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Can an intermittent cathodic protection system prevent corrosion of buried pipeline?

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ABSTRACT

Carbon steel pipelines are provided with corrosion prevention systems, namely an insulating coating and a cathodic protection (CP) system that reduces corrosion rate below 10 μm/a. CP is applied by a stationary cathodic current, which effectiveness on the metal surface is twofold: oxygen consumption and alkalinization (pH > 10) at the metal-to-electrolyte interface. The increase of pH is beneficial, promoting passive condition. In this paper, a preliminary study of the effect of intermittent CP has been carried out in order to investigate the effect of a temporary current interruption on the potential monitoring and on the residual corrosion of the metal. During the on period, oxygen is consumed and alkaline pH is established, during off period, the alkalinity and the slow oxygen replacement assure corrosion rates lower than in free corrosion condition. Test has been performed both in normal and overprotection condition, varying the off period duration, monitoring weekly the protection potential.

Key words: Cathodic protection; carbon steel; protection potential; oxygen reduction; overprotection.

INTRODUCTION

Buried carbon steel pipelines are provided with corrosion prevention systems, namely an insulating coating and a cathodic protection (CP) system that reduces corrosion rate below 10 μm/a, which is the maximum acceptable corrosion rate according to ISO (1) 15589-1. [1]

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(1) ISO – International Organization for Standardization, Chemin de Blandonnet 8, 1214 Vernier, Geneva, Switzerland (CH)

Carbon steel in aerated soil operates in protection condition if the IR-free potential (not affected by ohmic drop) is more negative than –0.850 V CSE (CSE = +0.318 V SHE). The effects of CP on carbon steel are well known and can be summarized as follows: 1) a thermodynamic effect, which consist on the lowering of the potential of the metal below the equilibrium potential, in order to stop corrosion (immunity condition), 2) a chemical effect, which consists on the alkalinization of the electrolyte in close proximity of the metal. [2] More precisely, in aerated environment where the cathodic reaction is oxygen reduction, the cathodic current provided in a stationary way by the anode consumes oxygen promoting an increase of pH according to the electrochemical reaction:

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{1}$$

Oxygen reduction is diffusion controlled and the maximum amount of oxygen available for steel corrosion is determined mainly by its diffusion rate in the electrolyte, i.e. by the oxygen limiting current density. At lower potential, hydrogen evolution takes place with higher cathodic current density due to the lower cathodic activation overvoltage with respect to oxygen reduction.

In this paper, a preliminary study of intermittent CP has been carried out in order to investigate the effect of a temporary current interruption on the potential monitoring and on the residual corrosion rate. This works is complementary to a previous research with the aim of studying the effects of direct current (DC) anodic non-stationary interference on buried carbon steel pipes under CP condition. [3] In this previous research, results showed the main important role of alkalinity not only during CP energizing but also during the anodic peak of interference (even at high current density). Due to the slow kinetic of diffusion phenomena, alkalinization is maintained for a few minutes during interference (the time depends on the intensity of anodic current density), avoiding during this period the strong corrosion of the metal. In principle, these considerations can be applied also in the absence of interference if an intermittent CP is applied. The main difference with the interference test is the duration of the off period (i.e. when the current is interrupted): while in case of DC interference CP is applied for most of the time and interference peaks last a few minutes, in case of intermittent CP the off period is in the order of hours.

In truth, intermittent CP is far from practical application (nowadays CP is applied by a stationary current, according to international standard). Nevertheless, it could be helpful in the better understanding of fault and poor CP condition or in application where the conventional electrical connection with AC power line is tough and the use of a solar power CP system could be considered. [4-5]

Otherwise, even if the aim and the mechanism is different, the positive effects of intermittent CP are more recognized in the rehabilitation of contaminated concrete, where the intermittent (or pulse) cathodic current can be helpful to remove chlorides from the cover concrete or to restore passivity condition with respect to the continuous application of current. [6-9]

EXPERIMENTAL PROCEDURE

Laboratory tests were carried out on carbon steel specimens type L360 (EN 10208 [10]), chemically equivalent to type API 5L X52 steel pipes, according to API (2) 5L. [11] After preparation and cleaning operations according to ASTM (3) G1-03 [12], specimens were placed in a PTFE cylindrical watertight sample holder (Figure 1), exposing a circular net surface of 1 cm^2 to the electrolyte, that simulates a coating defect of a steel pipe. A stainless steel screw on the top of the sample holder provides the electrical contact to the specimen. In order to prevent galvanic coupling effects, a glass tube has been placed around the screw to insulate the electrical contact (Figure 1).

