

**DETECTION OF A.C. CORROSION**  
**(PROTECTION CRITERIA, MEASUREMENT OF CORROSION**  
**RATE AND PH, USING THE CORREAC SYSTEM AND**  
**AN ELECTRICAL RESISTANCE PROBE)**

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**ABSTRACT**

Research in the field of alternating current (a.c.) corrosion has confirmed the specific criteria required for cathodic protection in the presence of an a.c., and has made it possible to measure the corrosion rate where these criteria are not met.

Since the protection criteria required when an a.c. is present are so strict, it is far better to detect corrosion when it occurs and to rectify it using earthing techniques.

CORREAC instruments and specially designed electrical resistance probes have led to significant improvements in detecting and measuring a.c. corrosion and in helping to understand the conditions under which it occurs.

**RESUME**

La poursuite des recherches sur les corrosions courants alternatifs induits a permis de confirmer les critères particuliers de protection cathodique en présence de courants alternatifs et d'évaluer les vitesses de corrosion lorsque ces critères ne sont pas satisfaits.

Les critères de protection en présence de courants alternatifs sont tellement contraignants qu'il est de loin préférable de déceler les situations de corrosion et d'y porter remède par des techniques de mises à la terre.

L'instrumentation correal et des sondes de résistance électrique adaptées au problème ont apporté des améliorations très conséquentes pour la détection et l'évaluation des corrosions par courants alternatifs, et pour aider à comprendre les conditions où elles se manifestent.

**ZUSAMMENFASSUNG**

Die Fortsetzung der Untersuchungen zu den Wechselstromkorrosionen hat dazu geführt, dass es möglich wurde, die besonderen Kriterien des kathodischen Schutzes bei Vorliegen von Wechselstrom zu bestätigen und die Korrosionsraten abzuschätzen, wenn diese Kriterien nicht erfüllt werden.

Die Schutzkriterien bei Vorliegen von Wechselstrom sind dermaßen zwingend, dass es bei weitem vorzuziehen ist, die Korrosionssituationen aufzuspüren und mit Hilfe von Techniken der Erdung darauf zu reagieren.

Die Correal-Apparaturen und die für das Problem angepassten Sonden für elektrischen Widerstand haben bei der Detektion und Bewertung der Wechselstromkorrosionen sowie beim Verständnis der Bedingungen, unter denen sie vorkommen, zu sehr bedeutenden Verbesserungen geführt.

## INTRODUCTION

This research continues that begun in 1996 on a.c. corrosion.

Previous results had shown that a.c. corrosion could be detected and measured if the exact state of electrochemical polarisation of the metal at any given moment during the a.c. period could be determined.

It had also been shown that ohmic drop errors were often much higher under the a.c. interference as the density of the a.c. currents is much higher than the d.c. currents for cathodic protection.

Therefore, in the first instance, a system has been developed to measure the true potential (without ohmic drop) during an a.c. period. This system is known as the 'CORREAC' system and is described in [1]. The CORREAC system simultaneously measures both the current density at any given moment during the a.c. period and the phase angle between the true potential and the current. The 3 values ( $E_{\text{true}}(t)$ ,  $i(t)$  and  $\phi$ ) have to be measured accurately to allow a rational and objective analysis of the corrosion induced by a.c. currents.

Once the system had been developed, a series of laboratory and field studies were carried out. In the laboratory, tests were performed to try to establish the corrosion rate and a correlation between the conditions of a.c. polarisation and the existence of corrosion. The field study involved identifying the points and conditions in the networks (pipelines and high-voltage power lines) where the risk of a.c. corrosion was much higher.

To establish the correlation sought in the laboratory, a system of double potentiostatisation has been developed whereby both the a.c. and d.c. polarisations could be kept constant over time.

These studies showed that corrosion can indeed occur in the presence of a.c. currents under chemical and polarisation conditions which would not cause corrosion if a.c. currents were not present [1]. In particular, it was found that conditions (chemical and polarisation) which acted as passivators under a d.c. current can become corrosive when the true potential fluctuates when affected by a.c. currents [1]. A series of interesting conclusions could also be drawn concerning local changes in the pH at the metal interface under the effect of cathodic polarisation, and the possibility to determine the surface pH using the CORREAC system based on the hydrogen evolution potential.

The work carried out here focussed on

- a more in-depth study of the influence of a.c. polarisation conditions on a.c. corrosion according to the chemical nature of the environment and the stability of passivating films with a view to establishing protection criteria in the presence of a.c.;
- researching the measurement of corrosion rates based on information provided by the CORREAC system;
- determining the surface pH of the metal in relation to hydrogen evolution using the information provided by the CORREAC system.

## **MATERIALS AND METHODS**

### **The CORREAC system**

The CORREAC system measures the electrode potential (without any ohmic drop), the current density and the phase angle at any given moment during the period. These measurements are carried out on a coupon connected to the pipeline and with a reference electrode placed right up against the coupon. The potential values are measured approximately 1 ms after disconnecting the coupon from the pipeline (this time period is adjustable). This disconnection takes place once per period, each time with a minor time lag to restore changes in the true potential during a period and so as to avoid inhibiting cathodic protection in between measurements.

The system displays and registers the synchronised curves  $E(t)$  and  $i(t)$ , and the corresponding Lissajous figures in an E-I plot.

The system also displays the potential and the maximum, minimum and average current density values of a.c. and d.c. currents and also the phase angle and the impedance.

All these curves and values are reproduced in each test report (see [Figure 2](#) onwards as an example.)

### **The d.c.+a.c. potentiostatisation system**

The method developed previously for controlled d.c.+a.c. polarisation has also been used for this application [2]. This system keeps the chosen polarisation conditions constant over time to obtain a clear measurement of the corrosion rate.

These polarisations and CORREAC measurements are carried out on the electrical resistance probes themselves.

### **Electrical resistance probes**

The electrical resistance probes were assembled with very thin steel sheets and using a technique similar to that used to assemble printed circuit boards. Every probe has a section that is exposed to the outside environment and a similar insulated section to ensure automatic temperature compensation. The device measures and displays the relationship between the two resistances and displays the material loss expressed in mm/year according to the initial reading, the final reading and the exposure time between the two readings assuming general corrosion. The dimensions of the probes and the sensitivity of the combination of probe and the measuring device have been selected to obtain sensitive probes, designed for short-term use. As such, the developed probes are inexpensive and disposable, and the overall resolution is 20  $\mu\text{m}/\text{year}$  for test periods of 60 minutes.

