A proposal of AC corrosion mechanism in cathodic protection

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ABSTRACT

Alternating current (AC) corrosion mechanism is not well understood, particularly as it applies in cathodic protection (CP) condition. The aim of this research is to propose an AC corrosion mechanism of carbon steel in CP conditions. Electrochemical tests were carried out on carbon steel in simulated soil conditions to identify AC corrosion risk related parameters during CP, like AC and CP current density ratio and protection potential. A corrosion risk diagram is proposed: overprotection seems to be the most dangerous condition in the presence of AC. A two-steps corrosion model is proposed: AC causes the local breakdown of the nanosized passive layer formed in CP condition (Step 1) and then high pH corrosion can occur (Step 2) due to the high alkalinity in overprotection condition. To study the effects of AC on passive films, corrosion tests were performed on an austenitic stainless steel in neutral solution in the presence of chlorides.

Keywords: AC corrosion, cathodic protection, passive film, corrosion mechanism.

1 INTRODUCTION

Buried pipelines used to transport hydrocarbons and dangerous fluids are provided with corrosion prevention systems, consisting of an insulating coating and a CP system. CP reduces the corrosion rate caused by soil corrosiveness below 10 μm/y, which is the maximum accepted damage, regardless the pipe wall thickness. The presence of AC may cause serious corrosion damages on metallic structures, even under CP. When a metallic pipe runs parallel to a high voltage transmission line (HVTL), AC-interference takes place by a conduction or an induction mechanism. If the pipeline is insulated with an integral organic coating, corrosion cannot take place, but when the coating has defects, AC-corrosion can occur in them due to high AC density. Factors that contribute to AC interference on pipelines include: (1) the growing number of HVTL, (2) AC operated high-speed traction systems, (3) high insulation resistance of modern pipeline coatings and (4) coatings integrity [1]. Nowadays, the mechanism by which AC causes corrosion is still under study.

The aim of this research is to propose a mechanism of AC-corrosion of carbon steel in CP conditions. Several publications offer a discussion about it, even in the absence of CP. Some of these are discussed in further detail below. Yunovich and Thompson [2] proposed an electrical equivalent circuit analysis to describe AC effects in absence of CP. They consider electrical components to describe the electrochemical behaviour of the metal when AC interference is applied. In their mechanism, the polarization of the metal by the AC signal imposed produces a net anodic current that leads to an accelered corrosion attack. Stalder [3] proposed that AC corrosion may be affected by the chemical composition of the environment at the steel-soil interface and its impact on the spread resistance. According to the theory, alkaline earth cations (such as Ca^{2+} and Mg^{2+}) in the soil promote the formation of highly resistive deposits, wih a higher spread resistance associated to the coating defects and a lower risk of AC corrosion. Nevertheless, this model doesn't propose a description of the mechanism related to corrosion due to AC interference but suggests that the chemical composition of the soil could be critical to identify areas where AC corrosion is most likely to happen. Furthermore, in the presence of a cathodic current, the chemical composition close to the metal is regulated by diffusion processes due to the electric field, therefore it could be very different to the soil-bulk composition.

The above theory by Stalder provided the basis for the alkalinization theory, which was developed by Nielsen et al. [4, 5]. In brief, this mechanism proceeds when hydroxyl ions produced by CP current accumulate in the near surroundings of the coating defect. The combined action of potential variation promoted by AC and high pH induces corrosion attacks. They suggests that, in the presence of AC, a non-protective film can be formed when the potential oscillates between the passivation and the immunity domain of Pourbaix diagram [6]. Oscillations can cause corrosion due to the different time constants associated with iron dissolution (fast) and the formation of the passive layer (slower) [4]. Other authors [7-10] also pointed out that the ratio of the anodic and cathodic Tafel slopes ($r = \beta a/\beta c$) determines the sensitivity of the corroding system with regard to the AC caused polarization and corrosion. Models consider that the nonlinear nature of the current–potential relation of a corroding system is responsible for the generation of a DC-current (rectification current), when a sinusoidal voltage is applied.

In this work an AC-corrosion risk diagram is proposed. Tests were carried out on carbon steel in simulated soil conditions varying CP current density and AC interference current density. The effect of AC interference on nanosized passive films was also studied by means of electrochemical tests on stainless steel in the presence of chlorides to investigate the effect of AC on critical chlorides threshold.

