

# **DETECTION OF AC CORROSION. INTERPRETATION OF INSTANTANEOUS IR-FREE POTENTIAL, CURRENT DENSITY AND PHASE ANGLE MEASUREMENTS**

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## **ABSTRACT**

A control system, acting on dc and ac polarization, was developed to keep max and min peak OFF-potentials within preset ranges during long periods of time in different environments. In this way, the absence or occurrence of corrosion has been correlated to potentials varying in immunity, corrosion ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ) and passivation conditions, with pH values from 9 to 14.

IR-free potential, current density and phase angle were measured on ac interfered coupons, using the CORREAC instrument. The results were computed as  $E_{\text{off}}$  and I versus time plots, and as Lissajous  $E_{\text{off}}$ -I plots throughout an ac period.

They confirmed the absence of corrosion when the  $E_{\text{off}}$  was below the immunity potential for the relevant pH at every moment of the ac period. Ac currents could impede the formation of protective oxides when the potential oscillates in the passivation domain or between immunity and passivation.

This calls for more detailed criteria for the cathodic protection of metals under ac interference.

## **RESUME**

Un système de contrôle, agissant sur la polarisation des courants continu et alternatif, a été mis au point pour maintenir les potentiels OFF de pointe maximal et minimal à l'intérieur de plages prédéfinies, et ce pendant des périodes prolongées et dans divers environnements. Ceci a permis d'établir un rapport entre l'absence ou l'apparition de corrosion et les variations dans les domaines d'immunité, de corrosion ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ) et de passivation, avec un pH allant de 9 à 14.

Le potentiel sans chute ohmique, la densité du courant et l'angle de phase ont été mesurés avec l'appareil CORREAC sur des éprouvettes subissant l'influence de courants alternatifs. Les résultats furent présentés en tant que courbes  $E_{\text{off}}$ -temps, I-temps et Lissajous  $E_{\text{off}}$ -I tout au long d'une période de courant alternatif.

Les résultats ont confirmé qu'il n'y a pas corrosion lorsque  $E_{\text{off}}$  est inférieur au potentiel d'immunité pour le pH concerné à tout moment de la période de courant alternatif. Les courants alternatifs pourraient empêcher la formation d'oxydes protecteurs lorsque le potentiel fluctue à l'intérieur de la zone de passivation ou oscille entre l'immunité et la passivation.

La protection cathodique de métaux soumis à l'influence de courants alternatifs nécessite par conséquent la définition de critères plus détaillés.

## ZUSAMMENFASSUNG

Ein Kontrollsystem, das die Gleichstrom- und Wechselstrompolarisation steuert, wurde entwickelt, um die Höchst- und Tiefstspitzenpotenziale OFF während langen Perioden und in unterschiedlichen Umgebungen innerhalb von vorher festgelegten Bereichen zu erhalten. Also konnte ein Zusammenhang zwischen Abwesenheit oder Auftreten einer Korrosion und Potentialschwankungen unter Immunitäts-, Korrosions- ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ) und Passivierungsbedingungen, mit pH-Werten zwischen 9 und 14, festgestellt werden.

Das IR-freie Potential, die Stromdichte und der Phasenwinkel wurden mit dem CORREAC-Gerät auf wechselstrombeeinflussten Proben gemessen. Die Ergebnisse wurden als  $E_{\text{off}}$ -Zeit-, I-Zeit-, und Lissajous  $E_{\text{off}}$ -I-Kurven über einer ganzen Wechselstromperiode verarbeitet.

Die Ergebnisse bestätigten, daß keine Korrosion auftrat, wenn  $E_{\text{off}}$  zu jedem Zeitpunkt der Wechselstromperiode niedriger als das Immunitätspotential für den betreffenden pH-Wert war. Wechselströme könnten die Bildung von Schutzoxiden verhindern, wenn das Potential innerhalb des Passivierungsbereiches oder zwischen Immunität und Passivierung schwankt.