Specimens were placed in a cylindrical cell (diameter 0.15 m; height 0.20 m, Figure 2) containing a soil-simulating solution consists of 0.2 g/dm^3 of $CaSO_4$ and 0.2 g/dm^3 of NaCl. The solution simulates the corrosion behavior of a carbon steel pipe in a soil with resistivity of about 50 $\Omega \cdot m$. Tests were carried

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(2) American Petroleum Institute (API), 1220 L St., N.W., Washington, DC 20005-4070.

(3) American Society for Testing Materials (ASTM International), 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959

out at room temperature (20 ± 2 °C). Carbon steel specimens were cathodically polarized by means of a Direct Current (DC) feeder (impressed current CP system) through an activated titanium insoluble anode (Ti-MMO counter electrode). CP was applied continuously for one month, applying a constant cathodic current density (galvanostatic mode). Two cathodic current densities were considered in order to study two levels of cathodic protection:

- 0.2 A/m^2, which simulates cathodic protection of steel in neutral and aerated soil where the cathodic reaction is oxygen reduction. Protection potential falls in the range between -0.85 V CSE (namely the protection potential according to international standard) and -1.2 V CSE;
- 1.0 A/m^2, which simulates the overprotection condition of steel (namely E < -1.2 V CSE), where hydrogen evolution overlaps to oxygen reduction.

Before starting the on-off cycles, the protection potential was monitored twice a week and the current was adjusted in order to obtain a steady potential. IR-free potential was measured by means of a high impedance voltmeter and an external Ag/AgCl/KCl$_{\text{sat.}}$ (+0.2 V SHE) reference electrode placed in close proximity to the metal surface in order to eliminate the ohmic drop contribution in solution during potential reading.

After one month of polarization, cathodic protection on-off cycles were applied, according to the schedule reported in Table 1. Three on-off time ratios were adopted (12 hours:12 hours; 8 hours:16 hours; 18 hours:6 hours). An automatic on-off switch, electrically connected to the specimen (Figure 2), interrupts and restores the cathodic current provided by the feeder. The potential of each specimen has been monitored once a week for five months by means of a data logger with acquisition frequency of 0.5 samples per second (Figure 3). Two specimens for each condition (and, for comparison purpose, a control specimen in free corrosion condition) were tested.

