Effect of intermittent cathodic protection on potential and corrosion rate of carbon steel in soil simulating solution

Andrea BRENNA[1], Silvia BERETTA[2], Marco ORMELLESE[3], MariaPia PEDEFERRI[4]

[1]Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Milan, Italy, andrea.brenna@polimi.it
[2]Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Milan, Italy, silvia.beretta@polimi.it
[3]Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Milan, Italy, marco.ormellese@polimi.it
[4]Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Milan, Italy, mariapia.pedeferri@polimi.it

Abstract

Carbon steel in aerated soil operates in cathodic protection (CP) condition if the IR-free potential is more negative than –0.850 V CSE, which corresponds to a corrosion rate lower than 0.01 $mm \cdot a^{-1}$.
CP is applied by a stationary current, which effectiveness depends on a thermodynamic effect, which reduces (or stops) corrosion rate, and on a chemical effect due to the alkalinisation at the metal-to-electrolyte interface. The increase of pH is promoted by the cathodic reactions (oxygen reduction and, at lower potential, hydrogen evolution) occurring on the polarized metal and can promote passive condition. 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 potential monitoring and on residual corrosion rate of steel in soil simulating solution. Test has been performed applying two cathodic current densities (0.2 and 1.0 $A \cdot m^{-2}$), varying the current-off period daily duration (6, 12 and 16 hours) and monitoring weekly the potential. During the on period (i.e. CP on), oxygen is consumed and alkaline pH is established; during the off period (i.e. when CP is interrupted), the alkalinity and the slow oxygen replacement assure corrosion rates lower than in free corrosion condition, especially if high cathodic current density is previously applied.

Keywords

Cathodic protection; oxygen reduction; alkalinisation; IR-free potential; Tafel's law.

Introduction

Buried carbon steel pipelines are protected by soil corrosiveness with an insulating coating and a cathodic protection (CP) system which reduces corrosion rate of coating defects below 0.01 $mm \cdot a^{-1}$, which is the maximum acceptable corrosion rate according to ISO 15589-1 [1].
Carbon steel in aerated soil operates in protection condition if the IR-free potential (not affected by ohmic drop contribution) is more negative than –0.850 V CSE ($Cu/CuSO_4$ reference electrode, +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 below the equilibrium potential of the metal, in order to stop corrosion (immunity condition); 2) a chemical effect, which consists on the alkalization of the electrolyte in close proximity of the metal [2]. More precisely, in aerated environment where the cathodic reactions are oxygen reduction and, at lower potential, hydrogen evolution, the cathodic current provided in a stationary way by the anode consumes oxygen and acidity promoting an increase of pH according to the electrochemical reactions:

(1) $$\frac{1}{2}O_2 + H_2O + 2e^- = 2OH^-$$

(2) $$2H^+ + 2e^- = H_2$$

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 diffusion limiting current density. At lower potential, namely lower than -1.10 V CSE for carbon steel in natural environment (e.g. soil, seawater), hydrogen evolution becomes significant and takes place with higher current density due to the lower cathodic activation overvoltage with respect to oxygen reduction reaction.
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]. Preliminary results showed the main important role of alkalinity not only during CP energizing but also during the anodic peak of interference (even at high anodic current density). Due to the slow kinetic of diffusion phenomena, alkalization 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 could 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].

Materials and Methods

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 5L [11]. After preparation and cleaning operations according to ASTM 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 coated 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 (0.2 $g \cdot dm^{-3}$ of $CaSO_4$ and 0.2 $g \cdot dm^{-3}$ 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 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 $A \cdot m^{-2}$, 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 $A \cdot m^{-2}$, 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 $Ag/AgCl/KCl_{sat.}$ (+0.20 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 on – 12 hours off; 8 hours on – 16 hours off; 18 hours on – 6 hours off). 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. Two specimens for each condition (and, for comparison purpose, a control specimen in free corrosion condition) were tested.

