromperiode entwickelt. Gleichzeitig werden die Stromdichte und der Phasenwinkel zwischen dem Strom und dem Elektrodenpotential gemessen. Das System wird CORREAC genannt und gibt nützliche Auskünfte über die sofortige und örtliche Wirkung der induzierten Wechselströme. In diesem Dokument wird folgendes dargelegt: die detaillierte Methode, die Apparatur, die Ergebnisse einer Feldstudie, die Datenauswertung, die Identifikation der Wechselstromkorrosionsbedingungen und einige spezifischen Eigenschaften der Wechselstromkorrosion von selbstpassivierenden Metallen.

Stichwörter : Wechselstromkorrosion, Passivierung, Kathodenschutz, Überwachung, Impedanz, IR-freies Potential

INTRODUCTION AND LITERATURE OUTLINE

AC induced corrosion has been a concern for about 50 years. It was a concern for structures (mostly pipelines) running parallel or close to overhead high voltage transmission lines (typically 15 kV and higher). The problem exists also in municipal areas, for example for structures near buried power distribution systems.
It is also a concern for concrete structures such as bridges with attached power cables and inside tunnels for electrified railway.

It is not uncommon to measure AC voltage in the range of 15 to 100 V_{rms} between a grounding rod and a coated pipeline exposed to AC induction. This may cause safety hazards and corrosion problems.

Early literature states that AC corrosion is only a small percentage of what it would be with a DC current density equivalent to the rms AC value. This percentage varies from the experimenters and is a function of the frequency, the nature of the metal, the soil resistivity, chemistry etc.
The percentages cited for steel vary between approximately 0.1 % and 2 to 5% [1-5].
Corrosion of Pb, Al, Cu and 50Sn50Sb can also be increased by AC in soils [2-4, 6].

An interesting observation was made for passive systems such as steel in concrete or stainless steel in sulfuric acid: AC currents produce a progressive shift of the zero-current potential.
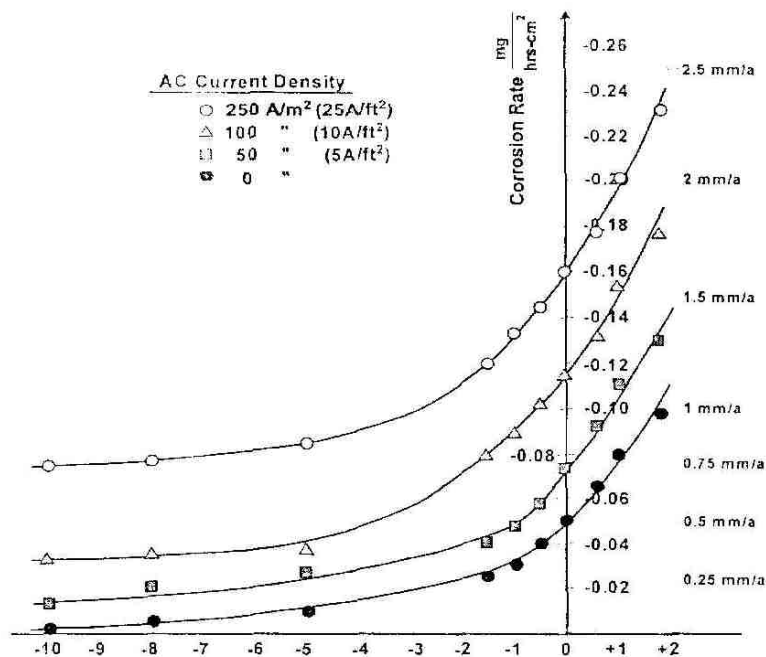
Fig. 1. Corrosion rates of iron as a function of AC and DC current densities in KCl 5%
[10,11]

The direction and the amplitude of the potential shift vary with the magnitude of the AC current density. Destruction of passivity by AC induced current was reported in several conditions [7,8].
These shifts of zero-current potentials were analysed as a function of the shape of the type of anodic and cathodic E-I curves, assuming that these curves do not change with time [1,9]. The potential shifts depend on the frequency, the slope of the Tafel lines (or the type of reaction : activation or diffusion control), the AC amplitude, the capacitance of the metal-electrolyte interface and the level of cathodic protection.