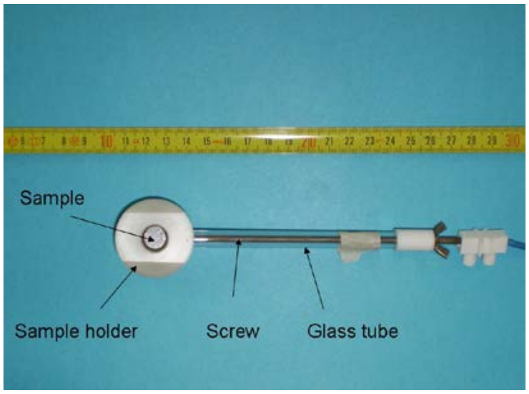

Figure 1: Carbon steel specimen

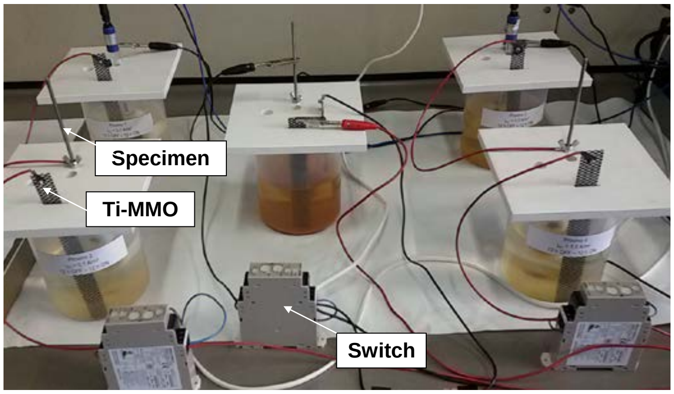

Figure 2: Corrosion cell and electrical circuit

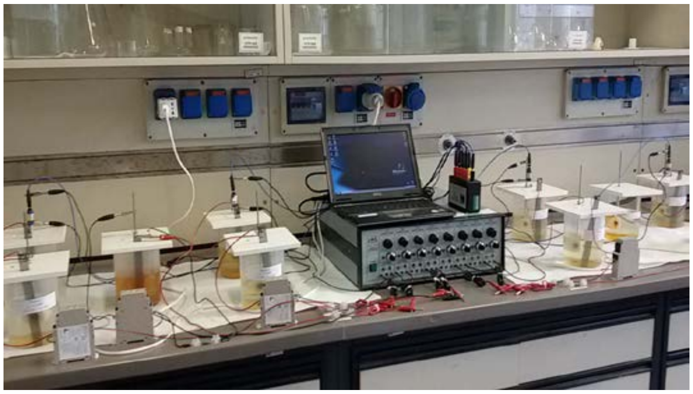

Figure 3: Galvanostatic tests of intermittent CP

Table 1
Experimental conditions: cathodic current density and duration of on-off period

Specimen		DC density (A/m^2)	on period (hours/day)	off period (hours/day)	on-off time ratio
Control		Free corrosion condition	---	---	---
A	**A.1**	0.2	12	12	1
	A.2	0.2	12	12	1
B	**B.1**	1	12	12	1
	B.2	1	12	12	1
C	**C.1**	0.2	8	16	1:2
	C.2	0.2	8	16	1:2
D	**D.1**	0.2	18	6	3:1
	D.2	0.2	18	6	3:1

RESULTS

After one month of CP, on-off cycles were applied by interrupting and re-energizing the cathodic current cyclically, as described in the previous paragraph.

The potential of each sample was weekly monitored for 24 hours in order to study the effect of the interruption of the current on the potential of the metal. For a sake of simplicity, the potential profiles of one sample for each tested condition (Table 1) are reported (values are converted with respect to CSE reference electrode). Figure 4 shows the potential of sample A.1 (0.2 A/m^2; 12 hours on – 12 hours off) during the five months of testing. In on condition, IR-free potential is in the range between -1.1 V CSE and -1.2 V CSE. Steel is in immunity condition and corrosion is not thermodynamically possible. After current interruption, the potential increases following an asymptotic behavior up to the free corrosion potential reached in a variable time in the range from few minutes (first weeks of testing) to about two hours (after about three months on-off cycles). Two dotted lines are reported: the -0.85 V CSE line, namely the protection potential according to ISO 15589-1 standard and the mean value of free corrosion potential measured during the test on the control specimen (-0.72 V CSE). After the off period, the cathodic current was re-energized and the potential decreases to the potential range measured before current interruption. The polarization is time-dependent, i.e. the transitory time from the free corrosion potential to the steady value of protection potential increases as the testing time increases.

Similarly, Figure 5 shows the potential of sample B.2 (1 A/m^2; 12 hours on – 12 hours off) monitored weekly. In on condition, IR-free potential is lower than -1.2 V CSE, as expected. Steel is in overprotection condition and the main cathodic reaction occurring on the specimen is hydrogen evolution. After current interruption, the potential increases instantly to about -1.1 V CSE. This potential variation of about 0.2 V is due to the fast kinetic of hydrogen activation overvoltage, not controlled by diffusion. Hydrogen activation overvoltage is eliminated in about 1 ms, [13] so that oxygen concentration overvoltage remains the only contribution during the off period. In the first two months, i.e. 60 on-off cycles, the potential moves to the free corrosion condition in about one hour or less; then, the transitory time becomes longer, in the order of a few hours.

Figure 6 and 7 show the potential profiles of specimens C.2 and D.2, exposed to a cathodic current density of 0.2 A/m^2 interrupted for 16 hours and 6 hours daily, respectively. The same previous considerations can be extended to these two cases: after current interruption, the potential increases following a logarithmic behavior up to the free corrosion potential.