Der Kathodenschutz von wechselstrombeeinflussten Metallen erfordert also die Bestimmung mehr detaillierter Kriterien.

## INTRODUCTION AND OUTLINE LITERATURE

AC induced corrosion has been a concern for more than 50 years, mostly for pipelines running parallel to overhead high voltage transmission lines. It is also a concern for concrete structures (bridges with attached power cables and tunnels for electrified railway).

It is not uncommon to measure AC voltage in the range of 15 to 100  $V_{\text{rms}}$  between a grounding rod and a coated pipe exposed to AC interference. 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 AC 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]. AC can also increase corrosion of Pb, Al, Cu and 50Sn50Sb in soils [2-4, 6].

An interesting observation was made for passive systems (steel in concrete, or stainless steel in sulphuric acid): AC currents produce a shift of the zero-current potential. Destruction of passivity by AC induced current was reported [7,8].

These shifts of potentials were analysed as a function of the shape of the anodic and cathodic E-I curves, assuming that these curves do not change with time [1,9]. The shifts depend on the frequency, the slope of the Tafel lines and 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, Dévay et al [10,11] showed that increasing cathodic dc currents superimposed to a constant amount of AC indeed decrease the corrosion rate, but not to a negligible amount.

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

A documented report was published in 1999 for the American Gas Association (PRC International) [11]. In 2000 CEOCOR published a booklet on « AC corrosion on cathodically protected pipelines. Guidelines for risk assessment and mitigation measures » [17].

The criteria to decide the implementation of AC corrosion mitigation methods are diverse. For safety reason, it is generally considered that the permanent AC voltage should be lower than  $50 V_{\text{rms}}$ . But AC corrosion may occur well below that value.

One criterion used in Germany suggests that there would be no AC corrosion when the rms AC current density is lower than  $2 \text{ mA/cm}^2$  ( $20 \text{ A/m}^2$ ) and that corrosion is highly suspected above  $10 \text{ mA/cm}^2$ . Between 2 and  $10 \text{ mA/cm}^2$ , corrosion may or may not occur depending on the nature of the soil [18].

If this is correct, the « safe » AC voltage (for less than  $2 \text{ mA/cm}^2$ ) can be calculated by a simplified expression, as a function of the size of the coating defect (diameter  $d$ ) and of the soil resistivity  $\rho$  [11]:

$$V_{\text{ac}} = I_{\text{ac}} \rho \pi d / 8 \quad (\text{units : V, A, ohm.m, m})$$

As an example, for a defect of  $1 \text{ cm}^2$  ( $d = 1,12 \text{ cm}$ ) and a low resistivity soil ( $2000 \text{ ohm.cm}$ ), the « safe » AC voltage would be  $1.75 V_{\text{rms}}$ . AC corrosion would be very probable above  $8.8 V_{\text{rms}}$ .

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 corrosion is almost certain; above 3, the risk is serious; below 2, the risk is less, although not necessarily totally absent.

Criteria based only on the AC current density probably have a limited significance. The criteria based on the ratio AC current density/DC current density consider a balance between the interference effects and the cathodic protection level, which is more reasonable. However, the criteria based only on current density are not fundamentally correct. It is much more sound scientifically to base a no-corrosion criterion on both the current density and the IR-free 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.

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

This system has now been used extensively in laboratory and field surveys to study the conditions, the mechanisms and the importance of AC corrosion and to identify where and when AC corrosion is taking place (depending on locations, parallelisms, power load, train traffic load ...).

Previous studies [22] suggested that, under some circumstances, corrosion could occur in passivating alkaline solutions, when the maximum AC peak potential is in a passivation domain. Conversely, corrosion is not possible when the IR-free potential is at all times below the immunity potential. But very high pH can exist in front of coating defects on pipelines under cathodic protection. In these conditions, the immunity potential is significantly lower than the classical CP criterion of  $-850 \text{ mV}_{\text{Cu/CuSO}_4}$ .

