Copyright 2010, ABRACO
Trabalho apresentado durante o INTERCORR 2010, em Fortaleza/CE no mês de maio de 2010.
As informações e opiniões contidas neste trabalho são de exclusiva responsabilidade do(s) autor(es).

A new thermodynamic criterion and a new field methodology to verify the probability of AC corrosion in buried pipelines

Zehbour Panossian[1], Sérgio E.A. Filho[2], Neusvaldo L. de Almeida[3], Diogo de L Silva[4], Mário L. Pereira Filho[5], Eduardo W. Laurino[6], João Hipólito L. Oliver[7], José A. C. Albertini[8], Gutemberg S. Pimenta[9]

Abstract

One of the current and important challenges faced by cathodic protection professionals is to access the corrosion probability of cathodically protected buried pipes subject to alternating current (AC) interference (i.e., AC corrosion). In practice, it is very common for cathodically protected pipes to be buried adjacent high voltage AC electrical power lines and electric energy distribution systems. These electric power systems can produce stray AC current in soil or induced AC current in the pipe. This AC current can cause severe corrosion on buried pipes which are supposed to be catholically protected. There are several criteria cited by the literature to evaluate the probability of AC corrosion; however, they are inefficient since failures due to AC corrosion have been reported on pipelines which displayed electric and electrochemical parameters within the acceptable limits of those criteria. This work has as an objective to propose a new thermodynamic criterion and presents all the necessary equipment for obtaining in the field the necessary electric and electrochemical parameters to apply the proposed criterion in a safe way. Those parameters are obtained from the waveform of pipe-soil interface AC+DC *off* potential. Two devices were developed: a probe composed of a modified permanent $Cu/CuSO_4$ reference electrode coupled with corrosion coupons and an electronic alternating switch device. Some measurements conducted on existing pipelines are also presented.

Keywords: cathodic protection, AC current, AC corrosion.

[1] Doutora em Ciências – Instituto de Pesquisas Tecnológicas
[2] Químico – Instituto de Pesquisas Tecnológicas
[3] Mestre em Engenharia – Instituto de Pesquisas Tecnológicas
[4] Técnico em Metalurgia – Instituto de Pesquisas tecnológicas
[5] Doutor em Engenharia Elétrica – Instituto de Pesquisas Tecnológicas
[6] Consultor Técnico – Petrobras/Transpetro
[8] Consultor Técnico – Petrobras/Transpetro
[9] Engenheiro – Petrobras/Transpetro
[10] Consultor Técnico – Petrobras/Cenpes

Introduction

Lately, AC corrosion in cathodically protected pipelines has attracted the attention of many professionals and researchers. Many studies have shown that the occurrence of AC corrosion depends on the AC current density, the AC frequency, the degree of cathodic protection and on soil characteristics. There are several criteria adopted by literature to evaluate the probability of AC corrosion (1-3).

However, these criteria are contradictory and inefficient since failures due to AC corrosion have been occurring on pipelines which displayed electric and electrochemical parameters within the acceptable limits of those criteria.

A critical analysis of the literature showed that all the above mentioned criteria are based on field measurements related individually to the AC or DC current densities that, are obtained experimentally by using corrosion coupons installed in fields.

Previous studies conducted by IPT (Institute for Technological Research) and Petrobras (4-7) introduced a new approach for AC assessment which consider the concept of coupling of AC current to the DC current and the potential-time waveform of this coupling.

Based on this new approach, a mechanism for AC corrosion was proposed (7). It was concluded that AC corrosion is a consequence of oscillation of metal/electrolyte interface, which depending on the electrolyte pH, puts the system alternatively within the active and immune domains or within the passive and immune domains. Steel corrosion occurs due to the irreversibility of an iron corrosion reaction in acid, in neutral or slight alkaline electrolytes and due to the impossibility of the formation of a passive film in alkaline electrolytes (pH <14). In excessively alkaline electrolytes (pH>14), an incipient corrosion occurs due to the formation and the reduction of a thin oxide film on metal surfaces.

Additionally, a new thermodynamic criterion for AC corrosion prediction was proposed which is as follows (7); AC corrosion does not occur when the peak of the IR-free AC plus DC coupling potential-time waveform remains below the equilibrium potential of the iron corrosion reaction.

But a new task arises from this proposal; how to obtain an AC plus DC potential versus time waveform without the influence of IR-drop .

Traditionally, IR-free DC potential (off-potential) is obtained by interrupting the current coming from the rectifier used for cathodic protection and simultaneously measuring the on and off pipe to soil potentials. When the current is interrupted, an immediate voltage shift occurs which is the result of eliminating the IR-drop as shown in Figure 1. The potential immediately after this shift (instant-off potential measured between 0.1 s and 1.0 s) is the IR-free pipe to soil potential.

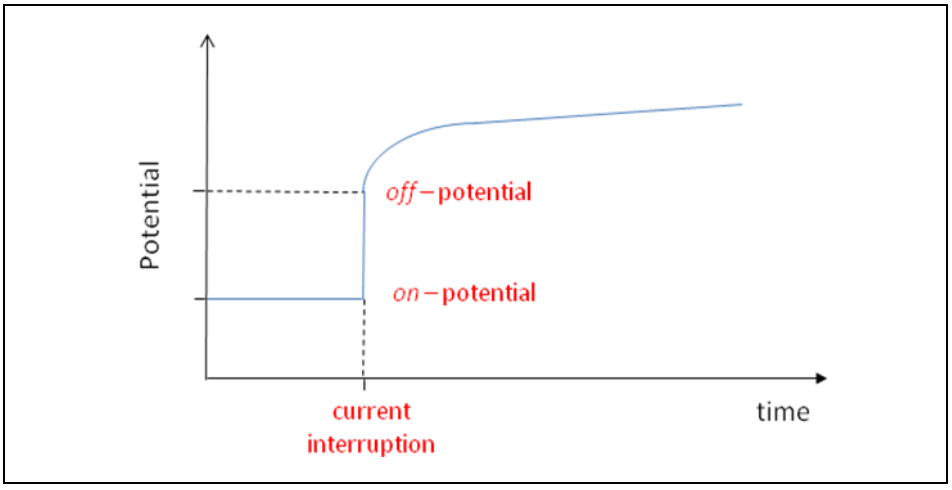


FIGURE 1 – Typical polarization decay curve indicating the on-potential and off-potential values

If there are installed corrosion coupons, the same procedure can be adopted. In this case, the current which passes through the coupon must be interrupted.