Already in 1967, evidences of the possible severe character of AC induced corrosion were given by Dévay et al [10] : they showed that in the presence of a same amount of AC, increasing superimposed cathodic DC currents indeed decrease the corrosion rate, but not to a negligible amount. Figure 1 shows the corrosion rate of iron in 5% KCl, under various 50 Hz AC and DC anodic and cathodic current densities. For example, an AC current density of 15 mA/cm² produces a corrosion rate of about 1 mm/y, even under a rather large cathodic DC current of 1 mA/cm² [10,11].

AC induced corrosion received a growing interest when a cathodically protected gas pipeline was perforated in Germany in 1986 [12] . The failure was attributed to AC. In 1987, a similar failure on a another gas pipeline in Switzerland was also attributed to AC [13]. Similar cases were reported in the US, Canada and France [14,16]. From the corrosion penetration and the lifetime of the pipelines, the penetration rate of AC corrosion was estimated in these cases at 0.8 to 1.4 mm/y [14-16].

A well documented report on experienced cases, mechanisms, laboratory results and mitigation was published in 1999 for the American Gas Association (PRC International) [11]. In 2000 CEOCOR finalised a booklet on « AC corrosion on cathodically protected pipelines. Guidelines for risk assessment and mitigation measures » [17], which will be published soon.

The criteria to decide the implementation of AC corrosion mitigation methods are diverse. First, for safety reason, it is generally considered that the AC voltage should be lower than 50 V_{rms}. But AC corrosion may occur well below that.
One criterion used in Germany suggests that there would be no AC corrosion when the rms AC current density is lower than 2 mA/cm² (20 A/m²) and that corrosion is highly suspected above 10 mA/cm². Between 2 and 10 mA/cm², corrosion may or may not occur depending on the nature of the soil [18].

If this is correct, the « safe » induced voltage (for a current density less than 2 mA/cm²) can be calculated by a simplified expression, as a function of the size of the coating defect (diameter d) and of the soil resisivity ρ [11]:
$V_{ac} = i_{ac}\rho\pi d / 8$ (units : V, A, ohm.m, m)
As an example, for a defect of 1 cm² (d = 1,12 cm) and a low resistivity soil (2000 ohm.cm), the « safe » AC voltage would be 1.75 V_{rms}. AC corrosion would be highly probable above 8.8 V_{rms}.

Another criterion was proposed more recently in France, on the basis of laboratory studies and field observations [19]: when the ratio "AC current density/DC current density" is above 10, AC induced corrosion is almost certain; above 3, the risk is serious; below 2, the risk is less, although not necessarily totally absent.

Criteria based solely on the AC current density probably have a limited significance. The criteria based on the ratio AC current density/DC current density considers a balance between the induction effects and the cathodic protection level, which is more reasonable. However, the criteria based on current density only are not fundamentally correct and could lead to wrong judgement. It is much more sound scientifically to base a no-corrosion criterion on both the current density and the electrode potential.

But the IR-free potential under AC conditions is difficult to measure. The ohmic drop error due to AC current can be much more important than the error due to DC cathodic protection currents. Until now, it was not possible to measure the IR-free electrode potential correctly, throughout the AC period.

This presentation deals with progress and experience gained recently in the measurement of the AC corrosion parameters.

A system to measure the IR-free potential at every moment of an AC period was developed in 1996, as an adaptation of the CORREAL system [20] and was modified in 1998 [21]. In 1999, a completely redesigned system, named CORREAC, was developed to measure altogether the IR-free potential, the current density and the phase angle throughout the AC period.

This system was used for two years in laboratory and field surveys, to study the conditions, the mechanisms and the conditions for AC corrosion and to identify where and when AC corrosion is taking place (depending on locations, parallelisms, power load, train traffic load …).

The final aim is to identify where mitigation techniques must be implemented and to verify their efficiency.

MEASUREMENT OF THE AC INDUCED CURRENT, THE ELECTRODE POTENTIAL AND THE PHASE ANGLE

The CORREAC system measures the IR-free potential, the current density and the phase angle throughout a period. It uses micro-controllers and advanced operational amplifiers for rapid measurements and data acquisition. The instrument is connected on one side to the pipeline, to a coupon and to a reference electrode, and on the other side to a portable computer. The results are computed and are represented on a screen as the sine curves for the IR-free potential versus time and the current density versus time, and as Lissajous figures in a E-I graph.