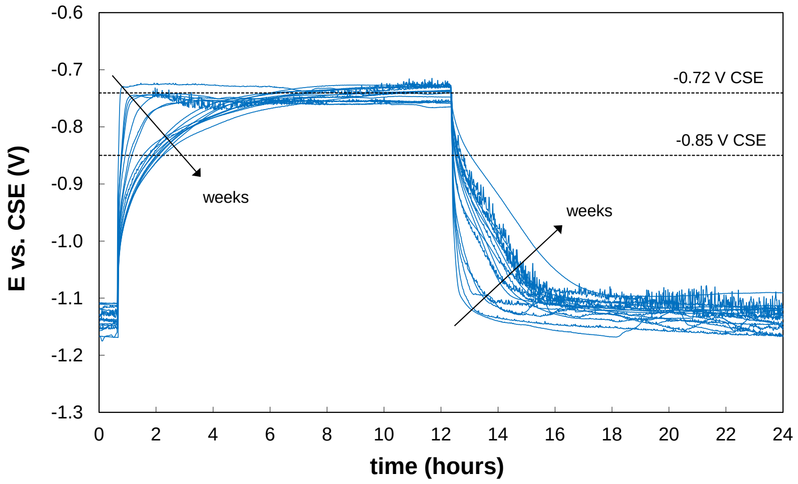

Figure 4: Potential during the off-period for sample A.1 (0.2 A/m^2; 12 hours on – 12 hours off)

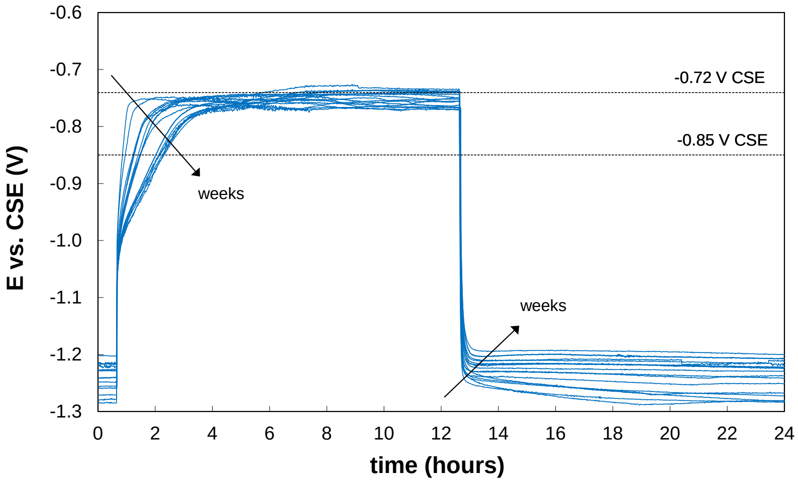

Figure 5: Potential during the off-period for sample B.2 (1.0 A/m^2; 12 hours on – 12 hours off)

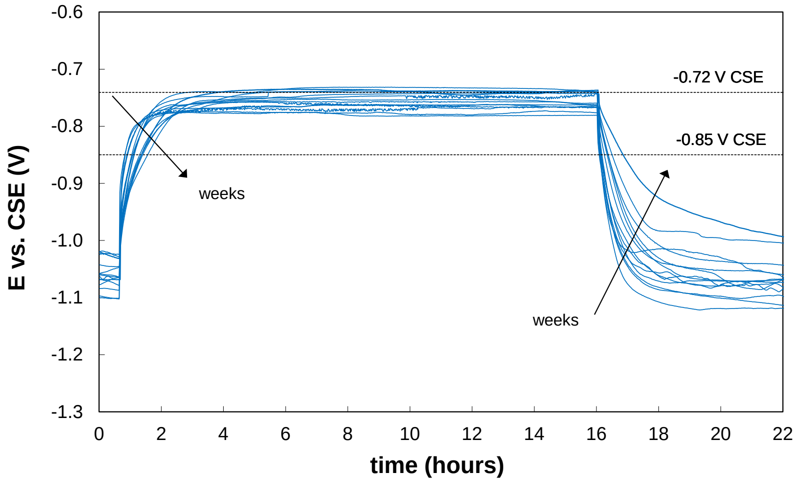

Figure 6: Potential during the off-period for sample C.2 (0.2 A/m^2; 8 hours on – 16 hours off)

