

A Study of the depolarisation phenoma in soils and remanence of corrosion protection after CP interruption

Clémence Rogier

RICE-GRTgaz

1-3 rue du Commandant d'Estienne d'Orves

92390 Villeneuve-la-Garenne

France

Tiphaine Lutzler

RICE-GRTgaz

1-3 rue du Commandant d'Estienne d'Orves

92390 Villeneuve-la-Garenne

France

Ahmed Fakhry

RICE-GRTgaz

1-3 rue du Commandant d'Estienne d'Orves

92390 Villeneuve-la-Garenne

France

Elisabeth Fleury

RICE-GRTgaz

1-3 rue du Commandant d'Estienne d'Orves

92390 Villeneuve-la-Garenne

France

David Sellam

GRTgaz

5 rue Ferdinand de Lesseps

60203 Compiègne

France

Laurent Henry

GRDF

6 rue Condorcet

75009 Paris

France

Yves Zannier

Storengy

1000 rue du Petit Etang

41700 Chémery

France

François Castillon

TEREGA

40 avenue de l'Europe

64010 Pau

France

ABSTRACT

Cathodic protection (CP) conveys an active protection against corrosion to pipeline steel surface in case of coating defect. This work studies depolarization phenomena that occurs after CP interruption. The term “depolarization” refers to the pipes returning to its free potential value after cessation of CP. Here we present a laboratory study in soils, using metallic coupons to simulate pipeline coating defect behavior with metallic surface exposed to the electrolyte. After CP interruption the potential value of the steel coupon doesn't return to initial value before CP (around -0.6 V/CSE) but remains higher (up to -0.2 V/CSE) for a long period of time (up to 11 days). This effect can be attributed to the formation of a passivation layer at the metallic surface due to pH increase during CP application. This passive layer confers a remanence to the protection against corrosion of the metallic surface after cessation of CP. This study focuses on understanding this depolarization behavior depending on various parameters: level

of CP, time duration of uninterrupted CP, shape of the metallic coupon, composition of the soil media. The objective is to give insight to pipeline operators as to the safety of cathodic protection interruptions on the network depending on environmental conditions.

Key words: Cathodic protection; corrosion; soils; free potential; depolarization phenomena; buried pipelines; remanence of protection.

INTRODUCTION

Oil and gas buried pipelines are protected against corrosion by both organic coatings, a passive protection system, and cathodic protection, an active protection system. When coating defects occur, CP controls the corrosion of the exposed steel surface. From an operating point of view, cathodic protection interruptions can occur on the network during interventions, consignments, or technical problems. Literature indicates that during CP interruption the corrosion rate of the metal remains lower than its free corrosion rate [1]. Application of CP confers a remanence of protection to the metal. The objective of this study is to determine the safe duration for cathodic protection interruptions depending on environmental and cathodic protection conditions.

Effects and mechanisms of CP have been greatly studied and are well-known. Two main effects have been reported (cf. Figure 1) 1) the activation polarization: a direct thermodynamic effect with the lowering of the potential below the equilibrium potential of the metal which confers immunity and stops corrosion; 2) the concentration polarization: an indirect chemical effect with an alkalinization at the metal/soil interface which confers corrosion protection thanks to passivity conditions [2, 3]. More precisely when the soil environment presents a good bedding (e.g. well compacted, fine material) [4], OH^- produced during the cathodic reaction is accumulated near the metallic surface and pH increases locally. A passive film is formed on the metallic surface that slows down corrosion phenomena and is directly linked to oxygen accessibility to the metallic surface. Effectiveness of CP can be correlated to the E_{IRfree} potential but also to the pH value at the metal/soil interface [4].