The instrument has a very high input impedance amplifier for the potential measurement and another precision amplifier for zero-resistance current measurement. There are rapid electronic switches for the switch-off process, range changes and data acquisition. The micro-controller controls the switch-off function, the data acquisition, the data storage and the communications with the PC.

The time between switch-off and measurement is adjustable. If the measurement is done to quickly after switch-off, the capacitance of the wiring interferes with the switch-off, and the « off » potential is not measured correctly. In resistive concrete, this time must be increased. The instrument is designed to work indifferently at 16.6, 50, 60 Hz etc.

The assembly coupon-reference electrode has a well defined geometry which is part of the system. The reference electrode is very close to the metal coupon because CP and stray currents flow around the coupon even during the switch-off periods. The metal coupon faces upward to avoid hydrogen accumulation on the simulated coating defect. The exposed surface of the coupon is small, because these are the most dangerous conditions for exiting AC currents. Coupons with different exposed surfaces are available, to reproduce the most likely coating defects.

MATERIALS AND METHODS

A series of situations with different AC induced effects was produced. The responses of the measuring system were examined. A correlation was made between corrosion or no-corrosion and the various DC+AC polarisation conditions. High pH were selected for many test conditions, because such high pH are detected as a result of cathodic protection.

Metal :

Coupons of carbon steel, mounted in epoxy resin and polished with 1200 SiC paper were used. The sizes were 0.1, 1 and 10 cm². Different geometries were tested : smooth surfaces facing upward or downward, or bare surface surrounded by a thick coating.

Solutions, soils :

Tests were conducted in various acid, neutral or alkaline solutions solutions and in different soils:
H_2SO_4 0.1M + 1000 mg/l Cl-
Na_2SO_4 0.01M
Na_2CO_3 0.1M
Na_3PO_4 0.01M + $NaHCO_3$ 0.1 M
Na_2CO_3 0.1M + $NaHCO_3$ 0.1M
NaOH, pH 13.75
Natural soils (sand and clay)

Polarisation :

Various AC polarisations between 10 and 100 mA/cm² were applied, with superimposed DC current between −70 and + 70 mA/cm². Several tests were conducted under conditions such that the true maximum peak potential would be either always in the immunity region, or at times in the immunity and at times in the passivation region, or always in the passivation region. Regulation of the DC and AC polarisation to achieve these conditions was made manually. Rather large current densities were applied to give results in a short time, because the control of the polarisation conditions is not easy. The tests lasted one hour or more. All potentials are expressed versus the saturated calomel reference electrode.

The outputs of the tests were the recordings of the IR-free potential and current throughout the period, the corrosion estimated from the aspect or from the electrical resistance of the coupon and the pH near the surface measured with pH paper.

RESULTS

E-i curves under AC polarisation

Figure 2 shows the E-i curve for an AC polarisation cycle on iron in an acid solution and at low potentials. The phase angle is almost zero, the impedance is low and the E-i curve is flat. Such a curve at low potentials is attributed to hydrogen evolution on a bare surface, with a very low transfer resistance and, hence, a very small phase angle.
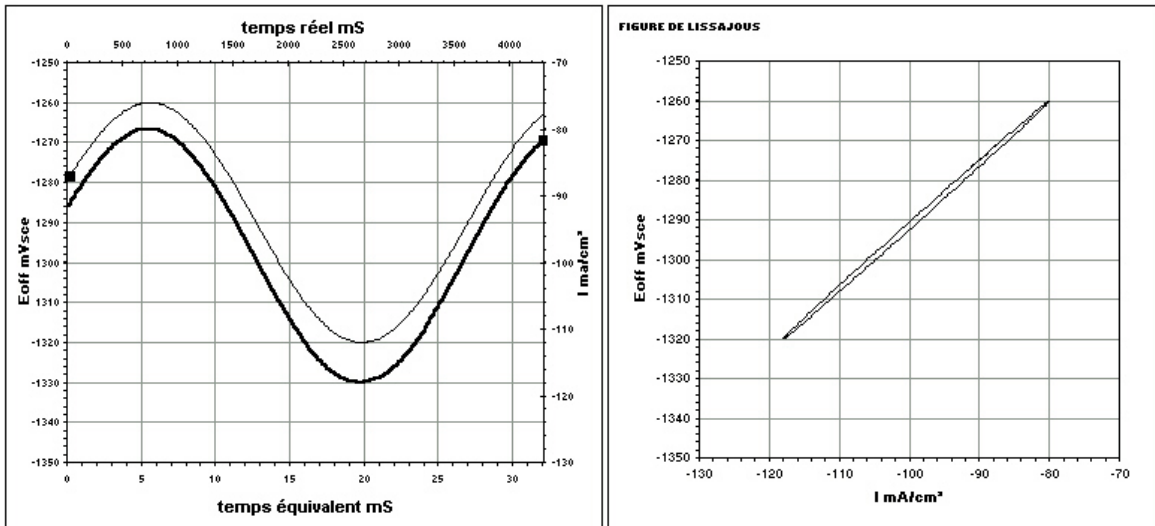
Fig. 2. E(t), i(t) and E-i curves for carbon steel in H2SO4 0.1M + 1000 ppm Cl- under 50 Hz, at low potentials (between –1320 and –1260 mV$_{sce}$)