2 AC CORROSION RISK

Long-term exposition tests were carried out on carbon steel, type API 5L X52, in CP condition and in the presence of AC stationary interference. Galvanostatic and potentiostatic tests were performed in soil (electrical resistivity 5÷10 Ωm) on carbon steel specimens (1 cm^2 net surface area): CP current density was applied in the range 0.2 ÷ 10 A/m^2 and AC density in the range 10 ÷ 200 A/m^2. DC and AC were applied using an electrical circuit, described elsewhere [11], that allows to separate the two signals by means of two independent meshes. At the end of the tests, after 120 days, corrosion rates were calculated by weight loss measurement: specimens were removed from the cells and subjected to ultrasonic cleaning in pickling solution, according to ASTM G1-03.

A corrosion risk diagram is proposed in Figure 1. The diagram reports the protection potential (E_{PROT}) versus the ratio between AC and CP current densities (i_{AC}/i_{CP}).

Figure 1: AC corrosion risk diagram
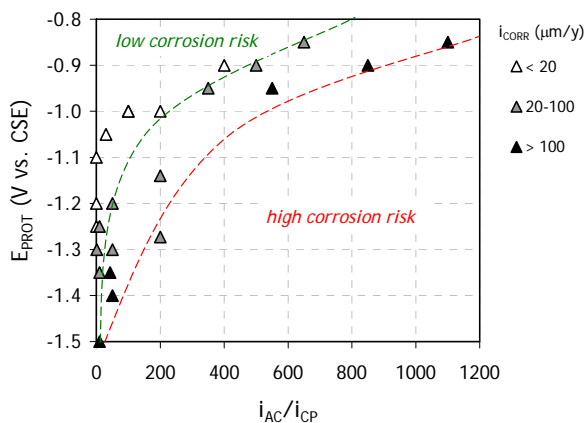
If 10-20 μm/y is considered the maximum acceptable corrosion rate, and 100 μm/y is considered high corrosion rate, three levels of corrosion risk may be identified: low, medium and high, as a function of potential and i_{AC}/i_{CP} ratio. The corrosion risk increases when the i_{AC}/i_{CP} increases and the protection potential decreases (i.e. overprotection conditions were reached). In any case, without AC interference, corrosion doesn't occur: the metal is protected by cathodic polarization. CP criteria in the presence of AC were discussed in a previous work [12]. From laboratory results, overprotection (E_{PROT} more negative than -1.1 V CSE) seems to be the most dangerous condition in the presence of AC. In fact, the critical value of AC density that may cause corrosion decreases as CP density increases (and so the protection potential becomes more negative). In the presence of AC interference, overprotection condition must be avoided. Therefore, AC density and CP current density are not sufficient to establish AC-related corrosion risk, since protection potential must also be taken into account.

3 AC CORROSION MECHANISM

Experimental results show that overprotection is the most dangerous condition with respect to AC corrosion. In this work a two-steps mechanism is proposed. In the first step (Step 1), AC causes the breakdown of the passive layer that CP allows to create of the metal surface. After the breakdown of passivity, corrosion can occur (Step 2) only if the pH at the metal/electrolyte interface reaches very high values (close to 14). Further details about each step are reported below.

3.1 Step 1: The film breaking mechanism

The cathodic current creates alkaline conditions close to the metal that can allow the formation of a nano-sized passive layer, with thickness of a few nanometers. In the passive condition, iron is covered by a thin film of $\gamma Fe_2O_3/Fe_3O_4$ oxide. The consensus view is that the γFe_2O_3 is responsible for passivity [13-14] while the Fe_3O_4 provides the basis for formation of the higher oxidation state but doesn't contribute directly to lower the anodic dissolution. At this stage of the research, experimental tests were mandatory to investigate the presence and the physical-chemical nature of the passive layer in CP.