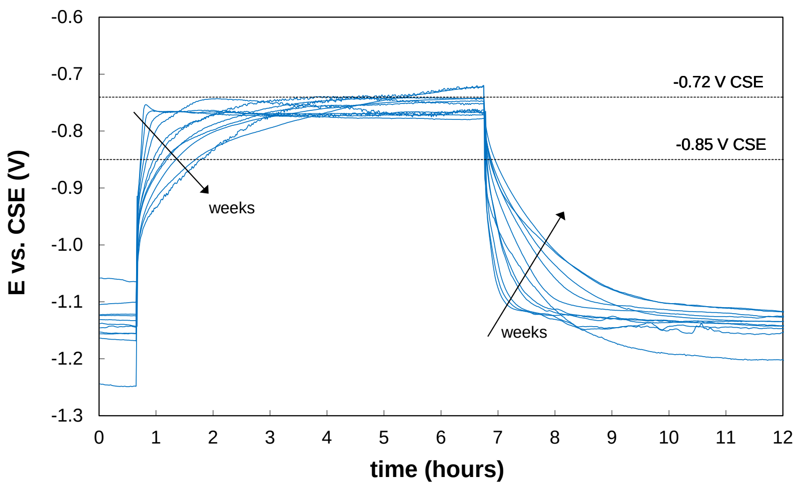

Figure 7: Potential during the off-period for sample D.2 (0.2 A/m^2; 18 hours on – 6 hours off)

DISCUSSION

Potential vs. time profiles showed that, during the current-off period, a not-negligible residual corrosion rate is expected. The potential of the metal, as soon as the current is switched off, increases and moves towards the free corrosion potential, where the corrosion rate is determined by oxygen availability in the electrolyte (oxygen diffusion limiting current density).

A simple electrochemical model using Tafel's law, i.e. the Evans diagram for most of active metals as carbon steel, can be used to estimate the corrosion rate during the off period. When the cathodic current is applied to the metal, corrosion rate is nil if the potential is equal or lower than the equilibrium potential, defined by Nernst equation. For iron in presence of 10^{-6} M iron ions (according to Pourbaix diagram) the equilibrium potential is -0.93 V CSE. Nevertheless, the practical protection potential is -0.85 V CSE, which corresponds approximately to a corrosion rate lower than 10 μm/a (in the following text, the approximated equivalence 1 A/m^2 = 1 mm/a is established) considered negligible in several applications as in case of pipeline for the transport of hydrocarbons.

In aerated natural environment, as waters and soil, corrosion rate is determined by the maximum amount of oxygen and its diffusivity in the electrolyte. In other words, corrosion rate is defined by the cathodic process (cathodic control) and is equal to the oxygen limiting current density, i_L, which ranges from a few to hundreds of mA/m^2. It follows that during the on period corrosion rate is nil (metal immunity) and increases with time after current interruption up to the maximum value, i_L. According to this model, corrosion rate (i, anodic current density) during the off period can be written as:

$$\eta = E - E_{prot} = b \cdot \log \frac{i}{i_{E=E_{prot}}} \qquad (2)$$

$$i = i_{E=E_{prot}} \cdot 10^{\frac{\eta}{b}} \qquad (3)$$

Where η represents the overvoltage calculated with respect the protection condition, i is the anodic current density (mA/m^2), $i_{E=Eprot}$ is the residual corrosion rate (10 μm/a) at the protection potential (E_{prot} = -0.85 V CSE), b is the Tafel's slope of iron dissolution reaction.

The model assumes a constant Tafel's slope (b) equal to 0.1 V for decade of current. As described in the following, this assumption may be too coarse due to the effect of CP on the electrochemical behavior of the metal during the on period. Indeed, cathodic reactions occurring on the metal surface may increase the anodic overvoltage due to the chemical changes induced by the cathodic current. Both cathodic reactions (i.e. oxygen reduction and hydrogen evolution) increases alkalinity of the electrolyte close to the metal surface (Equation 1) causing with time the formation of a passivity condition, as expected by Pourbaix diagram. It follows that, during the off period, the slope of the Evans diagram may be higher than 0.1 V for decade of current, due to the effect of the previous period of polarization. In other words, corrosion rate calculated by Equation 3 represents the corrosion rate during the off period, considering active carbon steel without any effect of passivation induced by the cathodic current. At the corrosion potential (measured on the control specimen, -0.72 V CSE), Equation 4 gives the theoretical corrosion rate:

$$i_{corr} = 0.01\frac{mm}{a} \cdot 10^{\frac{(-0.72+0.85)V}{0.1}} \cong 0.2\frac{mm}{a} \qquad (4)$$