<u>Figure 3</u> relates to the same acid solution, but at potentials well above the cathodic protection potential. The E-i curve has the shape of an ellipse. The impedance is shown by the slope of the large axis of the ellipse. The phase angle is shown by the ratio of the two axes.
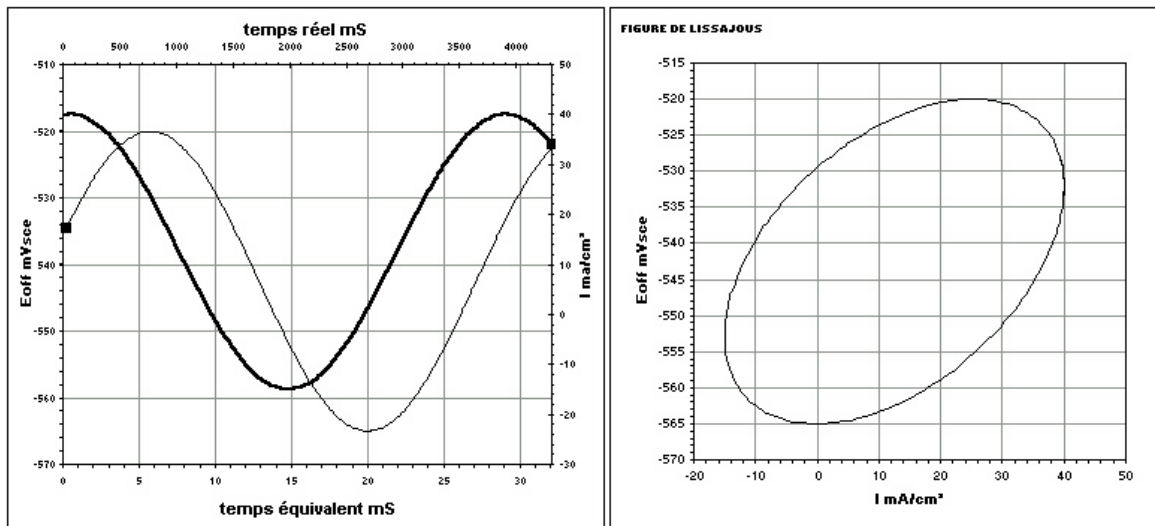

Fig. 3. E(t), i(t) and E-i curves for carbon steel in H2SO4 0.1M + 1000 ppm Cl- under 50 Hz, between –565 and –520 mV$_{sce}$)