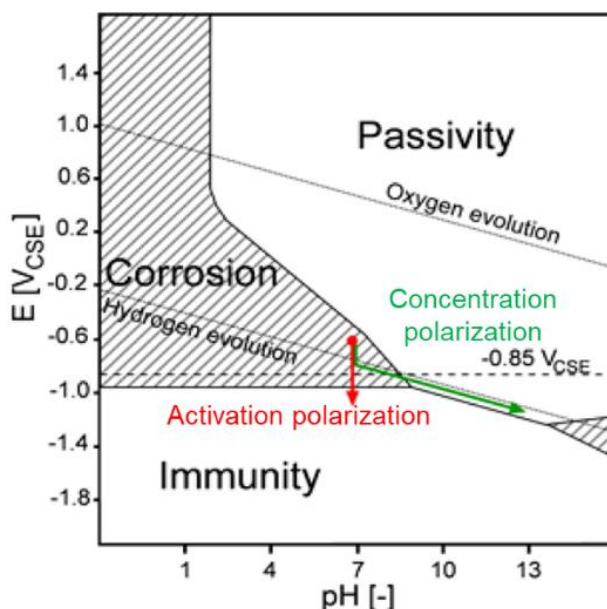


Figure 1 : Pourbaix diagram of iron and schematic representation of the mechanisms of CP adapted from [3]

The ISO 15589-1 [5] standard criteria states that corrosion rate is acceptable and stays below 0.01 mm/year if the IR-free potential of the metallic surface is under -0.850 V vs CSE (Cu/CuSO₄ reference

electrode, +0.318 V vs SHE). The potential (E_{ON}) measured between the metallic surface and a reference electrode (E_{ON}) is the sum of two contributions:

Equation 1

$$E_{ON} = E_{IRfree} + IR$$

where E_{IRfree} is the IR-free potential of the metallic surface, known as the “true” potential taken by the metal and on which the definition of the criteria is based, and IR is the ohmic drop [6]. The ohmic drop occurs in agreement with Ohm’s law due to the contribution of the flow current, the spatial distance between the reference electrode and the metallic surface, and the electric resistivity of the soil. Different measurements techniques are used by operators to determine E_{IRfree} and a common one is to interrupt the circulating current and measure the potential of the metallic surface very shortly after interruption (in the order of 10^{-3} to 10^{-2} s) and before depolarization of the metal. This is called ON-OFF measurements and the measured potential is the E_{OFF} potential [7].

In this paper we aim to understand the depolarization phenomena that occurs after CP current interruptions and evaluate the integrity risk for interruptions over a few hours and a few days since literature has shown that a remanence of protection could occur [1]. Various experiments were conducted in three electrodes cells in soils with metallic coupon under CP. Potential of the metallic surface was followed over a few days after CP interruptions and depolarization was studied depending on the applied CP and the environmental conditions. The parameters studied were as follows: CP level (E_{OFF} potential value before CP interruption), CP duration before its interruption, composition of the soil (sand or artificial soil), and shape of the metallic coupon (indented or flush-like).

EXPERIMENTAL PROCEDURE

Laboratory experiments were carried out in a soil media in a three electrodes cell configuration as represented in Figure 2 with:

- A reference electrode (RE): saturated copper/copper sulphate electrode (CSE) whose potential is verified before testing compared to a calibrated saturated calomel electrode (SCE).
- A counter-electrode (CE): metal grid in titanium covered with oxides of tantalum Ta_2O_5 and of iridium commonly called TiMMO.
- A working electrode (WE) depending on experimental conditions:
 - o an Electrical Resistance (ER) probe of 500 μm thickness and 1 cm^2 exposed surface to monitor the corrosion rate according to the different conditions applied. As advised by the supplier, the surface did not receive any treatment (such as polishing) but was only degreased. Carbon steel electrical resistance probe has been chosen to be able to monitor real time corrosion rate as general corrosion. The aim was to be able to associate specific conditions with a possible loss of metal.
 - o a Metallic Coupon with a 1 cm^2 circular exposed surface coupled with a pH probe positioned at the metal/soil interface. Carbon steel was chosen for the composition of the coupon (grade X70) and the surface is indented from its sample carrier by 2 mm to simulate coating defect. The pH probe was developed in our laboratory and is currently under patenting process and the detail of its operation is not given in this paper. It was calibrated in various media and allowed us to follow the evolution of the pH at the interface throughout the CP and depolarization processes. In this paper it is used to give an estimation of the pH value at the metal/soil interface at various points during the experiment.