To study the effects of AC on passive films, long-term exposition tests were carried out on austenitic stainless steel type X5 CrNiMo 17-12-2 in neutral solution. The use of stainless steel allows to find more general considerations on the corrosion behaviour of passive metals with AC interference, regardless the material under study. Specimens (15 x 15 x 2 mm) were obtained from commercial plane slabs; only one cross section (225 mm^2 net surface area) was exposed to the solution. The other surfaces and electrical connections were insulated with an epoxy resin-based coating. Tests were carried out in neutral solution, initially chlorides-free. Samples were placed in cylindrical cells (diameter 0.15 m, height 0.2 m) and connected to an external variable voltage transformer (variac device) to provide a voltage-adjustable source of AC electricity. Four values of AC density were applied for 60 days (stationary interference): 10, 20, 30 and 50 A/m^2. For each value of AC density, four specimens were prepared to ensure test repeatability. Chlorides were added in time (100 mg/L each week). The aim of the tests is to study the effect of AC on critical chlorides threshold, measured at the appearance of corrosion products on metal surface. Figure 2 reports critical chlorides threshold versus AC density. In the presence of AC interference, critical chlorides threshold decreases. This effect could be explained with a decrease of the corrosion resistance of the passive film due to the presence of AC. Nevertherless, some considerations should be done. Corrosion resistance of the nano-sized passive layer decreases for AC density higher than 10 A/m^2. No differences are observed in the presence of 10 A/m^2 with respect to the reference condition, without AC. This means that AC corrosion occurs only for AC density higher than a

critical threshold, as well as chlorides-induced corrosion. In the presence of 100 A/m² (results are not presented) localized corrosion occurs without chlorides in the solution.
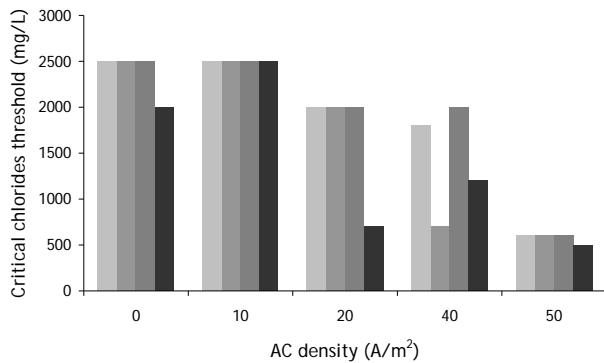

Figure 2: X5 CrNiMo 17-12-2 – critical chlorides threshold in the presence of AC interference

On the basis of laboratory results, a theory for breakdown of passive film is proposed: the film breaking mechanism. This theory was proposed in the field of anodic film breakdown mechanism by Vetter and Strehblow [15] and Sato [16] and requires the film breakdown, due to a mechanical stress within the film, to give anions direct access to the unprotected metal surface. Stress in anodic oxide films can arise for several reasons [16]: (a) interfacial tension of the film, (b) electrostriction pressure resulting from the presence of a high electric field in the film, (c) internal stress caused by the volume ratio of the film and the metal, (d) stress due to hydration or dehydration of the film, (e) local stress caused by impurities. In this paper, only of the interfacial tension and the electrostriction pressure are considered: passive films are extremely thin, hence interfacial tension cannot be negleted. The electric field that produces electrostriction pressure and causes the breakdown of the passive film is in the order of 10^6-10^7 V/cm [16]. The film pressure p that acts vertically to the film is determined by the atmospheric pressure p_0, the interfacial tension γ and the electrostriction pressure due to the presence of the electric field E. From a thermodynamic analysis of the nano-sized oxide film, the film pressure p is given by:

$$p = p_0 + \frac{\varepsilon(\varepsilon-1)E^2}{8\pi} - \frac{\gamma}{L} \qquad (1)$$

where ε is the dielectric constant of the film and L is the thickness of the film. The three terms influencing the film pressure are: the atmospheric pressure, the electrostriction effect and the interfacial tension effect. The electric field across the film can cause the breakdown of the passive film in the limiting condition that p is equal to the breakdown stress of the film. Furthermore, according to Eq. 1, there is a critical film thickness at which the film pressure is equal to the breakdown stress and beyond which mechanical breakdown of the film occurs. The critical thickness of film

breakdown decreases with increasing electric field strenght in the film.