The aim of this part of the study is to investigate detailed criteria for the occurrence and the importance of AC corrosion by considering the peak potentials and the polarity of DC + AC current peaks in particular at high pH and in passivating solutions.

## MATERIALS AND METHODS

The approach is to control the DC+AC polarisation conditions during long periods of time and to exploit the output of the CORREAC instrumentation to assess the existence and the importance of corrosion.

Details on the instrumentation are given in [22]. The results are represented as sine curves for the IR-free potential and the current density, and as Lissajous figures in an E-I plot. The exiting (anodic) current density and the impedance are also used for the interpretation.

Tests were conducted in three solutions:

- at pH 14, in NaOH 1 M (deaerated to prevent carbonation),
- at pH 10, in a Na<sub>2</sub>CO<sub>3</sub> - NaHCO<sub>3</sub> buffer, with a strong stirring to avoid an increase of pH due to CP,
- at pH 9.14, in a passivating solution (NaHCO<sub>3</sub> 0,1 M + Na<sub>3</sub>PO<sub>4</sub> 0,01 M).

At pH 10 (Na<sub>2</sub>CO<sub>3</sub> + NaHCO<sub>3</sub>), a series of CORREAC measurements under controlled DC + AC polarisation conditions were made in various potential ranges to show different reactions (hydrogen evolution, corrosion, passivation etc.).

Longer tests (one week) were conducted under selected pH and potential ranges, to show the absence or presence of corrosion and the type of corrosion and corrosion products. The conditions of these tests were selected as follows:

- at pH 14, permanently in the immunity domain (test nr.1),
- at pH 14, in the corrosion domain at high pH (test nr.2),
- at pH 10, between the immunity domain and the Fe<sub>3</sub>O<sub>4</sub> stability domain (test nr.3),
- permanently in the Fe<sub>3</sub>O<sub>4</sub> domain (test nr.4),
- at pH 10, oscillating between the Fe<sub>3</sub>O<sub>4</sub> domain and the Fe<sub>2</sub>O<sub>3</sub> stability domain (test nr.5),
- at pH 9, in a passivating solution, and permanently in the Fe<sub>2</sub>O<sub>3</sub> domain (test nr.6).

These conditions are represented in [figure 1](#).

A specially designed electronic regulator controlled separately the DC and AC polarisation.

Disk electrodes of carbon steel with 1 cm<sup>2</sup> exposed area limited by an O-ring were used. The steel was polished (1200) and weighted before the tests. After the tests, the samples were examined under binocular, analysed for surface films (EDAX, X-ray diffraction), pickled and weighted again. X-ray diffraction was of little help, because of the thin films.

## RESULTS

[Figure 2](#) shows the CORREAC results for controlled AC+DC polarisation in the whole potential range in a Na<sub>2</sub>CO<sub>3</sub> + NaHCO<sub>3</sub> solution at pH 10. These curves suggest that:

- hydrogen evolution occurs below about -1200 or -1300 -1400 mV<sub>sce</sub>,
- hydrogen evolution together with some corrosion occurs in the range -1200 to -1000 mV<sub>sce</sub>,
- a more rapid corrosion occurs in the range -1000 to -700 mV<sub>sce</sub>,
- corrosion occurs, with a tendency for some passivation, in the range -700 to -400 mV<sub>sce</sub>. The negative slope (indicative of a phase angle greater than 90°) corresponds to the transition between the corrosion peak and passivation,
- passivation without corrosion is observed between -300 and +800 mV<sub>sce</sub>,
- oxygen evolution is clearly seen above +1100 mV<sub>sce</sub>.

The results of the longer tests (one week under constant DC+AC polarisation) are summarised in [table 1](#). The solution, potential range, AC current and maximum anodic current density, phase angle, impedance, corrosion and corrosion products are indicated. Comments are given below:

- [Test nr.1](#) (always in the immunity domain: pH 14, between -1400 and -1300 mV<sub>sce</sub>).