### **Environments and solutions**

The different tests were carried out in one of the following solutions:

To study the protection criteria required against A.C. corrosion:

- municipal water (Brussels)
- $\text{H}_2\text{SO}_4$  0.1 M + 100 ppm  $\text{Cl}^-$  (pH 1)
- NaOH 40 g/l (pH 14)

- a buffer passivating environment, chloride-free (53.4 ml/l Na<sub>2</sub>CO<sub>3</sub> 0.1 M + 46.6 ml/l NaHCO<sub>3</sub> 0.1 M, pH 10)
- a soil sample, in the laboratory (garden soil)
- the same soil saturated with 1 g/l of Na<sub>2</sub>SO<sub>4</sub>
- the same soil saturated with 10 g/l of Na<sub>2</sub>SO<sub>4</sub>
- a real soil sample in the field (clayey soil with resistivity between 3,800 and 5,200 Ohm-cm)

To check the pH values measured

- pH 1.00: H<sub>2</sub>SO<sub>4</sub> 0.5 M
- pH 5.02: 99.2 ml KH<sub>2</sub>PO<sub>4</sub> 9.073 g/l + 0.8 ml Na<sub>2</sub>HPO<sub>4</sub> 2H<sub>2</sub>O 11.87 g/l
- pH 6.06: 88.9 ml KH<sub>2</sub>PO<sub>4</sub> 9.073 g/l + 11.1 ml Na<sub>2</sub>HPO<sub>4</sub> 2H<sub>2</sub>O 11.87 g/l
- pH 7.00: 41.3 ml KH<sub>2</sub>PO<sub>4</sub> 9.073 g/l + 58.7 ml Na<sub>2</sub>HPO<sub>4</sub> 2H<sub>2</sub>O 11.87 g/l
- pH 7.74: 53.0 ml Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 0.05 M + 47.0 ml HCl 0,1N
- pH 8.95: 83.5 ml Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 0.05 M +16.5 ml HCl 0.1N
- pH 10.00: 53.4 ml Na<sub>2</sub>CO<sub>3</sub> 0.1 M + 46.6 ml NaHCO<sub>3</sub> 0.1 M
- pH 11.00: NaOH 0.001 M
- pH 13.00: NaOH 0.1 M
- different soils.

### **A.c. polarisation conditions and a.c. protection criteria**

To complete previous results [2], tests were carried out in a soil sample (several times and using a method that could be repeated) under 3 characteristic polarisation conditions

- permanently in the immunity domain,
- oscillating between the immunity domain and the oxide stability domain,
- permanently in the oxide stability domain.

A.c. polarisations were applied after a sufficiently long time period for the pH to stabilise under the effect of cathodic protection. The potential in each case was lower than -800 mV<sub>ecs</sub> (including the a.c. components).

### **Measuring the a.c. corrosion rate using the CORREAC system**

Around 200 tests were carried out under controlled polarisation conditions, in very different solutions (acidic, alkaline, chloride, passivating, with/without a.c., with/without d.c. polarisation, etc.) and in 4 different soil types. Data was gathered from both the CORREAC system and readings detailing the corrosion rate provided by the electrical resistance probes.

### **Determination of the surface pH of the metal using the CORREAC system**

Previous results have shown [1] that it is possible to determine the surface pH of the metal by observing the reaction of hydrogen evolution. When the structure is exposed to a.c. currents, this reaction can be observed easily using the CORREAC system.

When no a.c. is present, or when the a.c. compound is too weak, it is advisable to superimpose a cathodic current for a very short period to show the hydrogen evolution. Since the potential of hydrogen evolution is linked to the surface pH, and the current increases very rapidly once the hydrogen evolves, the potential at which the cathodic current increases gives an accurate indication for the surface pH. CORREAC measurements have been carried out in

pH solutions known to contain large amounts of buffer and tests performed to study how the measurements indicate this pH.

## RESULTS

### A.c. polarisation conditions and a.c. protection criteria

The 3 polarisation conditions are shown in Figure 1 (1: permanently in the immunity domain, 2: switching between the immunity and passivating domains, and 3: permanently in the passivating domain).

The results of the CORREAC measurements are shown in Figures 2 to 4.

There is no corrosion in the immunity domain (condition 1). There is significant corrosion where the polarisation oscillates between the immunity and passivating domains (condition 2: 5.6 and 9.8 mm/year in our tests).

### A.c. corrosion rate measurement using the CORREAC system

Over 200 tests were carried out under different chemical and polarisation conditions. Depending on the corrosion rate, these tests lasted between 1 minute and 6 days. The results of the tests are shown in Figures 5 to 9.

The figures show the CORREAC readings of the true potential and the current density according to time during a period, the same values in the plan E-i (Lissajous figures) and the main parameters (peak potential, phase angle, impedance, etc.).

The corrosion rates are shown in the key to the each figure.

Comments on these results are given below.

### Determination of the surface pH of the metal using the CORREAC system

CORREAC measurements were taken in solutions containing significant quantities of buffer, and tests were carried out to determine if and under what conditions these measurements clearly delivered information to determine the pH. In particular, where there was no hydrogen evolution under natural polarisation conditions, a cathodic polarisation current was superimposed in order to observe it. So as not to alter the natural pH, it was important that this extra polarisation was added for only a short period of time.

The results are shown in Figure 2.

For each pH, 8 tests were carried out (under 2 different d.c. current densities, with/without agitation, and with/without superimposed cathodic current).

The results show that in general, the lower the minimum peak potential, the higher the pH.

This is particularly true for the lowest d.c. polarisations (here: 0.5 mA/cm<sup>2</sup>) where pH 12 was reached.

It was clear that the cathodic current must be applied for a short period only to ensure that it does not raise the pH value itself. Currents lasting more than 2 ms have systematically caused the minimum potential values to fall rapidly.

## DISCUSSION

### Protection criteria in the presence of a.c.

On the basis of both the 200 tests carried out now and previously [2], two important conclusions can be drawn:

- whenever the maximum true peak potential is higher than (less negative than)  $-1150 \text{ mV}_{\text{ecs}}$  (or  $-1200 \text{ mV}_{\text{Cu/CuSO}_4}$ ), there is a risk of corrosion. This risk is significant where the peak potential exceeds  $-800 \text{ mV}_{\text{ecs}}$ .

- where the maximum peak potential is always more negative than  $-1150 \text{ mV}_{\text{ecs}}$ , there is no corrosion, regardless of the environment and the value of the a.c. currents.