The electrostriction strain causes stress at the steel/nano-oxide interface due to the polarization of the dielectric. In the absence of the electric field, the oxide is formed by randomly-aligned electrical domains within the material. When an electric field is applied to the dielectric, the opposite sides of the domains become differently charged and attract each other, reducing material thickness in the direction of the applied field. At the steel/oxide interface, the strain is not allowed and causes a stress within the film that is proportional to the square of the polarization, i.e. of the electric field strenght. Stress higher than the breakdown stress of the film, causes cracks.

These considerations are general but could be extended in the case of AC induced corrosion: the breakdown of the protective film (with mean thickness L) on carbon steel in CP condition or on a passive material (like stainless steel) could occur by an electrostriction effect due to the alternating voltage across the film. This breakdown model could explain the existance of a critical threshold of AC density (i_{AC}), over which localized corrosion occurs. Furthermore, the sinusoidal physical nature of the alternating field could suggests a mechanical fatigue effect with tensile and compressive stresses at the steel/oxide interface due the alternating voltage. Nevertherless, this model needs confirmation by experimental tests. Using a metallurgical parallelism, the use of AC is known in the field of welding of passive metals, like aluminium, where AC voltage is used to cause the breakdown of the oxide layer and then the melting of the metal under the oxide.

This paper represents a first physical-mechanical approach but tests will be carried out to measure the alternating voltage that could cause the breakdown of the protective film. Nevertherless, also an electrochemical effect of AC must be considered to explain AC corrosion. This effect was described elsewhere [12, 17].

3.2   Step 2: High pH corrosion

After the breakdown of passivity, corrosion can thermodynamically occur only if the pH at the metal/electrolyte interface reaches a value close to 14 [6]. Experimental tests were carried out to measure the pH close to the metal surface in CP condition. A carbon steel specimen, type API 5L X52, was placed on the bottom surface of a cylindrical cell in which a Ti-MMO counter electrode allows to protect the metal by a cathodic current impressed by a galvanostat AMEL 2051. Tests were carried out in a synthetic soil solution containing 0.30 g/L of sodium sulfate (200 mg/L of sulfate ions) and 0.16 g/L of sodium chloride (100 mg/L chloride ions). Applied cathodic currents were 0.1, 1, 5 and 7 A/m². pH was measured by a pH electrode (±0.1 pH) and the distance from the pH electrode to the sample surface was gradually decreases by means of a mobile device, whose displacement was regulated by a screw with an accuracy of 0.2 mm for each

full rotation. Distance was measured by a digital caliber (accuracy ±0.01 mm). Figure 3 shows pH values as a function of the CP current density. In CP condition, the pH increases due to the high hydroxyl ions production due to cathodic reactions. A pH trend can be noticed, due to two effects: (1) diffusion transport due to chemical potential difference of hydroxyl ions from the metal/solution interface to the bulk and (2) electrophoretic effect due to the presence of the electric field between the working and the counter electrodes. In the presence of high current density (5 and 7 A/m^2) the pH value at the steel/electrolyte interface is between 13 to 14 and so corrosion is possible after the breakdown of the passive film that causes direct access of the solution to the unprotected metal. For these reasons, overprotection seems to be the most dangerous condition with respect to high pH corrosion because of the high CP current density.
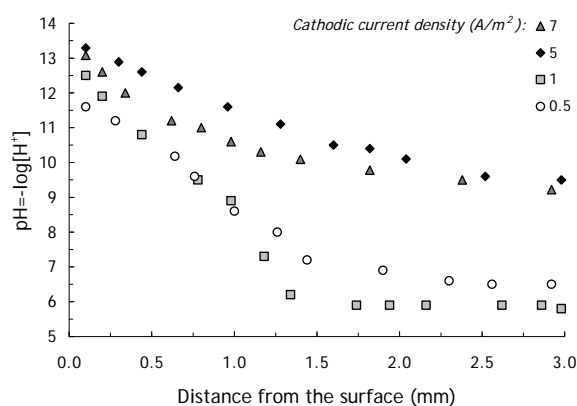

Figure 3: pH profiles varying CP current density

The anodic dissolution process on steel in alkaline environment might be due to the formation of $HFeO_2^-$ ions, with the secondary precipitation of $Fe(OH)_2$ [18]. Nevertherless, the identification of the corrosion reaction is still under study.

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