The Lissajous figure shows an ellipse with a lower part which is very slightly deformed towards a more linear shape, indicating some slight hydrogen evolution ([figure 3](#)). The AC current density is low (5.5 mA/cm<sup>2</sup>), and the phase angle is 40 to 50°. The impedance is rather low, compared to the other tests, indicating a very moderate reaction.

Binocular and weight loss examination indicate no corrosion, after one week.

- [Test nr.2](#) (in the corrosion domain at pH 14, between -1200 and -1000 mV<sub>sce</sub>).

The Lissajous figure does not give an indication of hydrogen evolution ([figure 4](#)). The very slightly deformed upper part of the ellipse suggests that the corrosion domain is approached.

The AC current density and the phase angle are higher (8 mA/cm<sup>2</sup> and 65°). Impedance is also moderate (8 Ohm/cm<sup>2</sup>).

After one week, a thin brown-black film covers the sample. Binocular and weight loss examination indicate a very slight general corrosion.

- Test nr.3 (in both the immunity domain and the Fe<sub>3</sub>O<sub>4</sub> domain, at pH 10, and between -1300 and -700 mV<sub>sce</sub>).

The Lissajous figure is composed of two ellipses. The upper one is more horizontal and indicates some corrosion (figure 5).

The AC current density is much higher (33 mA/cm<sup>2</sup>). The phase angle and the impedance are of the same magnitude as before (60° and 6 ohm/cm<sup>2</sup>).

A thicker brown-black film covers the sample. Binocular and weight loss examination indicate an important general corrosion. The highest corrosion rate for this test was estimated at 0.11 mm/y.

- Test nr.4 (in the Fe<sub>3</sub>O<sub>4</sub> stability domain at pH 10, between -800 and -500 mV<sub>sce</sub>).

The Lissajous figure is flat and has a negative slope (figure 6).

The AC current density is higher (74 mA/cm<sup>2</sup>), the phase angle is close to 180°, and the impedance is low (1,5 ohm/cm<sup>2</sup>). This corresponds to the zone of the polarisation curve between the oxidation peak at low potential and the passivation range, where the E-I slope is also negative.

A thick brown-black film on the sample corresponds to an important general corrosion.

- Test nr.5 (in both the stability domains of Fe<sub>3</sub>O<sub>4</sub> and of Fe<sub>2</sub>O<sub>3</sub> at pH 10, between -700 and +200 mV<sub>sce</sub>).

The curves clearly show a combination of two ellipses: the lower one (with a more horizontal slope) corresponds to corrosion in the Fe<sub>3</sub>O<sub>4</sub> domain, and the upper one with a large phase angle corresponds to a tendency to passivation, with formation of Fe<sub>2</sub>O<sub>3</sub> (figure 7). There is no corrosion on the exposed surface, but some crevice corrosion is present under the O-ring.

- Test nr.6 (in the Fe<sub>2</sub>O<sub>3</sub> stability domain, in a passivating solution at pH 9.14, between -200 and +400 mV<sub>sce</sub>).

The AC current is particularly low (1,6 mA/cm<sup>2</sup>), the phase angle is near 90° and the impedance is high (135 ohm/cm<sup>2</sup>) (figure 8).

A thin transparent film covers the sample, with no corrosion on the exposed surface. Crevice corrosion is again visible under the O-ring.

## DISCUSSION

The Lissajous curves produced by the instrumentation give a good indication of the various reactions that take place along a period. In particular, hydrogen evolution, corrosion, passivation, passivation breakdown and oxygen evolution can be clearly identified.

The test nr.4 is special, in the sense that its potential range corresponds to the upper part of a corrosion peak, where the current decreases as the potential increases. This corresponds to a phase angle greater than 90°, and in fact close to 180°.

While the current density is high and the impedance is low, the corrosion rate for test nr.4 is much lower than for test nr.3, which corresponds to the lower part of the corrosion peak. This indicates that the phase angle must be considered, together with the current density and the impedance to assess the corrosion rate. Such negative phase angles were also observed in the field.