The above mentioned procedure is suitable for the IR-free pipe to soil potential only in the absence of other DC or AC currents. Where cathodically protected pipes are influenced by AC or DC interferences, the obtained pipe to soil potential values are not IR-free.

Thus, the objective was to develop the necessary devices and equipment for obtaining, in the field, the necessary electric and electrochemical parameters to apply the proposed criterion in a safe way. Those parameters are obtained from the waveform of pipe-soil interface AC+DC *off* potential.

Initially, this paper describes the developed devices and equipment. Afterwards, their use is presented including the adopted methodology and the obtained results.

A description of corrosion probes

In the market, corrosion probes are available that contain a $Cu/CuSO_4$ reference electrode and a corrosion coupon. These probes are known as permanent reference electrodes. They are used on cathodically protected pipelines to estimate the corrosion rate and to monitor pipe to soil potentials. The corrosion coupon is electrically connected to the pipe through the test points (TP) and it is used to estimate the corrosion rates. The reference electrode is used to monitor the pipe to soil potential corresponding to the cathodic protection.

In general, these probes remain buried for long periods. In practice, errors in the measured values are observed with time. Experimental field inspection of long-term buried probes showed that these errors are a consequence of the passivation of the test coupon due to the diffusion of copper ions that passed through the porous plate of the reference electrode and moved toward the coupon and plated on it by galvanic deposition. This deposition is responsible for the passivation of the coupon.

As one of the objectives of this work was the monitoring of the pipe to soil potential using the above mentioned probes, it was first decided to modify the reference electrode in order to avoid the coupon passivation. Thus, a modification was introduced in the reference electrode to avoid the leakage of the copper ions and, consequently, coupon passivation.

The first modification consisted of replacing the porous plate of the traditional $Cu/CuSO_4$ reference electrode tip by a titanium plate. The intention was to avoid the leakage of copper ions from the reservoir of the reference electrode through the porous plate (Figure 2). The new electrode was named $Cu/CuSO_4$-Ti modified reference electrode.

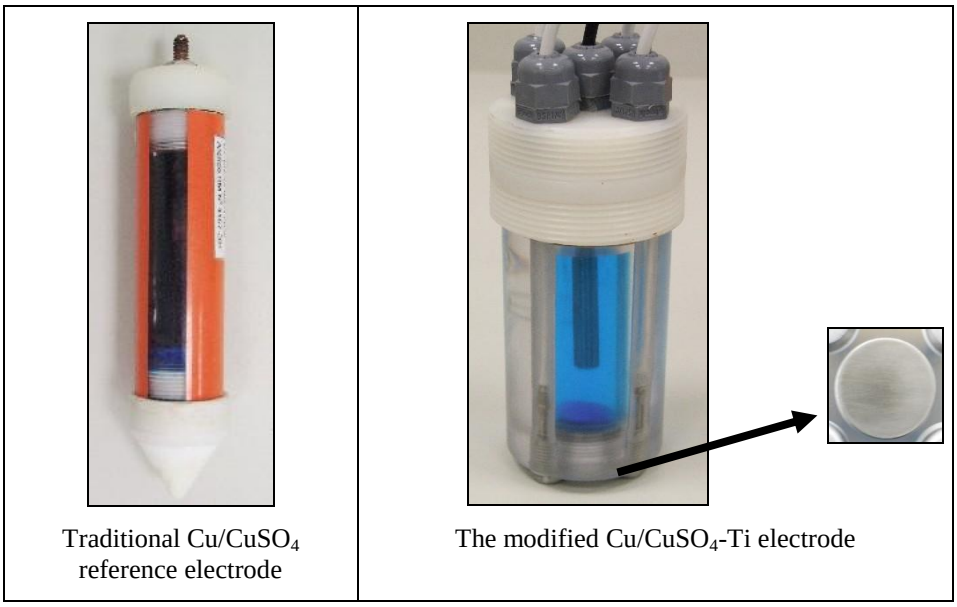


FIGURE 2 – The traditional $Cu/CuSO_4$ reference electrode and the modified $Cu/CuSO_4$-Ti electrode

To verify whether this substitution caused variations to the potential values, both electrodes, ($Cu/CuSO_4$ and $Cu/CuSO_4$-Ti) were checked with a standard hydrogen reference electrode. Both electrodes were also used for the determination of the interface potential of steel samples immersed in various aqueous solutions adopting nonpolarized (open circuit) and polarized conditions. The obtained values with the two electrodes were exactly the same.

The $Cu/CuSO_4$-Ti modified reference electrode was used in the field for five months, without presenting any type of problem.

Once the problem of passivation of the steel was resolved, a new corrosion coupon was developed. It was decided to use more than one corrosion coupon in order to obtain more than one corrosion rate value. This allowed the determination of a mean value for the corrosion rate. Additionally, the use of more than one coupon permitted the elimination of interference from stray currents present in the soil.