Figure 4 is in the same solution at even higher potentials: the impedance is low again and the phase angle is very small. This is attributed to a rapid corrosion.
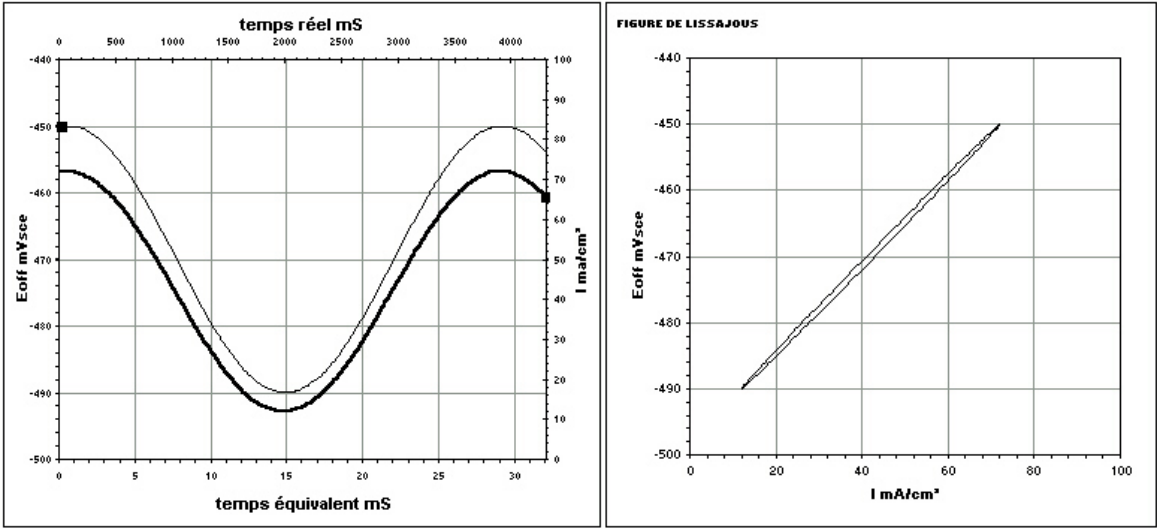

Fig. 4. E(t), i(t) and E-i curves for carbon steel in H2SO4 0.1M + 1000 ppm Cl- under 50 Hz, at higher potentials (between –490 and –450 mV$_{sce}$)

Figure 5 shows a series of curves obtained in NaOH at pH 13.75 with a rather large AC polarisation, around several average DC potentials. The hydrogen evolution, passivation and oxygen evolution can be seen.
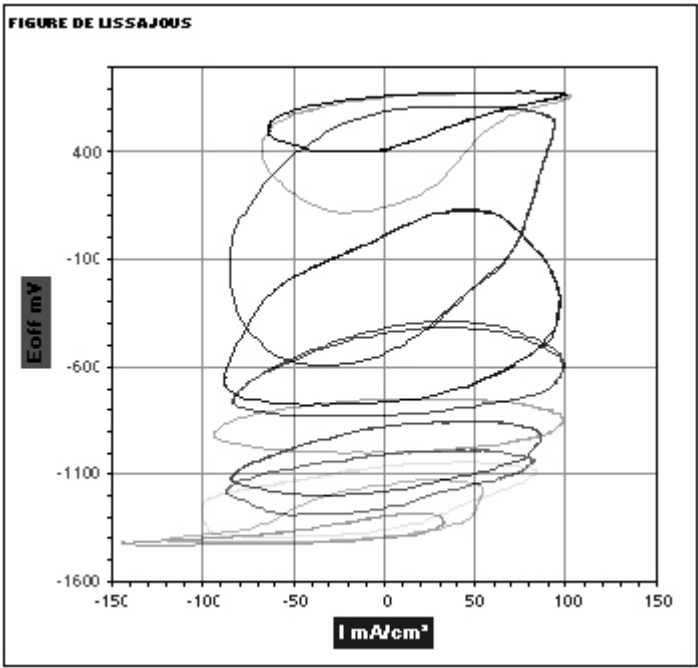

Fig. 5. E-i Lissajous curves for carbon steel in NaOH at pH 13.75, for various DC+AC polarisations