This value is comparable to the experimental corrosion rate measured by mass loss test (0.17 mm/a) on the control specimen at the end of the exposure test. Figure 8 shows corrosion rate distribution during the off period for specimen A.1 (0.2 A/m^2; 12 hours on – 12 hours off). For a sake of clearness, only one curve for month is reported. As discussed, for the first two months a rapid increase of potential (and consequently of corrosion rate) is observed. During the first weeks from the starting of intermittent CP, corrosion rate increases rapidly as soon as the current is turned off; nevertheless, corrosion rate is lower than corrosion rate in free corrosion condition (200 μm/a), due to the asymptotic increase of potential in the off period that slowly tends to the free corrosion potential. After one-month, maximum corrosion rate is in the order of 100 μm/a after 12 hours. The shape of the curve changes after about three months of exposure to cyclic intermittent CP: corrosion rate increases slowly with time and for the first two hours corrosion rate remains below 10 μm/a (i.e. the metal is in protection condition). Then, corrosion rate increases up to the maximum at the end of the off period, about 150 μm/a after five months testing. The higher corrosion rates can be misleading: these values are calculated from the potential variation (η) which is higher after four months. Nevertheless, the higher increase of potential may not be associated to a higher corrosion rate but to an increase of the slope b in Equation 3, due to a higher anodic overvoltage promoted by the alkalinity in CP condition. This aspect needs more investigations and further experimental measurements are necessary.

A similar behavior is observed for specimen B.2 (1.0 A/m^2; 12 hours on – 12 hours off, Figure 9). During the first weeks from the starting of intermittent CP, corrosion rate increases rapidly as soon as the current is turned off. After five months of intermittent CP, corrosion rate increases slowly with time and it remains below 10 μm/a in the first two hours. At the end of the off period, corrosion rate is in the order of 100 μm/a. In this case, besides the alkalinization effect, the main mechanism that explains the potential variation is the slow oxygen diffusion from the bulk solution to the surface. In cathodic protection, oxygen is reduced and its consumption rate depends on the cathodic current density supplied to the metal. In overprotection condition (1.0 A/m^2), the high cathodic current consumes the oxygen in contact with the metal during the 12 hours CP on, then oxygen is slowly replaced by diffusion in solution when CP is switched off. In case of intermittent CP of specimen C.2 (0.2 A/m^2; 6 hours on – 18 hours off, Figure 10), no appreciable differences are observed when the current is interrupted. The on period seems too short to promote a significant variation of oxygen diffusion rate and chemical variation on the metal surface. Potential slightly higher have been measured after three months of intermittent CP application, probably according to the mechanism described previously which finds a confirmation in the last tested condition. Indeed, for specimen D.2 (0.2 A/m^2; 18 hours on – 6 hours off, Figure 11) the on period is longer so that it can guarantee a stronger local alkalinization and increase of anodic overvoltage of the metal. The higher potential measured after three months is probably related to the described effect and it does not correspond necessarily to a higher corrosion rate. Nevertheless, in all the tested conditions, the calculated current density of the anodic process is lower than the theoretical one in free corrosion condition.

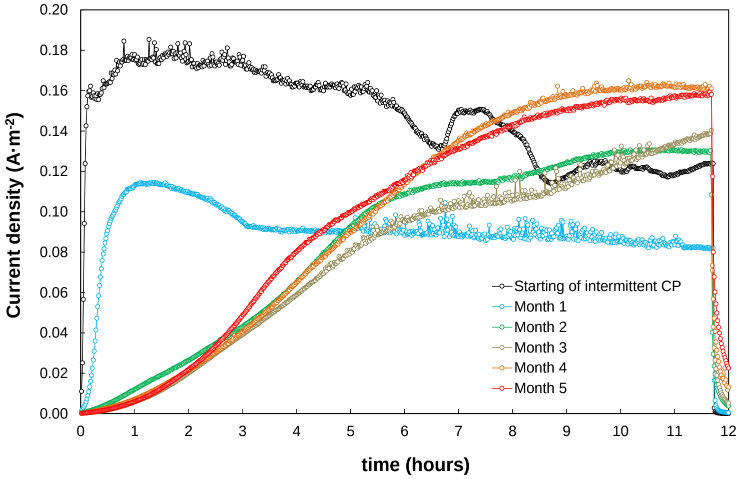

Figure 8: Current density during off-period for sample A.1 (0.2 A/m^2; 12 hours on – 12 hours off)