Tests here have confirmed that the protection criterion under a.c. interference is to keep the true potential (including the maximum peaks) within the immunity domain at all times. It is important to remember that in reality, the surface pH of the metal can be very high due to the cathodic protection. These high pH values will be more favourable where no a.c. is present but not where an a.c. is present.

The immunity potential is  $-1200 \text{ mV}_{\text{ecs}}$  at pH 14 and  $-950 \text{ mV}_{\text{ecs}}$  at pH 10. In all our tests where the potential was permanently below  $-1150 \text{ mV}_{\text{ecs}}$ , no corrosion was observed. This potential corresponds to the immunity limit at pH 13.

This protection criterion against corrosion in the presence of an a.c. current, which is different to that when no a.c. is present, is explained by the fact that non-protective films are formed by the a.c. polarisations oscillating between the passivating domain where the oxides form and the immunity domain where they disperse. From these tests, it can also be concluded that the electrochemical reactions rapidly follow the change in potential.

During this research, it has not been possible to investigate in any greater detail the intricate sequences of how the different oxide films are produced and dispersed. It would certainly be worthwhile carrying out additional research in order to refine these criteria.

### **Measuring the rate of A.C. corrosion using the CORREAC system**

In many cases the Lissajous figures can be broken down into several ellipses each corresponding to a specific situation or reaction: non-reactive metal and its double layer capacity, hydrogen evolution, corrosion, oxide formation and, at very high potentials, oxygen evolution. The corrosion rates can be measured using the section of the Lissajous figures that correspond to the corrosion reaction.

The target process is as follows:

- break down the Lissajous figures into individual ellipses and identify the ellipse that relates to corrosion (by doing so, the contribution of hydrogen evolution is eliminated from the total current),
- measure the maximum part of the anodic current which corresponds to corrosion, bearing in mind the resistive and capacitive components (phase angle).
- calculate the corrosion rate based on this current.

This process is under way with a view to compiling a guide to interpreting CORREAC information.

Even at this stage though, several provisional rules can be given where a.c. corrosion occurs (where a.c. protection criteria are not being met):

A situation which occurs frequently in soils is shown in [Figure 5](#). The Lissajous figure can be broken down into 2 ellipses, the upper one relating to corrosion. It is located below

-800 mV<sub>ecs</sub> and above -1150 mV<sub>ecs</sub>. In such cases, the estimated corrosion rate is between 0.02 and 0.1 mm/year per mA/cm<sup>2</sup> rms of a.c. current density. In the case of [Figure 5](#), the corrosion rate is 0.65 mm/year. For an equal a.c. current density, the corrosion rate is higher the further the lower ellipse extends into the immunity domain.

- If a Lissajous figure similar to that shown in [Figure 6](#) is observed (a single ellipse with  $\phi$  between 60 and 90°), it is possible either that an oxide film is forming in a strongly alkaline environment (and so the potentials are much higher, between -800 and -1150 mV<sub>ecs</sub>), or that there is immunity at lower pH values (and so the potentials are lower than -1150 mV<sub>ecs</sub>). The corrosion rate is approximately 0.25 mm/year per mA/cm<sup>2</sup> of a.c. current density in the first case, and zero in the second.

- Another situation that arises frequently is that of a single ellipse with  $\phi$  greater than 90° and high potentials (-800 to -1000 mV<sub>ecs</sub>, [Figure 7](#)). This corresponds to a protective film, and there is no corrosion. If the potentials are occasionally lower than -1150 mV<sub>ecs</sub>, a second ellipse appears and corrosion is measured at between 0.01 and 0.03 mm/year per mA/cm<sup>2</sup> of a.c. current density.

- A third situation, which appears to relate to the potential range between the corrosion and passivating domains produces 1 or 2 ellipses, each with  $\phi$  greater than 90° ([Figure 8](#)). There is less corrosion and the corrosion is reduced over time. At the same time, the curve changes to a single ellipse.

In most situations encountered in the field and where a.c. is present, a maximum true potential that is always below -1150 mV<sub>ecs</sub> guarantees that no corrosion occurs, and that maximum peak potentials above -800 mV<sub>ecs</sub> indicate very high levels of corrosion. According to the situations described above, when the potentials are within these limits (below -800 mV<sub>ecs</sub> but with peaks above -1150 mV<sub>ecs</sub>), the corrosion rate can be estimated at between 0.01 and 0.25 mm/year per mA/cm<sup>2</sup> of a.c. current density.

### **Determining the pH and hydrogen evolution using CORREAC measurements**

CORREAC measurements can be used to indicate pH value. Where the a.c. polarisation is significant, the lower parts of the Lissajous figures flatten out. This corresponds to hydrogen evolution and the lowest potential can be used to determine the pH value.

Situations where there is hydrogen evolution can be identified easily using the CORREAC system as in [Figure 9](#). The pH can be derived from the minimum potential (pH 1 for -650 to -690 mV<sub>ecs</sub>, pH 10 -1360 mV<sub>ecs</sub>, pH 14 up to -1500 mV<sub>ecs</sub>). The density of the cathodic current indicates how significant this evolution is.

In cases where the a.c. polarisations do not spontaneously reach the potentials of hydrogen evolution, very short cathodic currents were applied to measure the potential of hydrogen evolution. To use this method in the field, the intensity of this current must be adapted in line with local conditions (resistivity, induced a.c. current).

## **CONCLUSIONS**

By using sensitive, inexpensive and disposable electrical resistance probes, developed for this study, to measure the corrosion rate, it has been possible to calibrate the CORREAC for corrosion rate measurements.

Results confirmed that the cathodic protection criterion in the presence of a.c. is to keep the potential within the immunity domain at all times. Results also showed that local alkalisation via cathodic protection is very important in soils at the metal surface at coating faults

As such, it is recommended that maximum true potentials are kept below  $-1150 \text{ mV}_{\text{ecs}}$  at all times.

If the potential exceeds these values, the CORREAC measurements show the reactions when a.c. is present and speed up the corrosion rate.

The protection criteria in the presence of a.c. are so strict that it is far better to detect corrosion when it occurs and to avoid it using earthing techniques.

The disposable electrical resistance probes can also be used in the field for fast corrosion rate measurements.

Results also showed that the CORREAC system can indicate the hydrogen evolution for determination of the local surface pH of the metal.

## REFERENCES

1. A.Pourbaix, P.Carpentiers, R.Gregoor. "Detection of A.C. corrosion". Eurocorr 2001 (section: Cathodic protection), Riva del Garda 30 September – 4 October 2001, AIM.
2. A.Pourbaix, P.Carpentiers, R.Gregoor. "Detection of A.C. corrosion. Interpretation of instantaneous IR-free potential, current density and phase angle measurements", Cefra.c.or Symposium, Aix-en-Provence 6-7 June 2002.