Table 1: Cathodic protection current density and duration of on-off periods

Specimen			**DC density ($A \cdot m^{-2}$)**	**on period (hours/day)**	**off period (hours/day)**	**on-off time ratio**
Control			Free corrosion	---	---	---
A	A.1	A.2	0.2	12	12	1
B	B.1	B.2	1.0	12	12	1
C	C.1	C.2	0.2	8	16	1:2
D	D.1	D.2	0.2	18	6	3:1

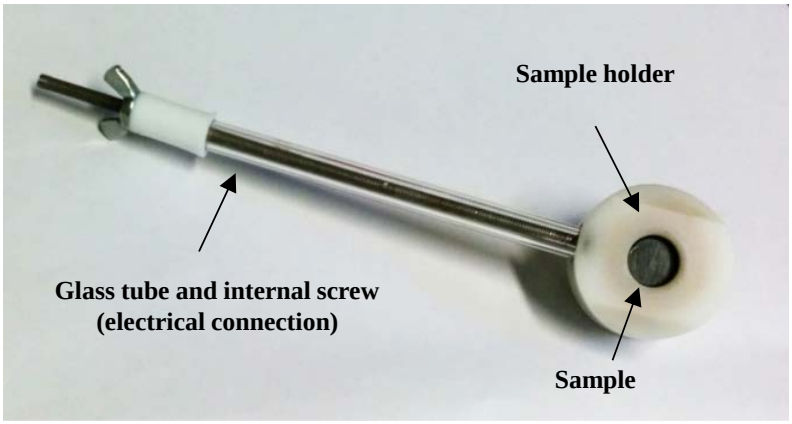

Figure 1: Carbon steel specimen

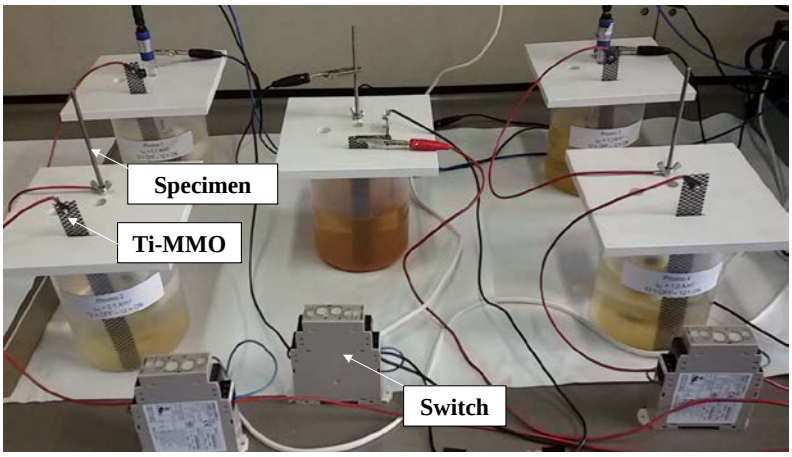

Figure 2: Corrosion cell and electrical circuit

Results

After one month of CP, on-off current cycles were applied by interrupting and re-energizing the cathodic current cyclically, according to Table 1.

The potential of each sample was monitored weekly 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 3 shows the potential of sample A.1 (0.2 $A \cdot m^{-2}$; 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 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 [1] 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 4 shows the potential of sample B.2 (1.0 $A \cdot m^{-2}$; 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 10^{-3} s [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.

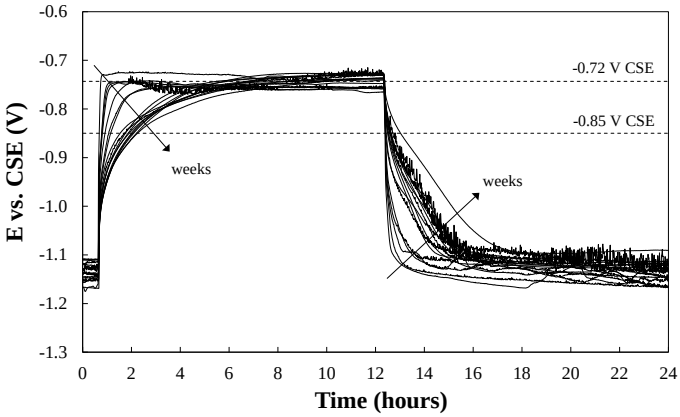

Figure 3: 24 hours potential monitoring for carbon steel specimen A.1 (0.2 A·m^{-2}; 12 hours on – 12 hours off)

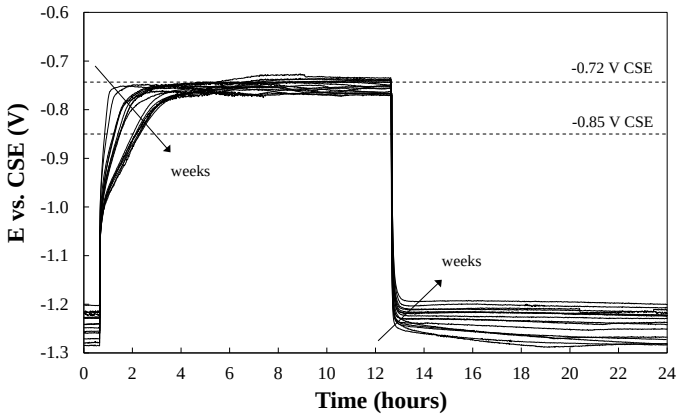

Figure 4: 24 hours potential monitoring for carbon steel specimen B.2 (1.0 A·m^{-2}; 12 hours on – 12 hours off)