To understand the concept of the elimination of the stray currents, all the currents captured by the coupons should be considered. These currents are the following ones:

- the current coming from the cathodic protection system passes through the cable used for the electric connection of the coupon with the pipe (test point);

- the stray AC or DC currents come through the soil from external sources.
- for example, currents come from high voltage transmission lines and/or from electric supplying systems.

Figure 3 shows a probe with four corrosion coupons symmetrically positioned around the $Cu/CuSO_4$-Ti reference electrode. Coupons **1** and **3** are positioned at the pipe x-axis cross section and coupons **2** and **4** at the y/axis cross section. In this example, the stray currents were represented by a system of Cartesian coordinates, with components $\mathbf{I_X}$ and I_Y, and the circulating current between the pipe and the coupon, through test point (PT), was represented by **I**.

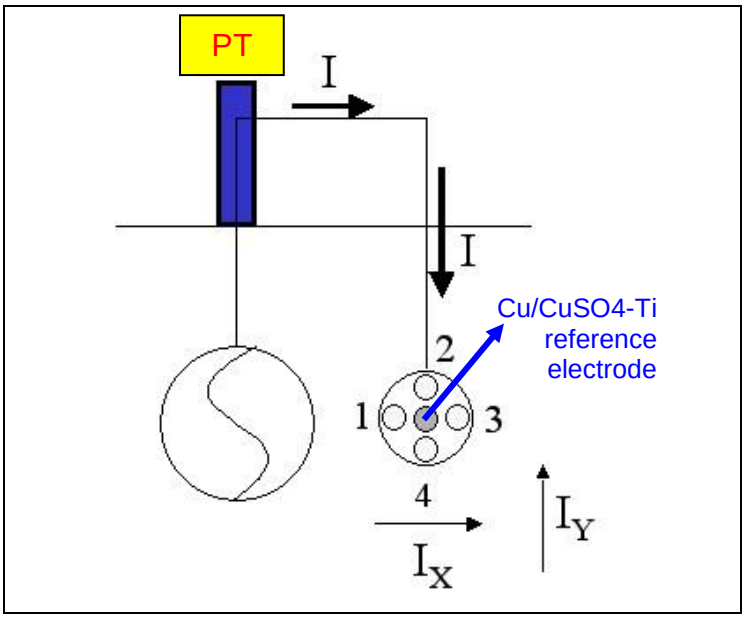


FIGURE 3 – The circulating currents through the corrosion coupons of the new corrosion probe

The potential of each coupon can be represented as follows:

In direction x

$$V_1 = I.Z_0 - I_x.\ Z_X$$

$$V_3 = I.Z_0 + I_x.\ Z_X$$

In direction y

$$V_2 = I.Z_0 + I_Y.\ Z_Y$$

$$V_4 = I.Z_0 - I_Y.\ Z_Y$$

Where:

I = total current

I_x = current (direction x)

I_y = current (direction y)

Z_0 = coupon impedance due to the current coming from the cathodic protection system which passes through the cable used for the electric connection of the coupon with the pipe (test point)

Z_x ou Z_y = impedance due to the stray AC or DC currents coming through the soil from external sources

In the measurement of the pipe to soil on-potential, the component due to the stray current coming from the soil and entering into **coupon 1** (I_xZ_x) is annulled by the component due to the stray current entering into **coupon 3** (I_yZ_y). Thus, the measured on-potential refers only to the CP current flowing to the pipe. The same consideration is valid for **coupon 2** and **coupon 4**.

The use of two coupons, disposed symmetrically to the reference electrode, is also suitable because the potential is annulled due to the stray currents coming from the soil. However, two values of a corrosion range were considered insufficient for the mean value estimation for the corrosion rate.

If three coupons were installed, the potential due to the stray currents coming from the soil could be annulled only if the reference electrode was put to the baricenter of the triangle formed by the position of the three coupons.

Thus, in order to simplify the construction of the corrosion coupon and to obtain four corrosion rate values, it was opted for a probe composed of four coupons.

Finally, it is worth mentioning that axis z (vertical direction) was not considered, as the four coupons are supposed to be installed on the same plane, parallel to the surface of the soil.

Using the developed probe and a portable oscilloscope, it is possible to obtain the AC plus DC coupling on-potential versus time waveform. From this on-potential waveform, it is possible to extract some important data of cathodically-protected buried pipes. These data include the cathodic protection on-potential (DC potential), the effective AC on-potential, the effective AC plus DC on-potential and the peak on-potential of the AC plus DC potential-time waveform. Additionally, it is still possible to analyze the harmonic content of the potential-time waveform and to map the possible interference sources in the measurement area. Figure 4 shows an example of an on-potential versus time waveform of buried cathodically protected pipe.

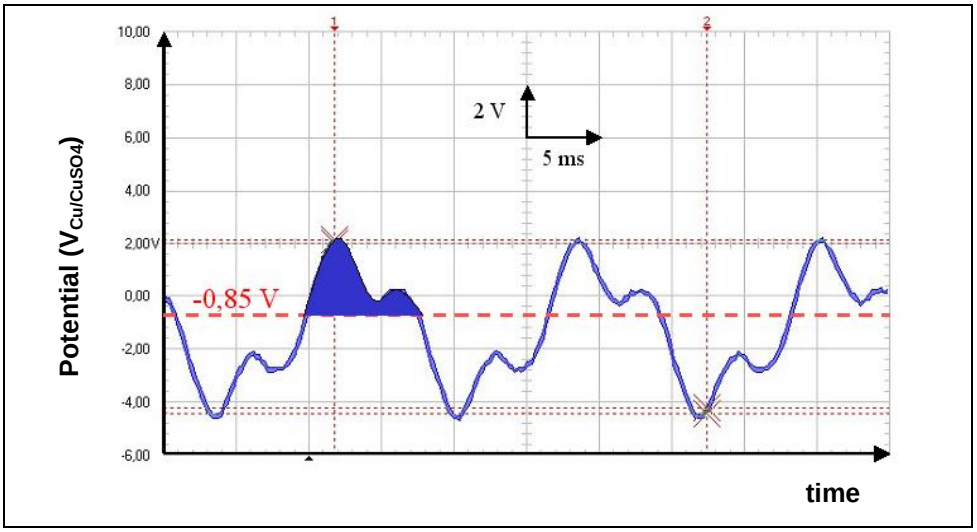


FIGURE 4 - AC plus DC on-potential versus time waveform obtained of a buried cathodically protected pipe. A four-coupon probe and a portable oscilloscope were used to obtain the waveform