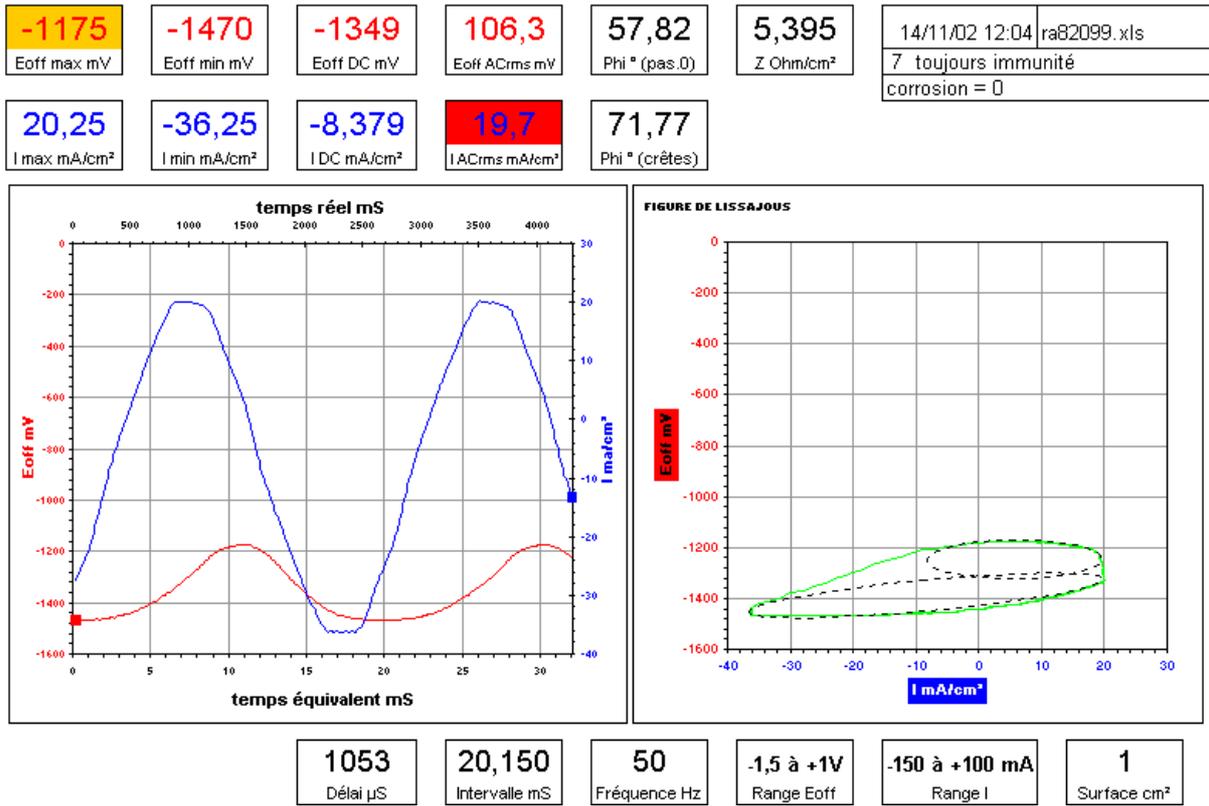


Figure 2 : Data from CORREAC in a soil, for 20 mA/cm<sup>2</sup> a.c., at potentials always more negative than -1150 mV<sub>sce</sub>. Two ellipses : hydrogen evolution and immunity. No corrosion.

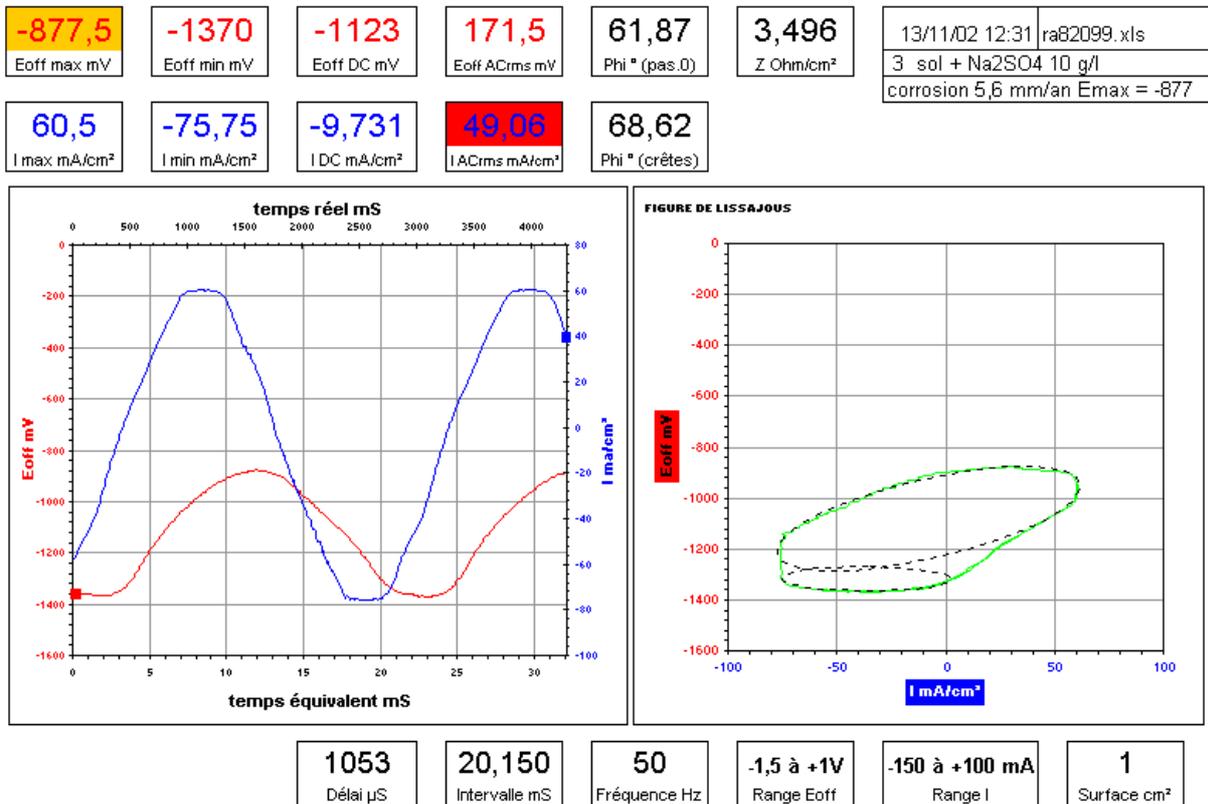


Figure 3 : Data from CORREAC in a soil, for 50 mA/cm<sup>2</sup> a.c., at potentials always more negative than -850 mV<sub>sce</sub>. Two ellipses : immunity and oxides. Severe corrosion : 5.6 mm/y.