An Origaflex Multichannel Potentiostat was used to:

- Apply the appropriate cathodic protection potential (E_{ON} potential) and measure the necessary current density delivered to reach this potential. By convention cathodic currents are negative in this paper. At the beginning of each experiment with a specific set of experimental conditions (CP level and soil media vary) the E_{ON} potential is fixed to correspond after stabilization to an E_{OFF} potential of either -800 mV, -950 mV or -1150 mV vs CSE.
- Measure the potential of the metallic surface throughout the experiment after CP interruption (Open Circuit Potential).

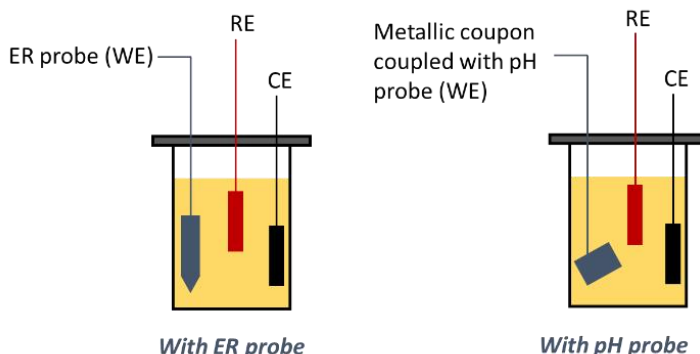
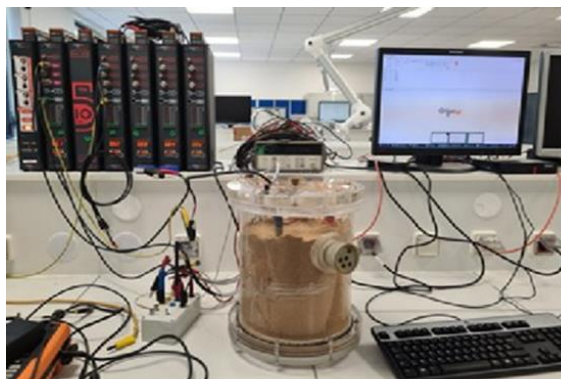


Figure 2: Scheme of the three-electrodes cell setup in soil media

A Rohde-Schwartz RTH1002 digital oscilloscope is used to follow the evolution of the potential during ON-OFF measurements performed with an electrical switch and E_{OFF} value is measured as the mean potential value on a 5-25 ms time interval after current interruption.

The following parameters were tested in this laboratory study:

- Duration of CP phase before interruption: 2 days or 2 weeks
- Level of CP Phase: E_{OFF} potential of -800 mV/CSE, -950 mV/CSE or -1150 mV/CSE
- Soil media: sand (granulometry below 2 mm moisturized with Na_2SO_4 at 10 g/L – pH 7,5 – 13% of absolute humidity) or artificial soil (20% kaolinic clay, 69% of fine sand with granulometry from 0.05 to 0.2 mm, 10% organic matter and 1% CaCO_3 – moisturized with tap water – pH 6.5 – 13% of absolute humidity).
- Surface of the metal: circular-shaped and indented (gravimetric coupon) or rod-shaped and flush (ER probe) as can be seen in Figure 3 below.

It can be noted that the electrolyte of the cell was not replenished throughout the experiments, and that the cell presents a small opening allowing for oxygen venting.

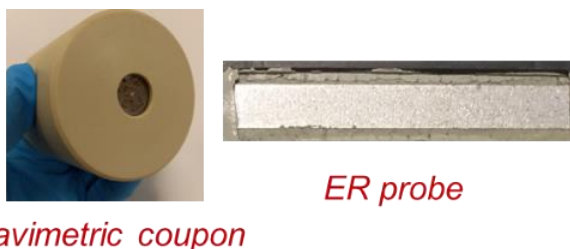


Figure 3 : Both types of metallic surfaces used in this study (circular indented gravimetric coupon and rectangular more flush-like ER probe)