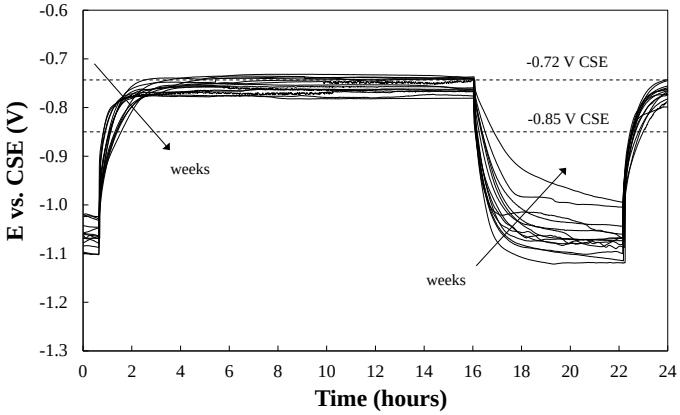

Figure 5: 24 hours potential monitoring for carbon steel specimen C.2 (0.2 A·m^{-2}; 8 hours on – 16 hours off)

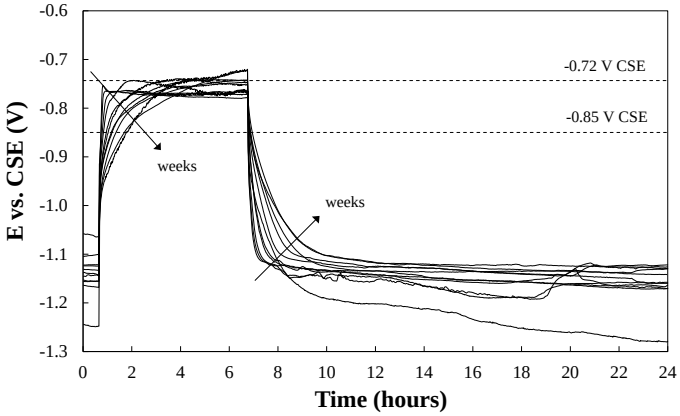

Figure 6: 24 hours potential monitoring for carbon steel specimen D.2 (0.2 A·m^{-2}; 18 hours on – 6 hours off)

Figure 5 and 6 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.

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 active metals as carbon steel in acidic and neutral electrolytes, 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 assures a corrosion rate lower than 0.01 mm·a^{-1}, considered negligible in several applications as in case of buried 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} (for carbon steel, the equivalence 1 mA·m^{-2} = 1.17 μm·a^{-1} is established by Faraday's law). 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:

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

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

where η represents the overvoltage calculated with respect the protection condition ($E - E_{prot}$), *i* is the anodic current density (or corrosion rate, $mA \cdot m^{-2}$ or $\mu m \cdot a^{-1}$), $i_{E=Eprot}$ is the residual corrosion rate (assumed 10 $\mu m \cdot a^{-1}$) at the protection potential (E_{prot} = -0.85 V CSE), b is the Tafel's slope of iron dissolution reaction. In other words, Equation 4 provides the instantaneous corrosion current density (i.e. corrosion rate) for each potential measurement during the off period. The model assumes a constant Tafel's slope (b) equal to 0.1 V for decade of current, measured experimentally by a preliminary anodic polarization test. As described in the following, this assumption may be too coarse due to the effect of CP on the electrochemical behaviour of the metal during the on period. At the corrosion potential (measured on the control specimen, -0.72 V CSE), the corrosion rate calculated by Equation 4 is 200 $\mu m \cdot a^{-1}$.

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:

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

where the meaning of the symbols is known.

With a simplified approach, the effective corrosion rate (C_{rate}) can be estimated by calculating the mean corrosion current density during the off period, considering five potential profiles for each specimens (one profile per month) (Table 2). This value can be compared with the corrosion rate that results by neglecting the slow depolarization of the metal during the off period, i.e. by weighing the free corrosion rate (200 $\mu m \cdot a^{-1}$) for the period without cathodic protection current (off period). A significant reduction of corrosion rate up to 60% for specimens in over-protection condition (DC density = 1.0 $A \cdot m^{-2}$) is measured. In all cases, corrosion rate reduction is more than 50%, even if no particular effect of the duration of the on period before current interruption is observed.