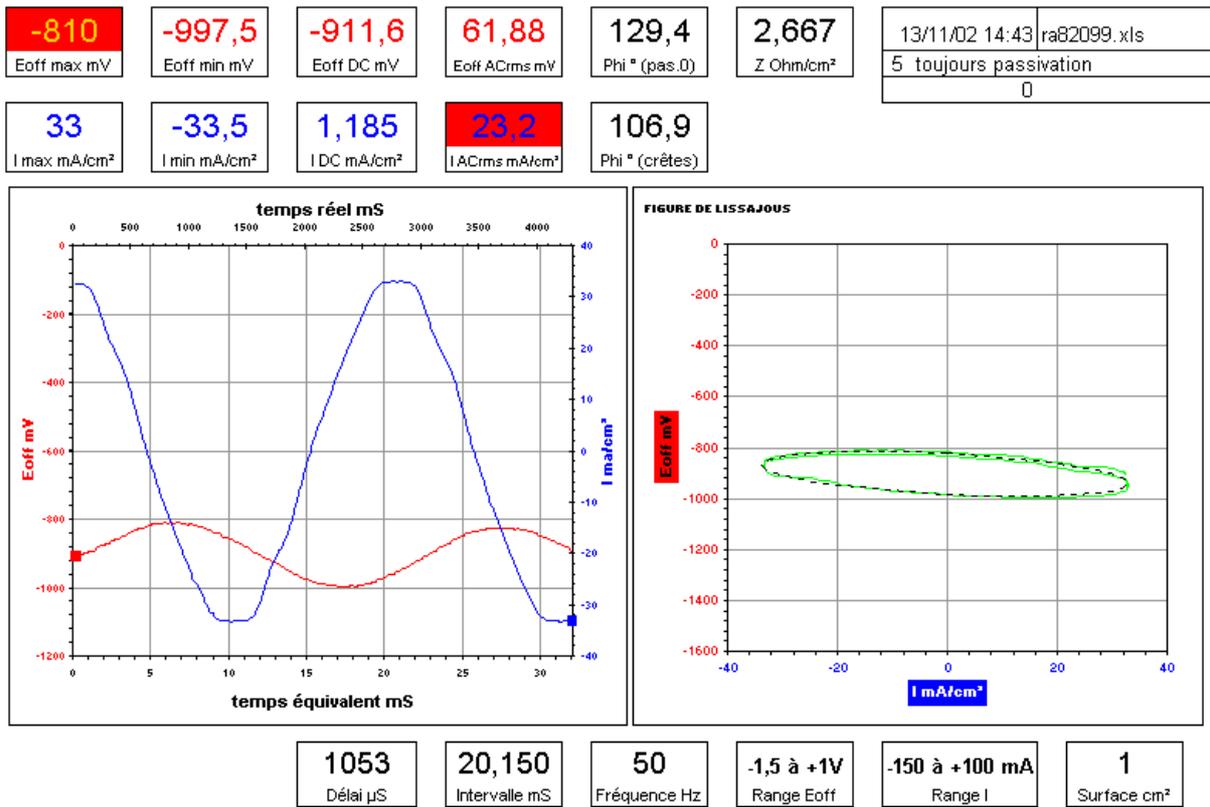


Figure 4 : Data from CORREAC in a soil, for 23 mA/cm<sup>2</sup> a.c., at potentials always more negative than -800 mVsce. One single ellipse,  $\varphi > 90^\circ$  : oxide only. No corrosion.

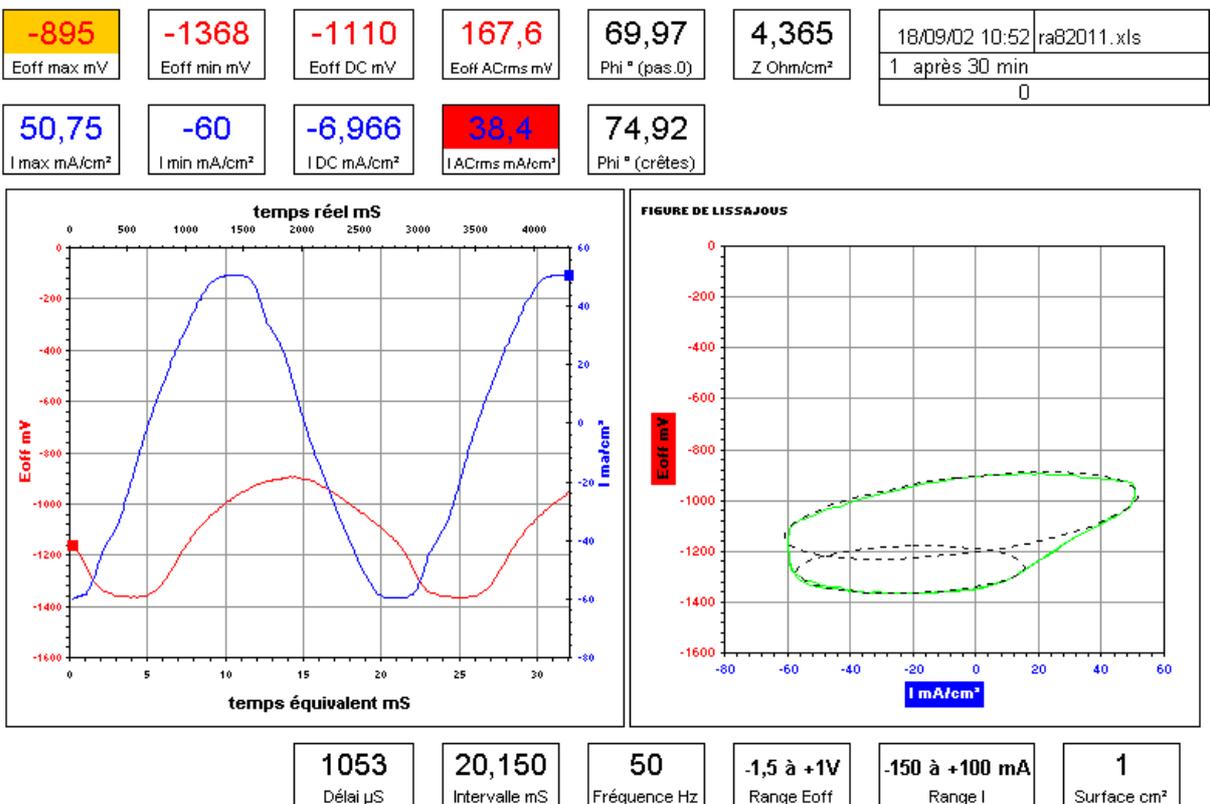


Figure 5 : Data from CORREAC in a soil, for 40 mA/cm<sup>2</sup> a.c., at potentials always more negative than -900 mVsce. Two ellipses : immunity and oxide. Constant corrosion (0.65 mm/y) for 2 hrs.