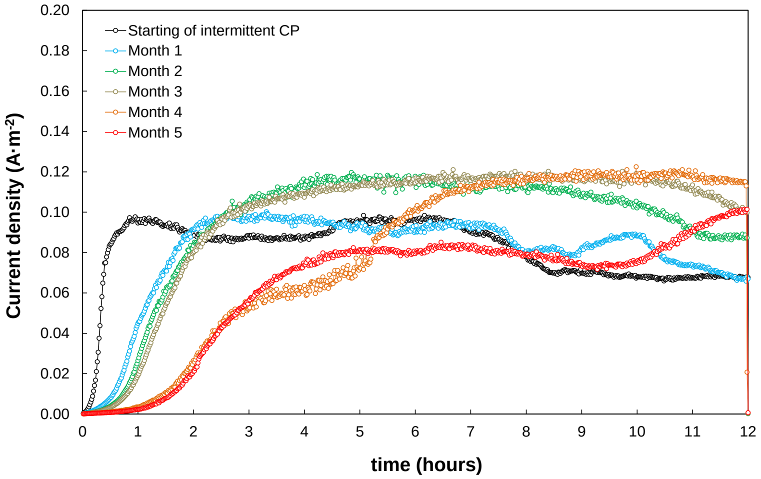

Figure 9: Current density during off-period for sample B.2 (1.0 A/m^2; 12 hours on – 12 hours off)

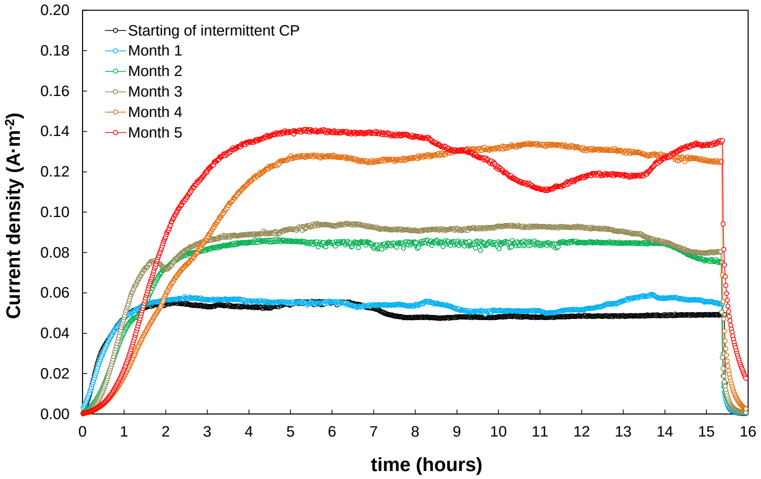

Figure 10: Current density during off-period for sample C.2 (0.2 A/m^2; 8 hours on – 16 hours off)

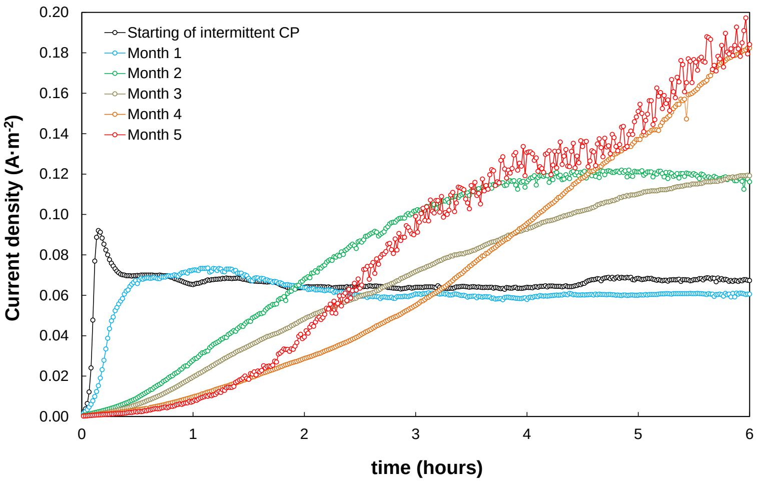

Figure 11: Current density during off-period for sample D.2 (0.2 A/m^2; 18 hours on – 6 hours off)