The analysis of the Lissajous curves, of the potential range, of the current densities and of the impedance allows making a correct, if not fully precise, assessment of the AC corrosion rate.

It is noted that CORREAC measurements made in the field on smaller coating defects occasionally showed maximum anodic current densities twice as high as those reproduced in the laboratory.

The shape and the potential ranges for the various aspects of the Lissajous curves can give an indication on the actual pH and hydrogen evolution conditions. For example, hydrogen evolution that occurs only at

potentials lower than  $-1450 \text{ mV}_{\text{sc}}$  is indicative of a pH value around 14. The actual pH is indeed important to determine the protection criteria under AC interference.

It was again confirmed that corrosion could occur under the influence of AC currents in environments and in potential ranges that would be perfectly passivating if AC currents were absent. This is a special feature of AC induced corrosion that deserves a more fundamental study.

Presently, the protection criteria under AC influence are clear: the maximum IR-free potential must remain at all time in the immunity domain, and the existence of very high pH must be considered to define the immunity potential. Protection criteria may thus be more severe in the presence than in the absence of AC, because superimposed AC currents can destroy passivation films that would be perfectly protective in the absence of AC.

## CONCLUSIONS AND FUTURE WORK

Previous results on AC induced corrosion were confirmed and detailed during this study.

Some corrosion was observed in potential and pH ranges where, in the absence of AC, steel would be perfectly protected by passivating films. The detailed reasons for this deserve a more fundamental study.

In the presence of AC currents, cathodic protection should thus maintain the potential permanently in the immunity domain, even at high pH.

The importance of AC induced corrosion is linked to a series of parameters such as the IR-free potential range, the value of the AC current density and the polarity of the peak value of the current, the impedance, the phase angle as well as the type of reactions and the local pH. All these parameters can be identified by the CORREAL system.

The future actions in this research are aimed at calibrating the output of the measuring system in terms of corrosion penetration rates for different sizes of defects.

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## TABLE AND FIGURES

**Table 1 : Summary of test results under controlled DC+AC polarisation**

Test nr. Test conditions	iAC mA/cm <sup>2</sup> rms	imax mA/cm <sup>2</sup>	$\phi$ °	Z $\Omega$	p mm/y	corrosion-no corrosion
nr.1 In the immunity domain (pH 14, -1400 to -1300 mV <sub>sce</sub> )	5.5	3.0	50	7	0.000	no corrosion
nr.2 In the corrosion domain (pH 14, -1200 to -1000 mV <sub>sce</sub> )	8.0	12.5	65	8	0.046	very slight general corr.
nr.3 In immunity and Fe <sub>3</sub> O <sub>4</sub> domains (pH 10, -1300 to -700 mV <sub>sce</sub> )	33.0	43.0	60	6	0.119	important general corr.
nr.4 In the Fe <sub>3</sub> O <sub>4</sub> domain (pH 10, -800 to -500 mV <sub>sce</sub> )	74.0	103.0	170	1.5	0.078	general corrosion
nr.5 In Fe <sub>3</sub> O <sub>4</sub> and Fe <sub>2</sub> O <sub>3</sub> domains (pH 10, -700 to +200 mV <sub>sce</sub> )	17.0	26.0	80	17	0.056	crevice corrosion
nr.6 In the Fe <sub>2</sub> O <sub>3</sub> domain (pH 9.14, -200 to +400 mV <sub>sce</sub> )	1.6	2.5	80	135	0.026	crevice corrosion