The waveform shown in Figure 4 is the fingerprint of the pipe to soil on-potential of the inspected pipe. From this waveform, the harmonic content, as shown in Figure 5, can be obtained. Additionally, a map of the possible interference sources (see Table 1) can be obtained, as the harmonic content presents a direct relationship with the source of the AC stray currents (AC interferences).

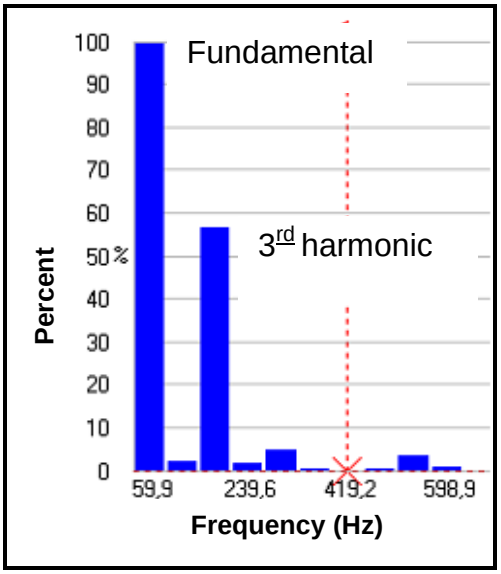


FIGURE 5 – Harmonic content of the pipe to soil on-potential versus time waveform presented in Figure 4 (percentage normalized in relation to the fundamental component (60 Hz)

TABLE 1
MAPPING OF POSSIBLE BURIED-PIPE INTERFERENCE SOURCES BY CHECKING HARMONIC CONTENT OBTAINED FROM AC PLUS DC ON-POTENTIAL VERSUS TIME WAVEFORM

Harmonic content	Main interference source
High 60 Hz component and low 180 Hz component	High voltage electric transmission lines
High 60 Hz component and high 180 Hz component	Electric supplying system
Low 60 Hz component and high 180 Hz component	Electric current coming from the neutral cable of electric supplying system
120 Hz component	Cathodic protection system

Analyzing the harmonic content shown in Figure 5, together with the mapping shown in Table 1, a strong influence of a high electric supplying was verified.

All the above discussion is related to AC plus DC coupling on-potential. However, for the adoption of the proposed thermodynamic criterion, it is necessary to obtain AC plus DC coupling off-potential versus time waveform.

The DC off-potential value procedure for cathodically protected pipes without stray current interferences is already established, as described previously. The same principle was used to obtain DC plus AC coupled off-potential versus time waveform. A device of electronic keying was projected of capable interrupting, in a synchronized way, the circulating current from the pipes to the coupons in an adequate time to obtain the *on*-potential AC + DC waveform and *off*-potential AC + DC waveform. In general, this time interval can be in order of milliseconds and it is depending on the waveform frequency. As an answer for this interruption, a curve is obtained that contains several on-potential and off-potential values, as will be shown later.

From the DC plus AC coupled off-potential waveform, it is possible to extract some important data of cathodically-protected buried pipes. These include the DC off-potential, the effective AC off-potential, the effective AC plus DC off-potential and the off-potential peak of AC plus DC waveform.

An assessment of AC current interference can be performed by comparing the peak of AC plus DC coupled off-potential waveform with the traditionally established value, that is $-0.85\ V_{Cu/CuSO4}$.

Field tests and their results

In order to validate the proposed thermodynamic criterion for the probability of AC corrosion occurrence and to test the a new probe, three probes were installed for five months at an existing buried pipe. One probe was installed at the OBATI site near the V 05-04 valve and two probes were installed at the test point (TP 34) of OPASA. Simultaneously, a coupon

corrosion reference electrode was installed at V 05-04 and TP 34 to verify corrosion rate and pitting depth.

During the exposition, periodic measurements were conducted in order to evaluate the evolution of the pipe to soil AC plus DC on- and off-potentials.

Initially, at each site, an AC plus DC coupled on-potential versus time waveform was obtained using a traditional $Cu/CuSO_4$ reference electrode positioned on the surface of the soil immediately above the pipe. Figure 6 shows one of the obtained waveforms. The peak of the on-potential waveform shown in Figure 6 corresponds to 52 $V_{Cu/CuSO4}$. This potential is very far from the pipe to soil interface potential as it is strongly influenced by IR due to the long distance between the pipe and the reference electrode.