Obviously, the mean corrosion rate in the presence of intermittent CP (considering both the on and the off period) depends on the ratio between the off and on time. Mean corrosion rate during the off period (given by the mean integral theorem) is "spread" on all the exposition time. Effective corrosion rate (C_{rate}) can be written as:

$$C_{rate} = \frac{t_{off}}{t_{off}+t_{on}} \cdot \bar{i}_{corr} = \frac{t_{off}}{t_{off}+t_{on}} \cdot \frac{1}{t_{off}} \int_{t=0}^{t=t_{off}} i_{E=E_{prot}} \cdot 10^{\frac{E(t)-E_{prot}}{b}} dt \qquad (5)$$

$$C_{rate} = \frac{1}{t_{off}+t_{on}} \cdot \int_{t=0}^{t=t_{off}} i_{E=E_{prot}} \cdot 10^{\frac{E(t)-E_{prot}}{b}} dt \qquad (6)$$

Where the meaning of the symbols is known.

In a simplified and conservative approach, the effective corrosion rate (C_{rate}) can be estimated considering the maximum corrosion rate measured during the off period. The values at the end of the exposure test (month 5) are considered (Table 2). Corrosion rate in presence of intermittent CP is reduced and depends on the duration of the off period, as expected, and on the intensity of cathodic current density. The beneficial effect of the alkalinity promoted by the cathodic current during the on period is clearly shown considering specimen B.1 and B.2: although the on period is 50% of the total exposure time, the corrosion rate is reduced from 200 μm/a to about 50 μm/a (75% lower). In case of specimens A.1 and A.2, the reduction of corrosion rate is about 60%, lower with respect to sample B due to the small cathodic current density, i.e. low alkalinity reserve formed in the on period.

For specimen D.1 and D.2 (18 hours on – 6 hours off) the calculated corrosion rate could be misleading according to the mechanism reported previously. Indeed, corrosion rate calculated by the proposed model considers active steel with a constant Tafel's slope of 0.1 V/decade; nevertheless, potential monitoring and calculated current density (Figure 11) show that this assumption can be too restrictive in presence of an increase of anodic overvoltage promoted by alkalinity of cathodic reaction.

Even if this aspect needs more investigations, a simple calculation can be proposed in order to explain this behavior. At the corrosion potential (-0.72 V CSE), the overvoltage η (Equation 2) is 0.13 V CSE. According to Tafel's law, this potential variation corresponds to a corrosion rate of 200 μm/a considering a Tafel's slope (b) of 0.1 V/decade. Corrosion rate decreases to 45 μm/a considering a slope of 0.2 V/decade up to fall down to 10 μm/a with a slope b higher than 1 V/decade, which corresponds to a strong passivation effect on the surface (for a passive material the slope can be considered in the order of 10 V/decade). A revised model, which considers Tafel's slope changing with time, could be helpful for the better understanding of the electrochemical changes promoted by intermittent CP, in order to have a proper estimation of corrosion rate.

Table 2
Effective corrosion rate in the presence of intermittent CP

Specimen		DC density (A/m^2)	on-off time ratio	$t_{off}/(t_{off} + t_{on})$	C_{rate} μm/a
Control		---	---		200
A	**A.1**	0.2	1	0.5	80
	A.2	0.2	1	0.5	75
B	**B.1**	1	1	0.5	55
	B.2	1	1	0.5	50
C	**C.1**	0.2	1:2	0.66	100
	C.2	0.2	1:2	0.66	90
D	**D.1**	0.2	3:1	0.25	50
	D.2	0.2	3:1	0.25	60

CONCLUSIONS

A preliminary study of intermittent CP has been carried out in order to investigate the effect of a temporary current interruption on the potential monitoring and on the residual corrosion of the metal. In the on period, oxygen is consumed by the cathodic current and alkaline pH is established at the metal-to-electrolyte interface. During the off period, the alkalinity and the slow oxygen replacement assure corrosion rates lower than in free corrosion condition, especially if high cathodic current density (1 A/m^2) is applied previously.

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