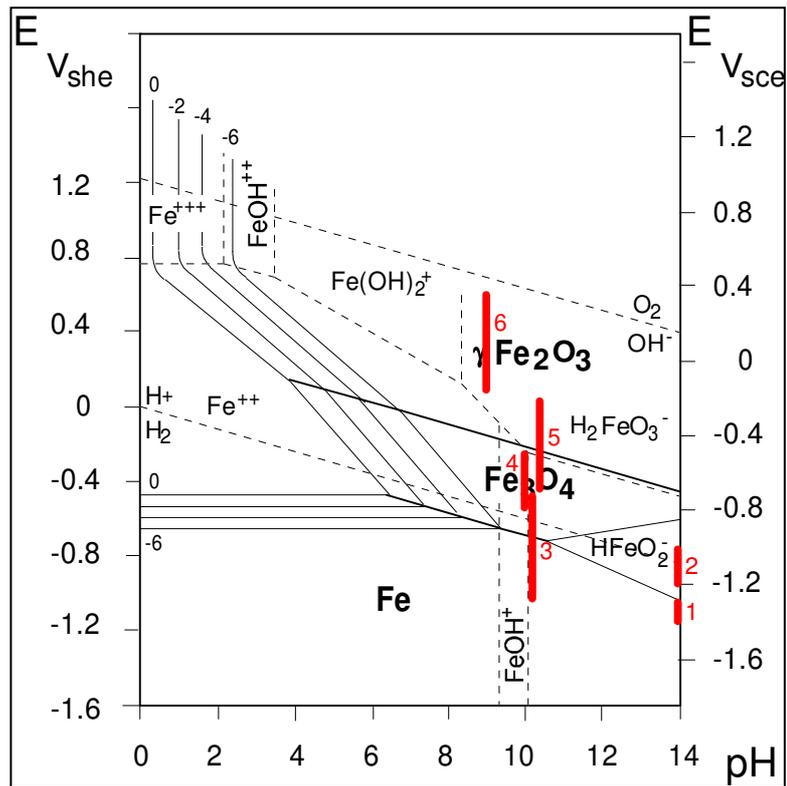


Figure 1 : Selected test conditions, under controlled DC+AC polarisation

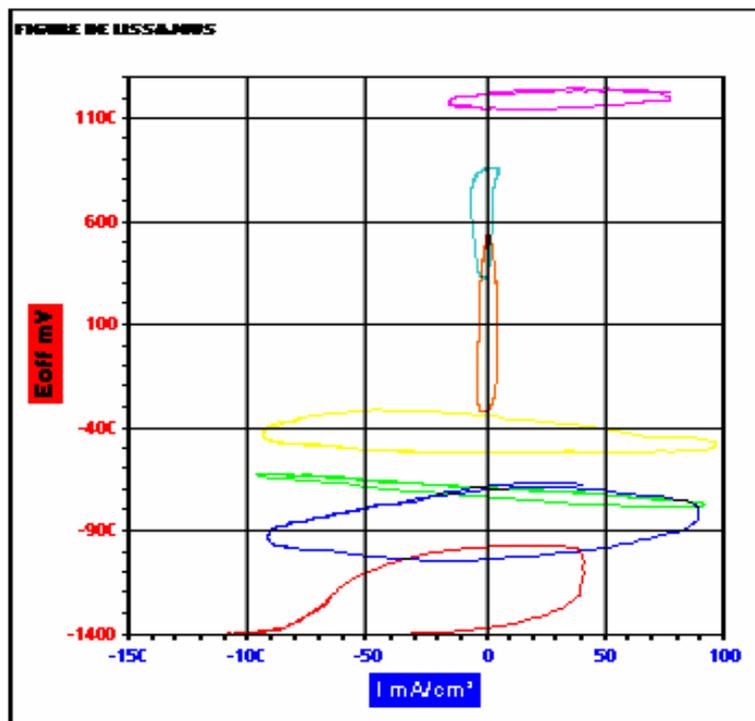


Figure 2: CORREAC responses for controlled AC+DC polarisations in the whole potential range.