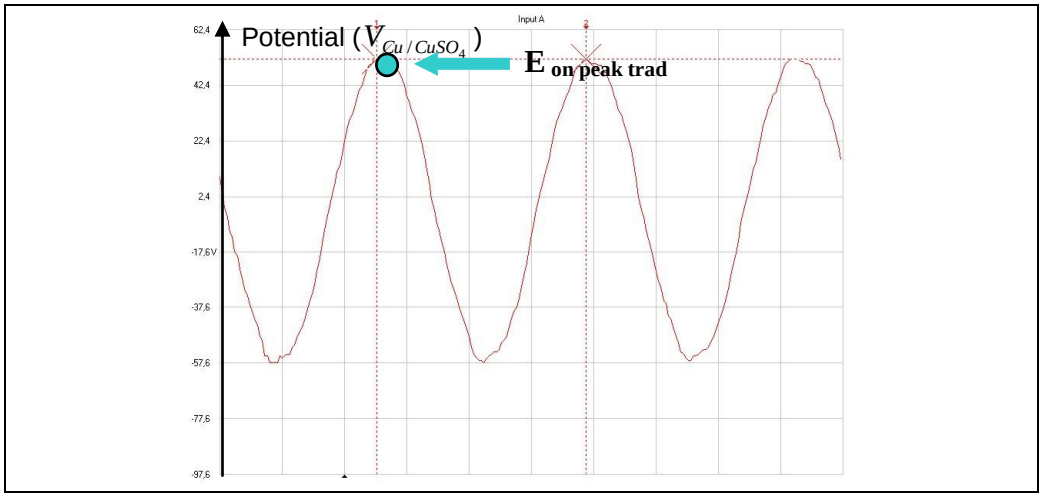


FIGURE 6 – AC plus DC on-potential versus time waveform obtained with the cathodically protected pipe at V-05-04. This waveform was obtained by using a traditional $Cu/CuSO_4$ reference electrode.

As described previously, for a thermodynamic assessment of AC corrosion it is necessary to obtain the IR-free AC plus DC coupled off-potential waveform.

Thus, a curve was obtained using the new probe (see Figure 7). As mentioned before, this curve contains several on-potential values (signed green points) and several off-potential values (signed with red points). With the former values, an AC plus DC coupled on-potential versus time waveform was obtained and with the latter an IR-free DC plus AC coupled off-potential waveform was obtained, as shown in Figure 8.

The peak of the on-potential waveform obtained with the probe is 8 $V_{Cu/CuSO4-Ti}$ is much lower than the one obtained with the traditional reference electrode (52 $V_{Cu/CuSO4-Ti}$ - Figure 6). This important difference is a consequence of the proximity of the $Cu/CuSO_4$-Ti reference electrode to the corrosion coupon which decreases the influence of IR-drop. The complete elimination of the IR influence is possible only when IR-free DC plus AC coupled off-potential waveform is considered.

In order to predict the occurrence of AC corrosion, the peak of AC plus DC coupled off-potential waveform was used that was 0 $V_{Cu/CuSO4-Ti}$. This value is higher than the

traditionally established -0.85 $V_{Cu/CuSO4}$. Thus the inspected pipe is subjected to AC corrosion.

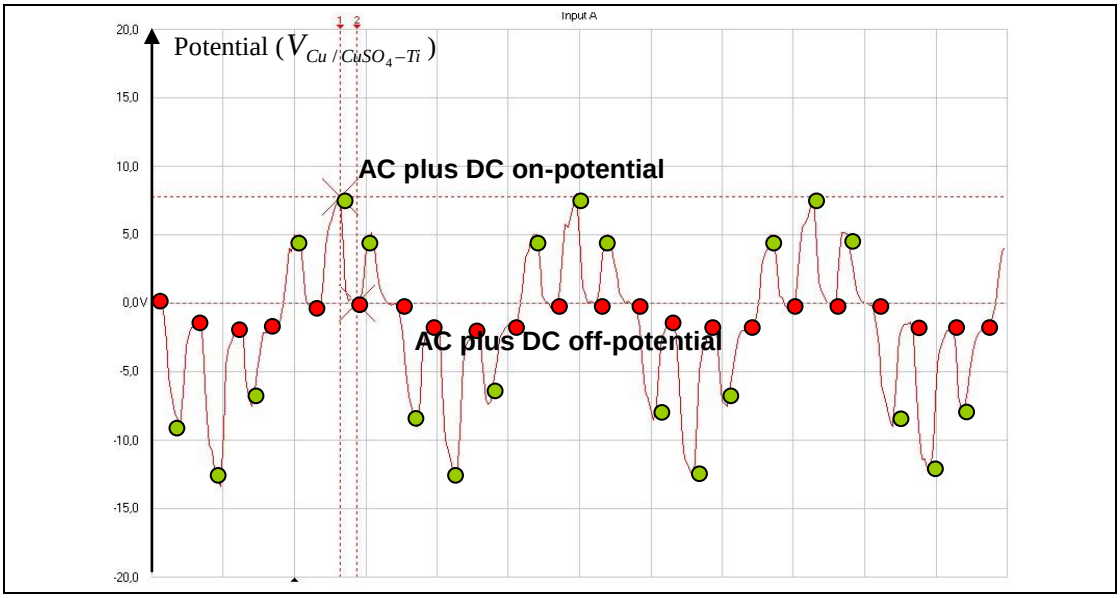


FIGURE 7 – AC plus DC potential versus time waveform obtained with the cathodically protected pipe at V 05-04. This waveform was obtained by using a developed probe.