Figure 6 was obtained in a soil. Two distinct reactions are seen : hydrogen evolution, with a low impedance and a small phase angle that suggests a resistance controlled kinetics, and passivation or corrosion, with a larger phase angle.
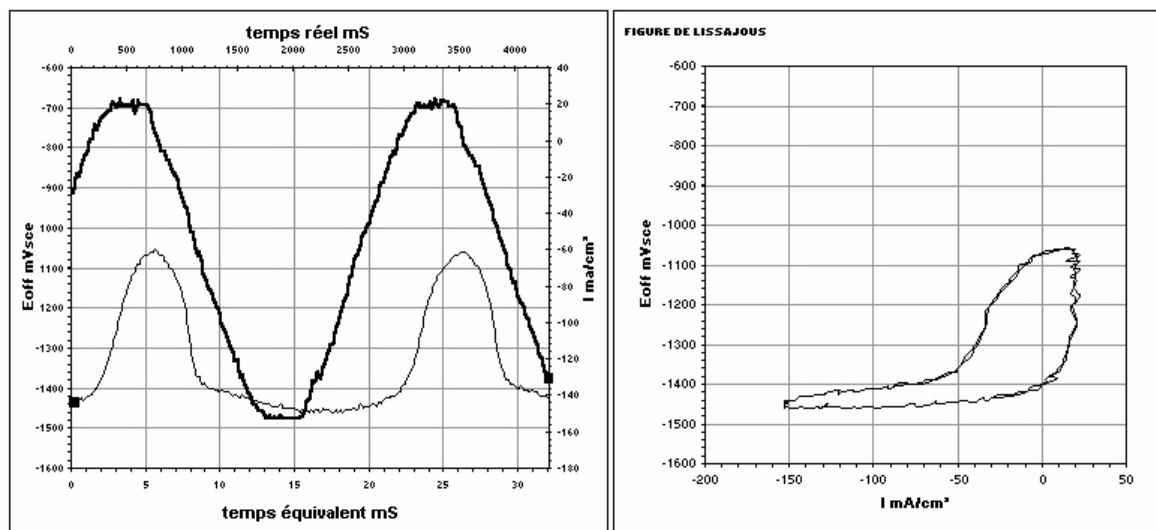

Fig. 6. E(t), i(t) and E-i curves for carbon steel in a soil, under 50 Hz, between −1460 and −1350 mV$_{sce}$

Conditions for AC corrosion

It was shown earlier, by field tests and by laboratory tests, that corrosion is possible (although not systematic) when the instantaneous IR-free potential is occasionally above the immunity potential, whatever the frequency and the environment is [21-23]. Conversely, corrosion is not possible when the IR-free potential is at all times below the immunity potential.

This calls for a correct determination of the immunity potential : under cathodic protection, the pH near the metal is increased, sometimes significantly. Tests in the laboratory with a cathodic DC polarisation of 10 mA/cm², with or without a superimposed 10 mA$_{rms}$/cm² AC polarisation, in various solutions (city water and buffered solution at pH 10.8) and soils (sand and clay) showed that pH 13 or more is measured on the metal surface after 1 minute or less. At pH 13, the immunity potential for iron is −852 mV$_{she}$ (or -1093 mV$_{sce}$, or −1168 mV$_{Cu/CuSO4}$). It was also shown before [22-24] that passive layers can behave in a special manner, in the presence of AC current. For example, iron was tested in Na_3PO_4 0.01M + $NaHCO_3$ 0.1M (bulk pH : 9.15). In the absence of AC, iron does not corrode in this solution, which has no chloride and which is nicely passivating. But, in the presence of a DC+AC polarisation such that the true peak potentials oscillate between the immunity region and the passive region (between −1150 and −470 mVsce), corrosion was measured at 2.08 mm/year [22,24].

In this work, similar observations were reproduced in other solutions. Table 1 summarizes the results of a series of laboratory tests. The same correlation between film formation, corrosion, pH and polarisation conditions was also observed in clay soils.
Table 1 : Correlation between film formation, corrosion and DC+AC polarization conditions

(carbon steel in NAOH, pH 13,75)

IR-free	potentials (Vsce)	Potential domain covered	Film	Corrosion	Duration
Min	max	in a period			(hours)
-1,20	-0,80 to -0,90	immunity and passivation	yes	yes	3
-1,30	-0,90 to -1,00	immunity and passivation	yes	? (*)	3
-1,35	-1,00 to -1,10	immunity and passivation	yes	? (*)	3
-1,42	-1,10 to -1,20	immunity only	no ?	no	3
-1,45	< -1,20	immunity only	no ?	no	3
-1,10	-0,90	passivation only	yes	yes	120

(*) corrosion is difficult to quantify, but a porous film is visible, thus corrosion is suspected.

Because of the special behaviour of passive layers under some conditions of AC polarisation, and because at the high pH measured at the metal-environment interface under cathodic protection (around pH 13), it is reasonable to consider that a risk of AC induced corrosion is possible when the IR-free maximum peak potential is higher than the immunity potential for those pH. Such potentials are possibly dangerous only because of the presence of AC. AC corrosion is thus possible if simultaneously the IR-free maximum peak potential is higher than the immunity potential for the actual pH on the metal (for example –1093 mV$_{sce}$ at pH 13) and the peak current is at least temporarily anodic (exiting currents). The latter corresponds to cases where the AC induced current density is at least as high as the cathodic protection current density.