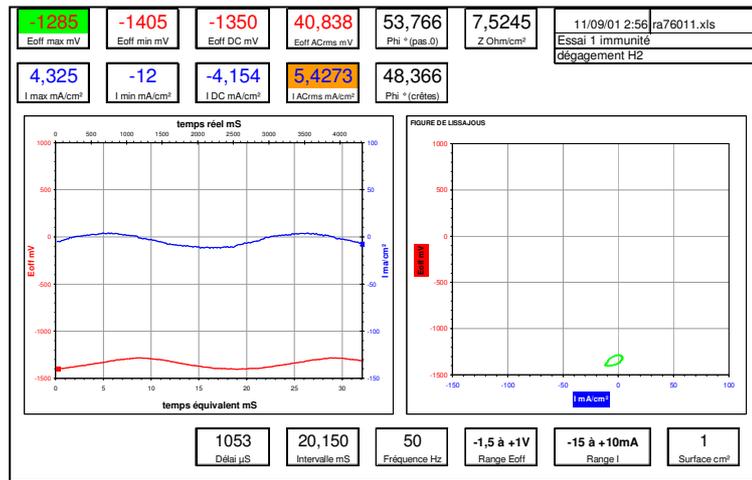


Figure 3 : IR-free potential and current density versus time, and E-I Lissajous curve for steel at pH 14, between -1400 and -1300 mV<sub>sce</sub> (test nr.1)

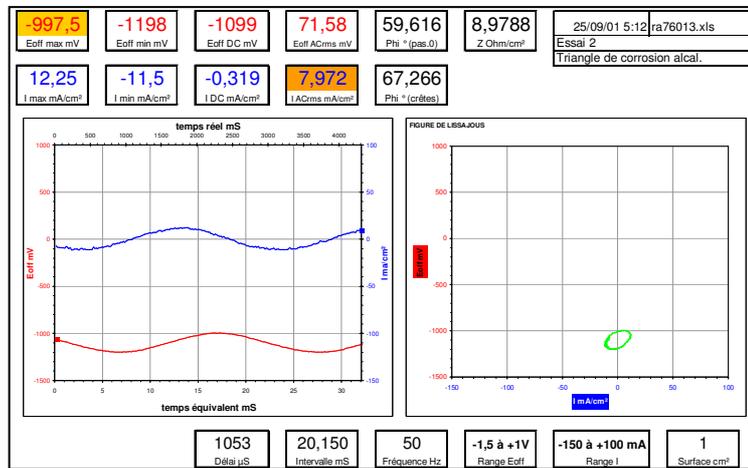


Figure 4 : IR-free potential and current density versus time, and E-I Lissajous figure for steel at pH 14, between -1200 and -1000 mV<sub>sce</sub> (test nr.2)

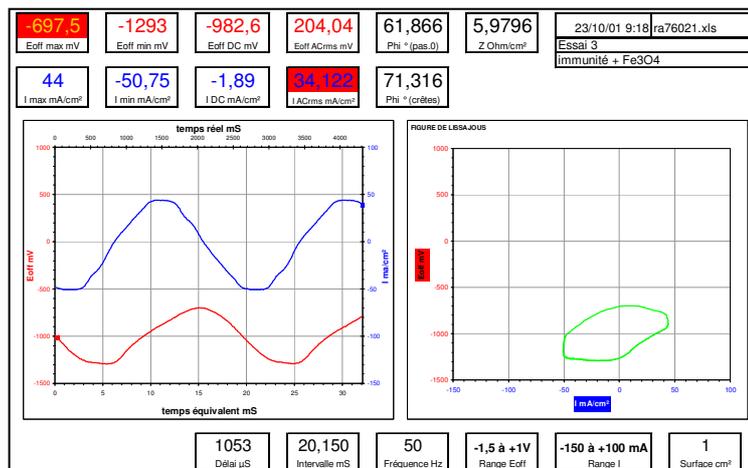


Figure 5 : IR-free potential and current density versus time, and E-I Lissajous figure for steel at pH 10, between -1300 and -700 mV<sub>sce</sub> (test nr.3)