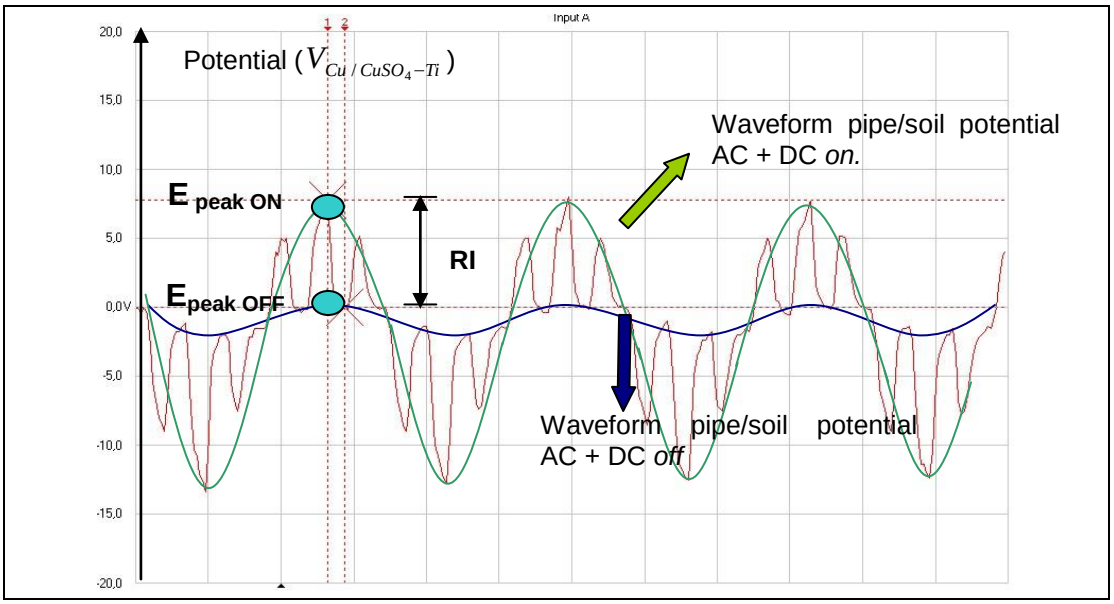


FIGURE 8 – AC plus DC coupled on-potential versus time waveform and IR-free AC plus DC coupled off-potential waveform was obtained, as shown in Figure 8.

Using the same above mentioned procedure, curves similar to Figure 6, Figure 7 and Figure 8 were obtained at the three selected site after 1, 2, 3, 4 and 5 months of exposition. From these curves, the $E_{on\ peak\ trad}$, $E_{on\ peak}$ and the $E_{off\ peak}$ values were obtained.

Figure 9 shows the $E_{on\ peak\ trad}$, $E_{on\ peak}$ and the $E_{off\ peak}$ values with the probe installed at OBATI (V 05-04) pipe. Figure 10 shows the same values except for the $E_{on\ peak\ trad}$. The difference between $E_{on\ peak\ trad}$ and $E_{on\ peak}$ is represented by **IR-1** and the difference between $E_{on\ peak}$ and $E_{off\ peak}$ is represented by **IR-2.**

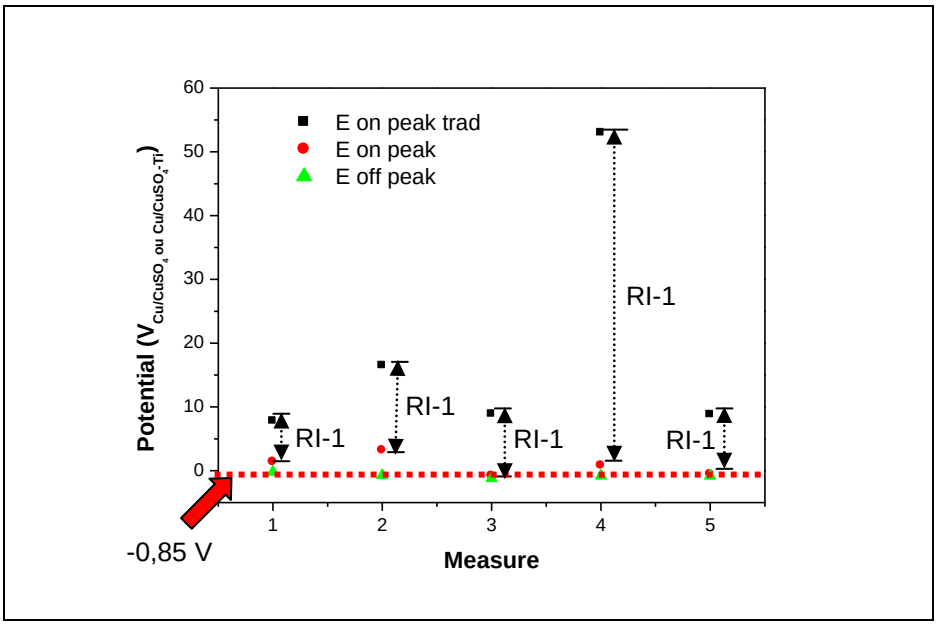


FIGURE 9 – $E_{on\ peak\ trad}$, $E_{on\ peak}$ and the $E_{off\ peak}$ values obtained at V 05-04.