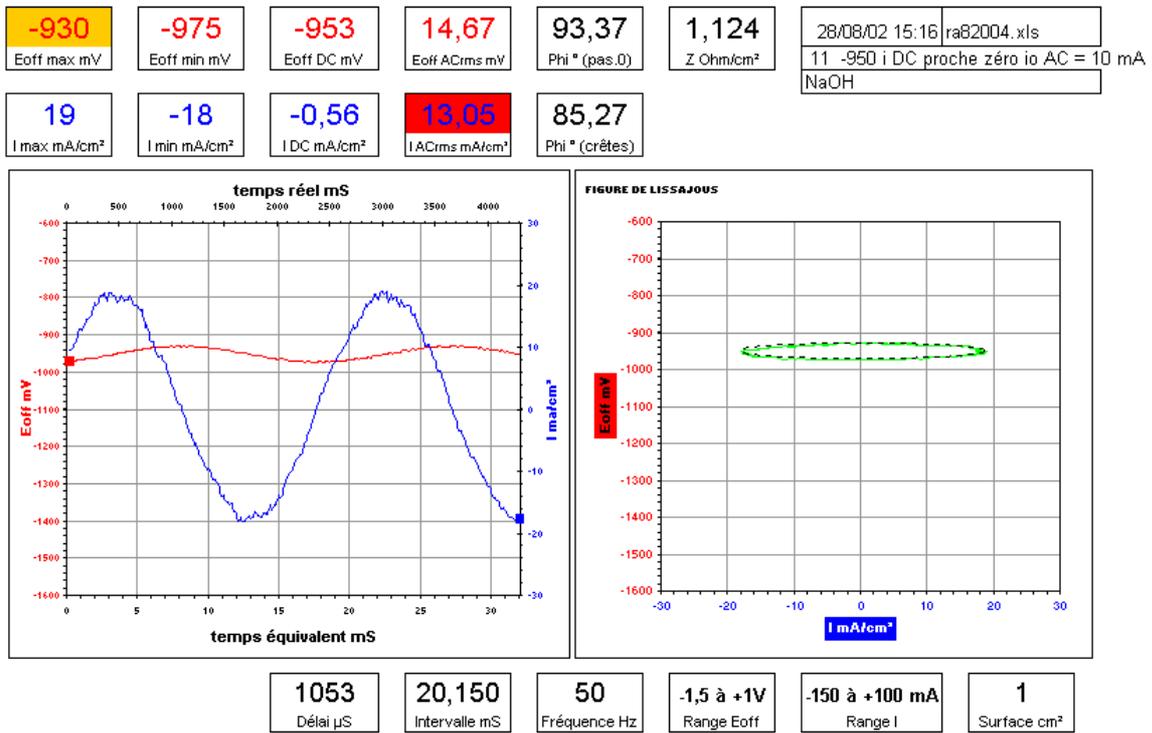


Figure 6 : Data from CORREAC in a very alkaline solution, for 10 mA/cm<sup>2</sup> a.c.. One single ellipse : oxide. Corrosion rate : 2.2 mm/y.

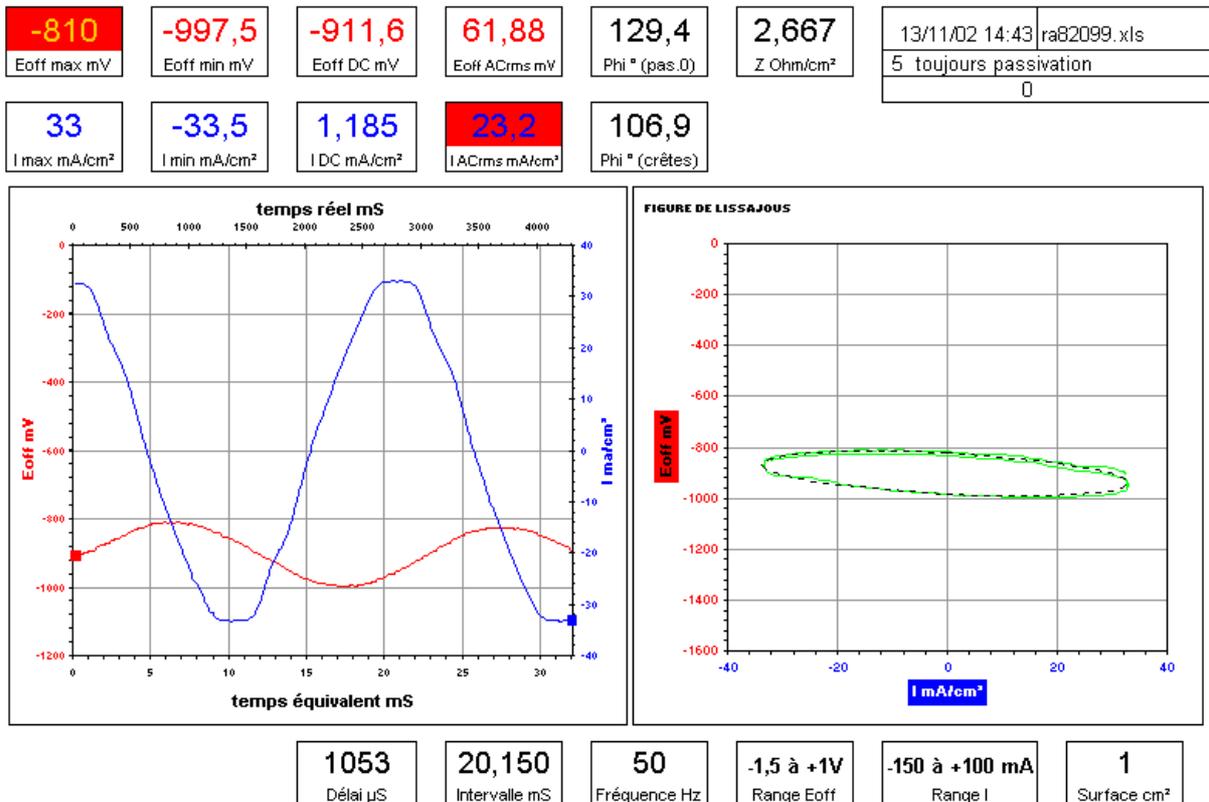


Figure 7 : Data from CORREAC in a soil, for 23 mA/cm<sup>2</sup> a.c., at potentials always more negative than -800 mV<sub>sce</sub>. One single ellipse :  $\varphi > 90^\circ$  : oxide only. No corrosion.