In this study, the films were not fully characterized for their composition, morphology and protective properties. There are indications that, under some conditions, corroded iron may redeposit on the surface as a porous and non protective deposit. A new programme has been launched to study in more detail the phenomena occurring when the potential oscillates between the immunity and the passive range.

Aspects

The corrosion of coated pipelines which is attributed to AC induced currents has often the aspect of a small sphere, extending underneath an even smaller defect of the coating. This sphere is built on top of a hard oxide layer [18].

Depending on the soil composition, the alkalization produced by cathodic protection may precipitate insoluble compounds or not, depending if compounds of Ca and Mg are present.

When insoluble compounds are formed, the spread resistance near the defect is increased and the current on the defect decreases with time. This reduces the AC induced effects.
On the contrary, some of the soluble Na and K compounds are hygroscopic and may attract water. This would decrease the resistivity and increase the current with time [25]. AC induced effects are increased.

The two situations (decrease and increase of the current densities) were indeed observed, both in the lab and in the field.

The formation of iron oxides is sometimes abundant under certain conditions of DC+AC polarisation. This may contribute to the formation of these hard deposits.

Size and shape of the coupon

Under DC cathodic protection, small coating defects are generally well protected, while large defects may not be enough polarised in resistive soils.
Under AC, anodic currents are possible under certain conditions of DC+AC polarisation and, contrarily to DC cathodic protection, smaller defects are more prone to see larger anodic current densities and, therefore exhibit more corrosion.
Small coating defects are thus more dangerous than larger defects, when AC effects are present. It is often considered that 1 cm² is representative of practical conditions for AC corrosion surveys. But it may not be small enough in all cases. The real or the most probable defect size must be used for surveys. The CORREAC system uses coupons of 0.1, 1 and 10 cm².

Side observations

The practical experience in the lab and in the field shows that :
- there is evidence that defects oriented downwards can retain hydrogen bubbles and increase the resistance of the electrolytic pathway. For this reason, the system uses coupons that are oriented upwards.
- attempts to integrate coupons of several sizes in the same coupon holder were unsuccessful, because stray currents would occasionally flow through the different coupons even when disconnected. Therefore, the system uses separate supports with coupons of different sizes.
- the switch-off method is sometimes difficult to apply in sandy soils. It seems that sand may exhibit some kind of capacitance with discharge times around 15 s, especially for large current densities. These difficulties can be identified reasonably well, for example by checking the potential decay between two distant reference electrodes after switch-off.
- the duration of an optimum sequence for detailed AC measurements is 4 s. If faster transients are expected (for instance passage of fast speed trains), it is possible to program the system for shorter sequences.
- it happens that AC effects are produced by cathodic protection rectifiers. This is generally easily identified from the shape of the curves (higher harmonics from rectified AC, or sharp flanks from thyristor action).

DISCUSSION

Shape of curves, equivalent circuits

The simultaneous measurement of the IR-free potential, of the current density and of the phase angle provides an interesting set of new information :
- The instantaneous IR-free electrode potential can be interpreted with respect to calculated equilibrium potentials : immunity potential, hydrogen evolution potential, pitting potential etc.
- The AC current is made of different components : the current that is in phase with the potential represents a resistance controlled reaction, and it is a good indication of the rate