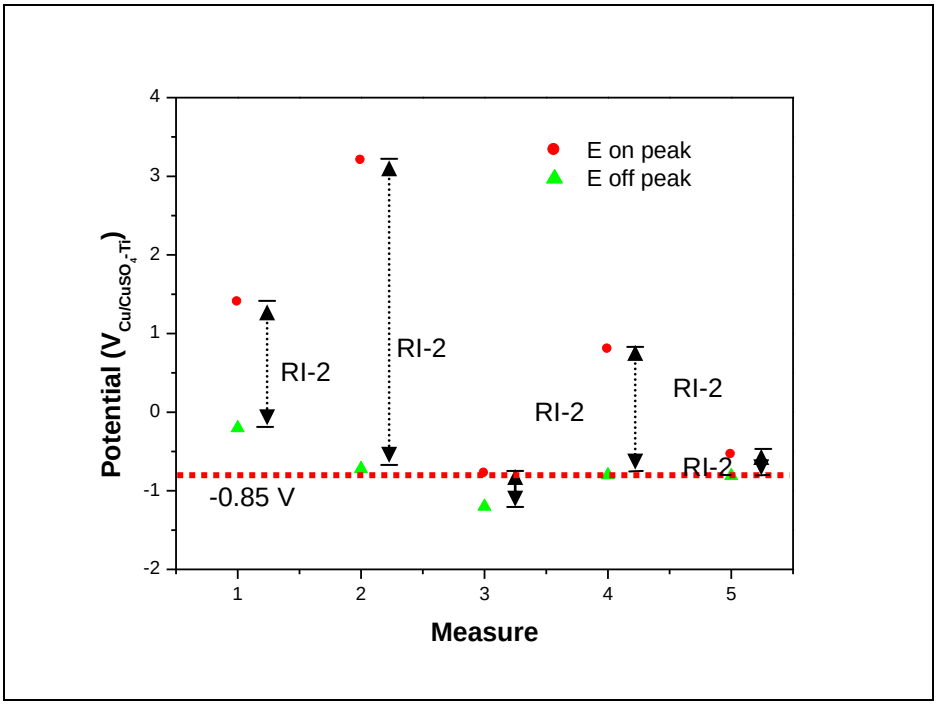


FIGURE 10 - $E_{on\ peak}$ and the $E_{off\ peak}$ values obtained at V 05-04.

Based on the results shown in Figures 9 and 10, it's possible to verify the strong influence of the IR-drop and the necessity of adopting a procedure which permits obtaining a IR-free pipe to soil potential. The simple approximation of the reference electrode to the pipe surface does not guarantee the complete elimination of the IR-drop. It is necessary the approximation of the reference electrode to the corrosion coupons.

By adopting the proposed thermodynamic criterion, it is possible to conclude that, the pipe are subject to AC corrosion. Only in one measurement was $E_{off\ peak}$ lower than the acceptable -0.85 $V_{Cu/CuSO4}$ value.

Figure 11 shows the $E_{on\ peak\ trad}$, $E_{on\ peak}$ and the $E_{off\ peak}$ values obtained for one of the probes installed at OPASA (TP 34) pipe. Figure 12 shows the same values except for the $E_{on\ peak\ trad}$. Again, the same conclusion obtained with the Figures 6 to 8 may be obtained.

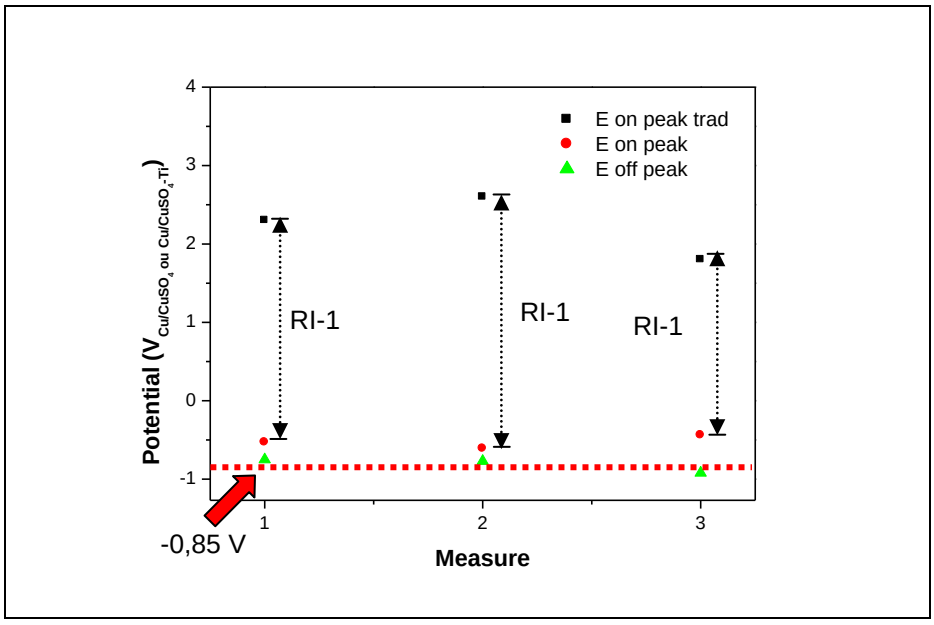


FIGURE 11 - $E_{on\ peak\ trad}$, $E_{on\ peak}$ and the $E_{off\ peak}$ values obtained with one of the probes installed at OPASA (TP 34)

The validation of the above results was obtained with the results presented in Table 2. In this Table, the coupon aspects and the mean corrosion rate are shown. It can be clearly verified that all the test coupons displayed generalized corrosion. This is in agreement with the results obtained by the probes which indicate, the coupons were not cathodically protected due to AC corrosion.