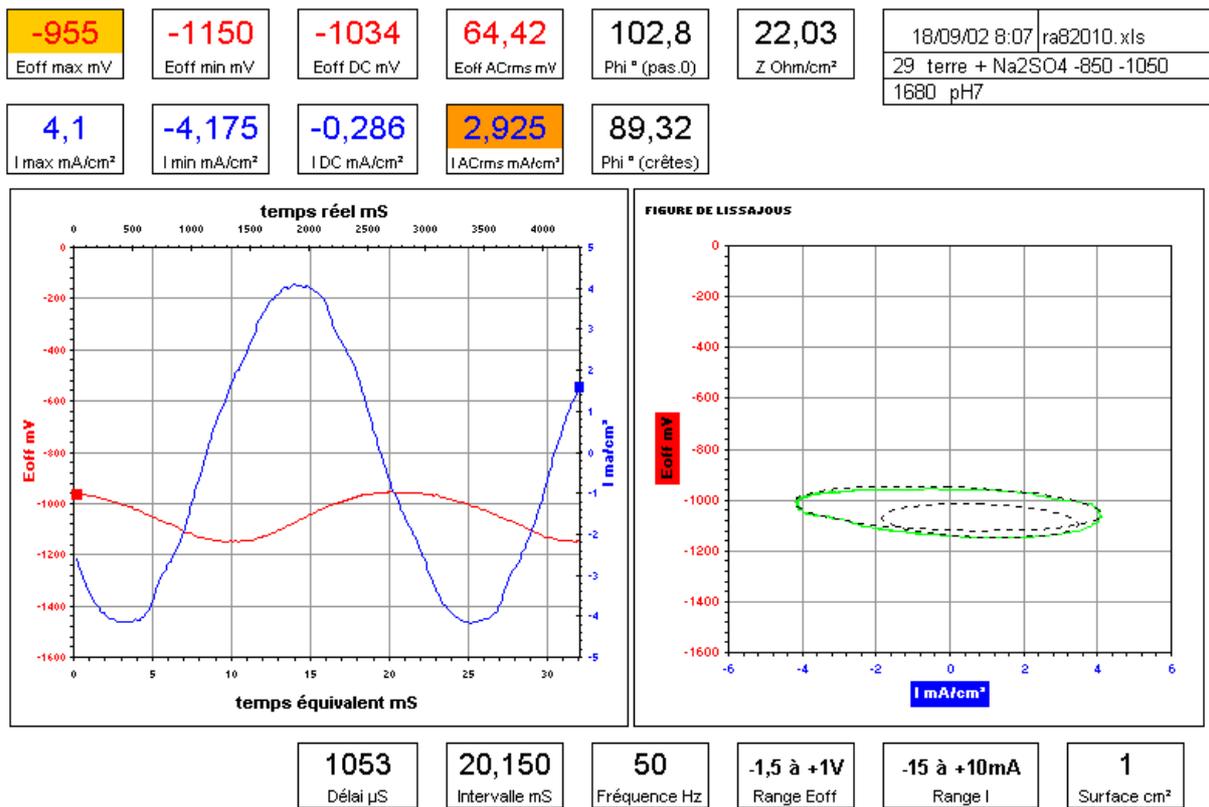


Figure 8 : Data from CORREAC in a soil, for 6 mA/cm<sup>2</sup> a.c., at potentials always more negative than -900 mV<sub>sce</sub>. Two ellipses :  $\phi > 90^\circ$  : immunity and oxide. No corrosion after 840 h.