of the reactions.
- A phase angle is representative of a capacitance. This capacitance is explained by the different equivalent electrical circuits that represent metal/solution interfaces. As a first simplified approach, the interface is described as a capacity in parallel with the transfert resistance R_t, which is directly related to the rate of reaction. The capacity represents the double layer capacity.
- When the reactions include a transport by diffusion or convection (transport of Fe^{++} or of H_2…), the faradaic impedance Z_f is composed of two impedances in series : Z_t is a transfert impedance and Z_d is a diffusion impedance. The physical meaning of Z_t may be described by the fact that, in corrosion reactions, Fe^{++} ions must leave the metal surface and their movement is slowed down by the compacity of the soil, and Z_d by the fact that their transport is also controlled by a concentration gradient.
  When the surface is covered by a film, the interface is described as a capacitance (capacitance of film or coating) in parallel with a resistance R_p (porosity of film or coating) in serie with the parallel circuit of the double layer capacitance and the transfert resistance R_t.. Other comments on various equivalent diagrams may be found in the literature. The corrosion rate is best described by the transfert resistance R_t.
  The impedance for the frequency of the AC current is given by the IR-free potential, the current density and the phase angle, but the transfer resistance R_t is not known precisely. AC impedance spectroscopy (measured with a small ΔE and at varying frequencies) could in principle help to suggest the equivalent diagrams. But the procedure requires longer times that are not compatible with the AC induced conditions.
  Our current work covers the study of how to determine R_t (and thus the reaction rates) with procedures that are compatible with the presence of AC currents.
- Phase angles higher than 90°C were measured both in the lab and in the field and this is not interpreted, yet. This indicates perhaps equivalent diagrams with several resistances and capacitances both in series and in parallel. More work on this is under way.
- The curves of <u>figure 5</u> show clearly the hydrogen evolution reaction, at low potentials. Due to the hydrogen evolution reaction, the true potential can hardly become more negative than -1400 mV$_{sce}$, in this high pH solution. This suggests that any potential measured in cathodic protection that is more negative than about -1400 mV$_{sce}$ is probably erroneous, because of an IR drop error.
- Some curves do not show an elliptical shape, but can be decomposed into several ellipses or lines (<u>figure 6</u>, for example). This indicates the simultaneous occurrence of more than one reaction, during one period.
- It is important to make measurements on coupons of the same size as the actual defects. If no better information is available, 0.1 or 1.0 cm² is considered to represent pinholes or stone damages satisfactorily.
- Mitigation techniques using Zn or Mg anodes, polarisation cells and electrolytic capacitors have been discussed [11]. Developments of techniques based on polarisation cells have been compared with the usual mitigation techniques and will be reported later.

CONCLUSIONS

An instrument and a software system (CORREAC) were developed to measure the AC induced effects on metallic structures. The IR-free potential, the current density and the phase angle are measured throughout a period, on a coupon connected to the structure.
This system is useful for the interpretation of AC corrosion situations and to clarify the various mechanisms of AC corrosion. In particular, the IR-free potential can be interpreted by

comparison with calculated equilibrium potentials.

Many types of E-i curves throughout AC periods were obtained from laboratory tests and during field surveys.

It was confirmed that one or more electrochemical reactions can occur or stifle rapidly and successively during the short time of an AC period, depending on the amplitude of the AC polarisation and on the level of electrode potential attained.

The analysis of the true potential, of the current density and of the phase angle allow to separate and identify these various reactions. In some cases, it is possible to have an idea of the rate of corrosion or of hydrogen evolution.

It was shown that under specific polarisation conditions, passive films are damaged by AC induced currents. This has consequences on the identification of conditions under which AC corrosion can occur.

The changes with time of the AC induced current is also indicative of the risk of AC corrosion.

Several recommendations were presented on the coupons used in the system. Their size should be directly related to the size of the possible defects of the coating. Smaller defects are more dangerous for AC corrosion. The AC monitoring system uses coupons of several sizes, most often 0.1, 1 and 10 cm².

Field surveys conducted with the system allowed to identify various levels of risks of AC corrosion.

More work is under way to develop criteria for AC corrosion, on the basis of the data provided by the measuring system. A special attention is given to the identification of the transfert resistance R_t and to the behaviour of passive films when exposed to DC+AC.

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FIGURES

Fig. 1 : Corrosion rates of iron as a function of AC and DC current densities in KCl 5% [10,11]

Fig. 2 : E(t), i(t) and E-i curves for carbon steel in H2SO4 0.1M + 1000 ppm Cl- under 50 Hz, at potentials between -1320 and -1260 mV$_{sce}$

Fig. 3 : E(t), i(t) and E-i curves for carbon steel in H2SO4 0.1M + 1000 ppm Cl- under 50 Hz, at potentials between -565 and -520 mV$_{sce}$

Fig. 4 : E(t), i(t) and E-i curves for carbon steel in H2SO4 0.1M + 1000 ppm Cl- under 50 Hz, at potentials between -490 and -450 mV$_{sce}$

Fig. 5 : E-i Lissajous curves for carbon steel in NaOH at pH 13.75, for various DC+AC polarisations

Fig. 6 : E(t), i(t) and E-i curves for carbon steel in soil, under 50 Hz, at potentials between -1460 and -1350 mV$_{sce}$