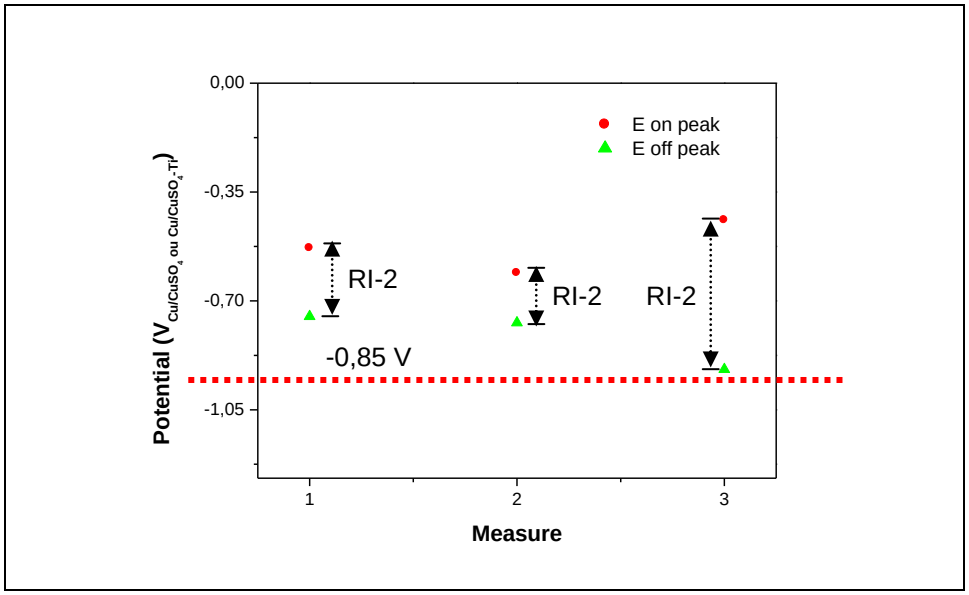
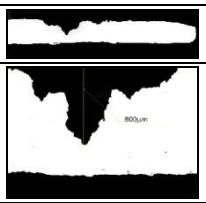
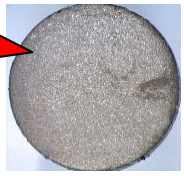
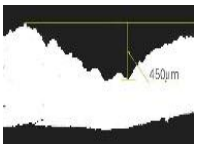
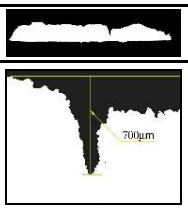
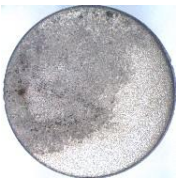


FIGURE 12 - $E_{on\ peak}$ and the $E_{off\ peak}$ values obtained with one of the probes installed at (TP 34)

TABLE 2

FIELD TESTS RESULTS: VISUAL ANALYSIS, CORROSION RATES AND DEPTH PITTING CORROSION OF COUPONS INSTALLED AT (V 05-04) AND (TP 34)

Location	Coupon number	Photo	Magnified photo	Metalografic test	Corrosion rate (μm/year)	Depth pitting corrosion (μm)
V 05-04	CP 01			---	58	---
	CP 02			---	65	---
	CP 03				76	800
	probe			---	Average (4 cupons) = 52 Deviation = 6	---

TP 34	**CP 19**				88	450
	CP 20				92	700
	probe 1			---	Average (4 cupons) = 71 Deviation = 4	---
	probe 2			---	Average (4 cupons) = 68 Deviation = 7	---

Conclusions

A new probe consisted of a modified $Cu/CuSO_4$ reference electrode, with four corrosion coupons symmetrically positioned around the reference electrode and an electronic keying device capable of interrupting the circulating current from the pipes to the coupons in an adequate time to obtain the *on*-potential AC + DC waveform and *off*-potential AC + DC waveform in a synchronized way. This time interval depending on the waveform frequency.

With this probe and a portable oscilloscope, it is possible to obtain IR-free AC plus DC coupled off-potential versus time waveform. The peak potential of this waveform, $E_{off\ peak}$, is used for the prediction of AC corrosion on cathodically protected pipes using the proposed criterion. The criterion is AC corrosion does not occur when the peak of the IR-free AC plus DC coupling potential versus time waveform remains below the equilibrium potential of the iron corrosion reaction (-0.85 $V_{Cu/CuSO4}$).

Referências bibliográficas

1. S. GOIDANICH; L. LAZZARI; M. ORMELLESE; M.P. PEDEFERRI, “Influence of AC on carbon steel corrosion in simulated soil solutions”, INTERNATIONAL CORROSION CONGRESS, 16, paper n. 04-03. (Beijing, China, 2005)
2. D. FUNK, W. PRINZ, H.G. SCHONEICH, “Investigation of Corrosion of Cathodically Protected Steel Subjected to Alternating Currents”, 3R International 32, (1992)
3. NACE INTERNATIONAL 2007, “AC Corrosion State-of-the-Art: Corrosion Rate,

Mechanism, and Mitigation Requirements", Corrosion/07, paper no. NACE TG 327, (Nashville, TX: NACE, 2007)

4. PANOSSIAN, Z.; ABUD FILHO, S. E.; NAGAYASSU, V. Y.; ALMEIDA, N. L.; LAURINO, E. W.; PIMENTA, G. S. "Estudo das variações de pH nos ensaios de corrosão", INTERCORR/08, paper no. 105, (Recife-Brasil, 2008)
5. ABUD FILHO, S. E.; PANOSSIAN, Z.; ALMEIDA, N. L.; PEREIRA FILHO, M. L.; SILVA, D. L.; LAURINO, E. W.; OLIVER, J. H. L.; PIMENTA, G. S.; ALBERTNI. J. A. C. "Proposição de um mecanismo e de um critério de previsão de corrosão por corrente alternada em dutos enterrados", INTERCORR/08, paper no. 106, (Recife-Brasil, 2008)
6. ABUD FILHO, S. E.; PANOSSIAN, Z.; ALMEIDA, N. L.; PEREIRA FILHO, M. L.; SILVA, D. L.; LAURINO, E. W.; OLIVER, J. H. L.; PIMENTA, G. S.; ALBERTNI. J. A. C. "Estudo de corrosão por corrente alternada em dutos instalados em corredores com linhas de transmissão elétrica", INTERCORR/08, paper no. 107, (Recife-Brasil, 2008)
7. NACE INTERNATIONAL 2007. PANOSSIAN, Z.; ABUD FILHO, S. E.; ALMEIDA, N. L.; PEREIRA FILHO, M. L.; SILVA, D. L.; LAURINO, E. W.; OLIVER, J. H. L.; PIMENTA, G. S.; ALBERTNI. J.A.C. "Effect of Alternating Current by High Power Lines Voltage and Electric Transmission Systems in Pipelines Corrosion", Corrosion/09, paper no. NACE 09451, (ATLANTA, GA: NACE, 2007)