The lower corrosion rate in the off period is interpretable considering two effects. Firstly, cathodic protection in the previous on period consumes oxygen in the electrolyte close to the metal surface, in particular in over-protection condition where the cathodic current density is higher. The slow depolarization rate to the free corrosion potential indicates the slow oxygen diffusion and replacement at the metal-to-electrolyte interface. Secondly, cathodic reactions (oxygen reduction and hydrogen evolution) increases alkalinity on the metal surface, promoting passive conditions with increased of the anodic overvoltage.

The effect of alkalinity is not considered in this simplified calculation even though potential measurements, especially after four month of testing, show that the metal tends to passivate thanks to the alkalinity produced in CP condition. It is reasonable to think that alkalinity promotes an increase in anodic overvoltage with two consequences: on the one hand, the value of Tafel's slope should be revised (b in Equation 4); on the other hand, the potential measurement would assume a new and different interpretation. For instance, at the free corrosion potential, the depolarization η is 0.13 V and the corrosion rate results 200 $\mu m \cdot a^{-1}$, 45 $\mu m \cdot a^{-1}$ and 10 $\mu m \cdot a^{-1}$ with Tafel's slopes of 0.1, 0.2 and 1 $\mu m \cdot decade^{-1}$, respectively. It follows that higher polarizations do not necessarily correspond to high corrosion rates.

Table 1: Effective corrosion rate in the presence of intermittent CP

DC density	ON period	OFF period	% t_{off}	$C_{rate,0} \cdot$ % t_{off}	C_{rate}	Variation %
A·m^{-2}	**hours/day**	**hours/day**		**μm·a^{-1}**	**μm·a^{-1}**	
Free corrosion	0	24	100%	200 ($C_{rate,0}$)	---	---
0.2	18	6	25%	50	29	**-53%**
	18	6	25%	50	18	
	12	12	50%	100	50	**-56%**
	12	12	50%	100	39	
	8	16	66%	130	73	**-52%**
	8	16	66%	130	53	
1.0	12	12	50%	100	39	**-60%**
	12	12	50%	100	41	

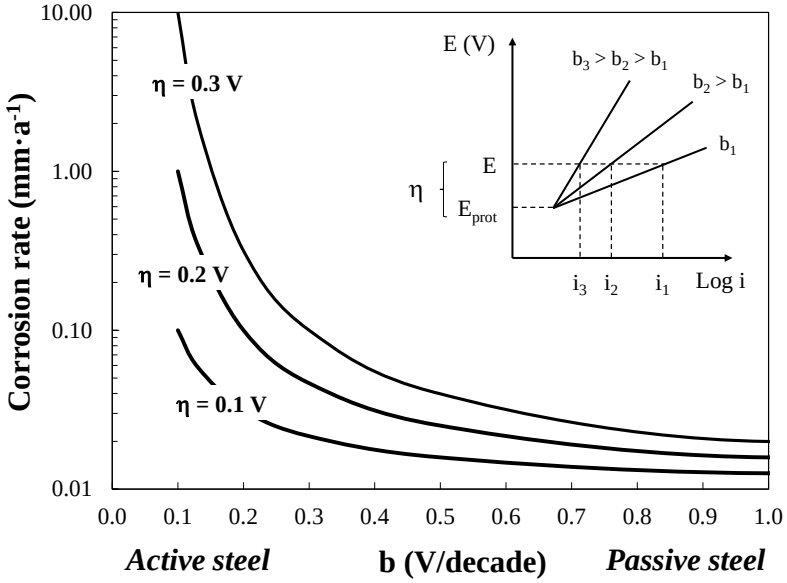

Figure 7: Corrosion rate calculation (Equation 4) by varying Tafel's slope and anodic overvoltage ($\eta = E - E_{prot}$).

Figure 7 shows corrosion rate for different value of potential (i.e. overvoltage η) with respect to Tafel's slope (b), calculated by Equation 4. According to the described mechanism, the increasing of Tafel's slope of carbon steel promotes a decrease of corrosion rate, even if the overvoltage is higher. In other words, the potential measurement can be misleading if it not related to the proper electrochemical behaviour of the metal.

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 (1.0 A·m^{-2}) is applied previously.

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