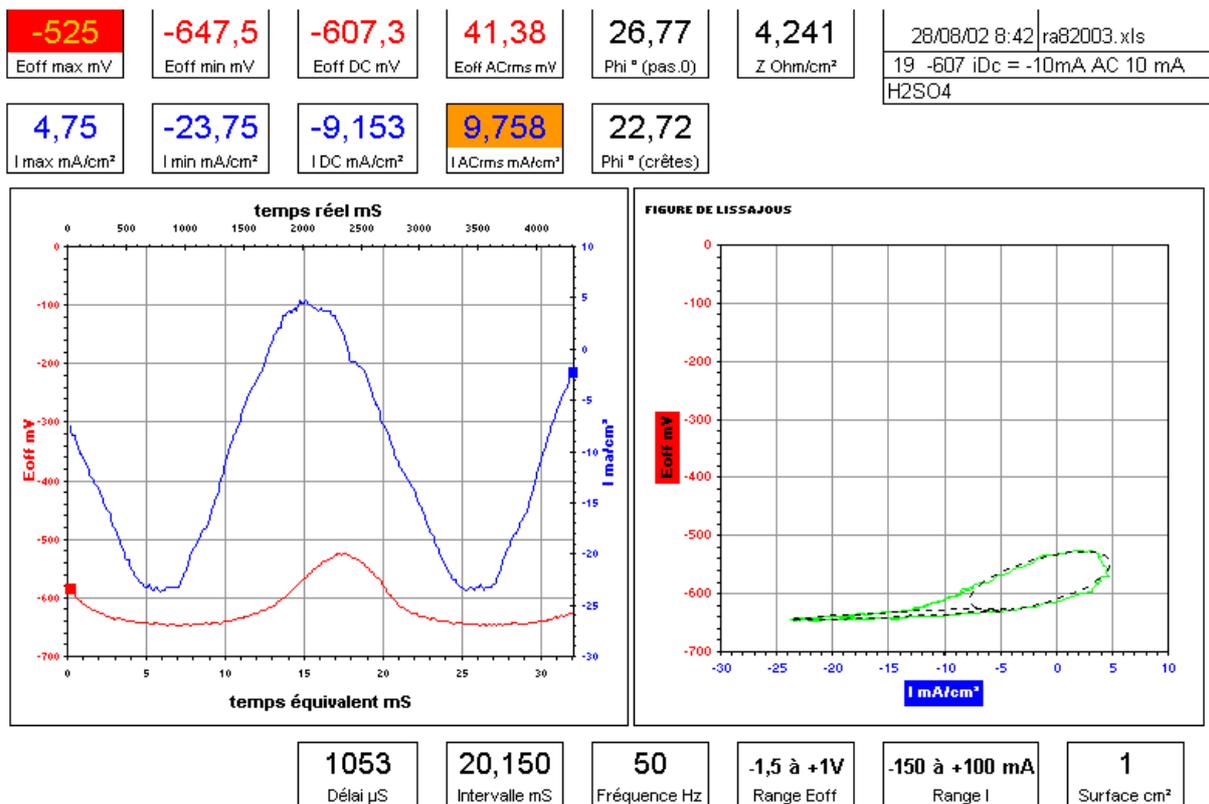
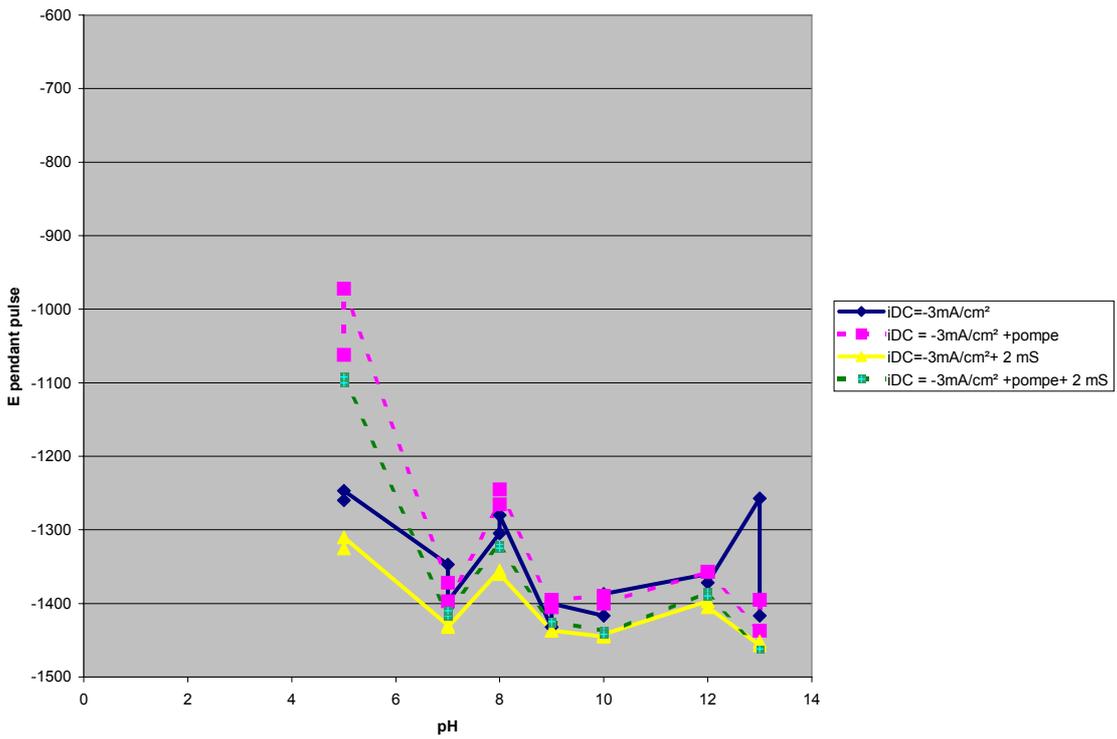
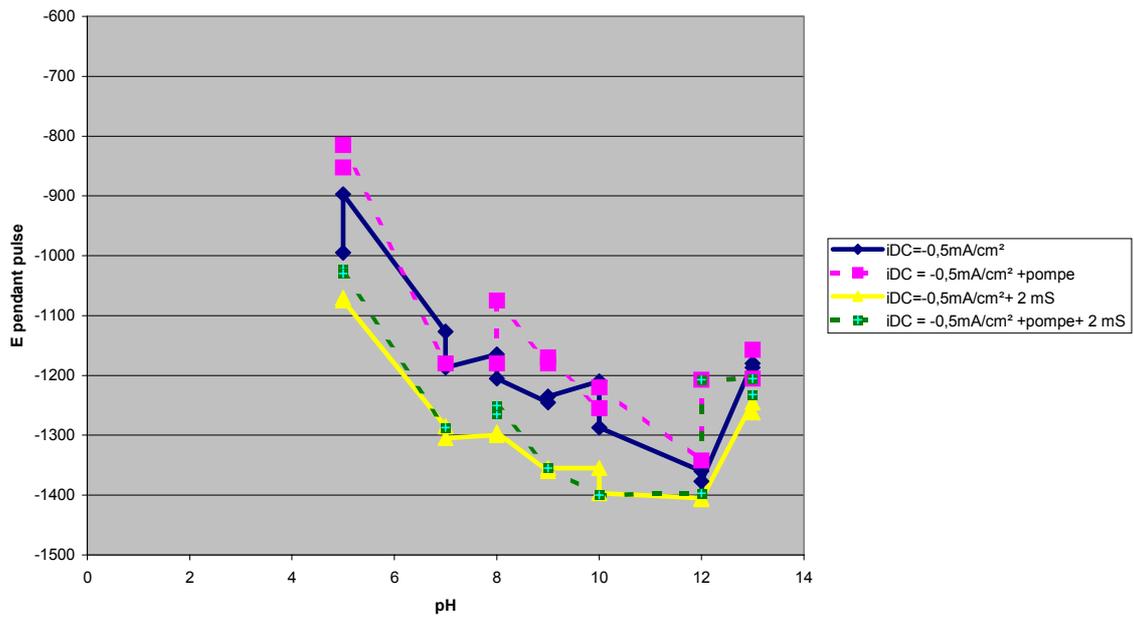


Figure 9 : Data from CORREAC in an acid solution, under cathodic polarisation + 10 mA/cm<sup>2</sup> a.c.. Two ellipses. Corrosion rate : 3.4 mm/y and hydrogen evolution. The cathodic polarisation is not enough to lower the potential.



**Figure 10** : Results for the tests to evaluate the pH at the metal surface by using the CORREAC system, with an added cathodic pulse.