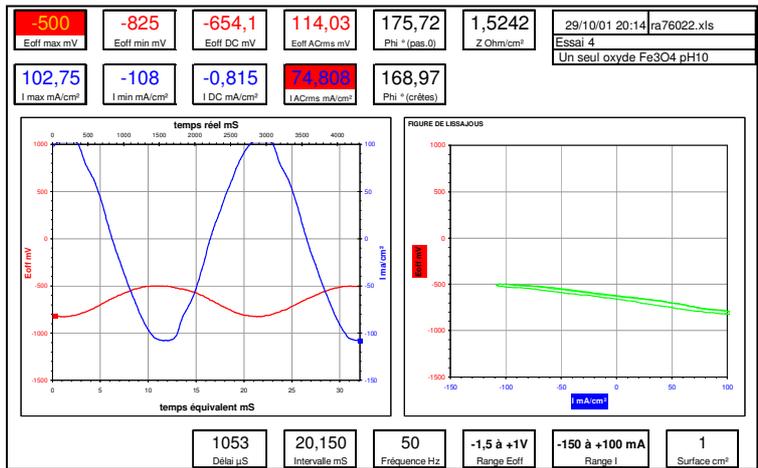


Figure 6 : IR-free potential and current density versus, and E-I Lissajous figure for steel at pH 10, between -800 and -500 mV<sub>sce</sub> (test nr.4)

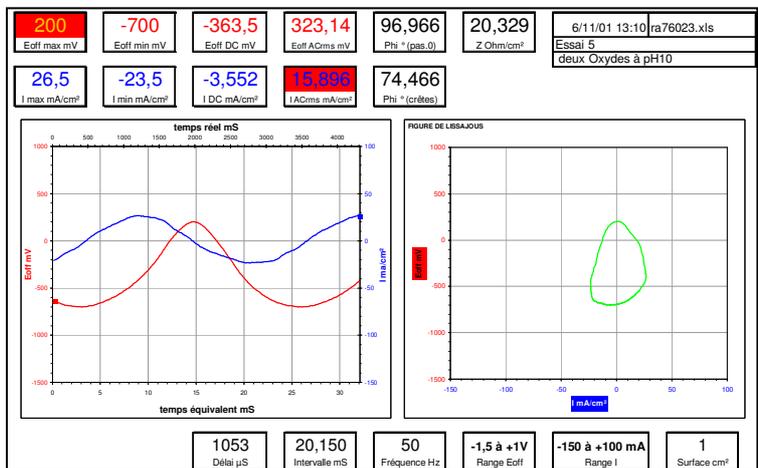


Figure 7 : IR-free potential and current density versus time, and E-I Lissajous figure for steel at pH 10, between -700 and +200 mV<sub>sce</sub> (test nr.5)

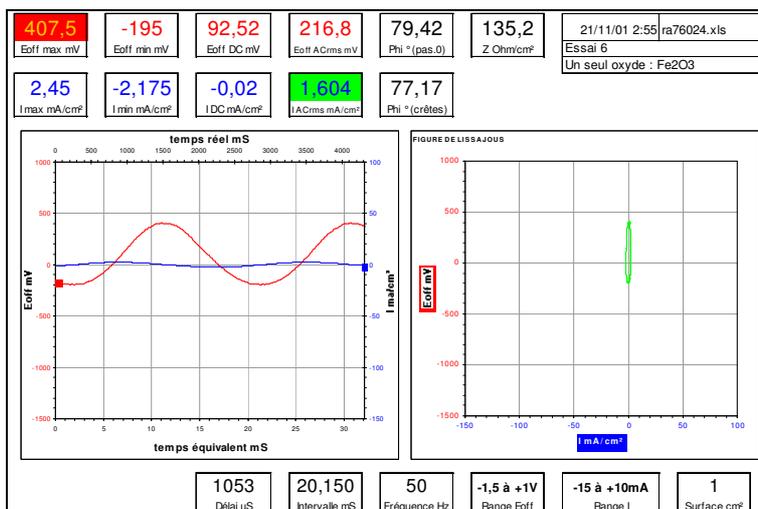


Figure 8 : IR-free potential and current density versus time, and E-I Lissajous figure for steel at pH 9.14, between -200 and +400 mV<sub>sce</sub> (test nr.6)