Corrosion Science 73 (2013) 222–229

Contents lists available at SciVerse ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Estimation of residual corrosion rates of steel under cathodic protection in soils via voltammetry

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ARTICLE INFO

Article history:
Received 14 December 2012
Accepted 25 March 2013
Available online 10 April 2013

Keywords:
A. Steel
C. Cathodic protection
B. Cyclic voltammetry
B. Weight loss
B. Polarization

ABSTRACT

Steel coupons were buried in soil for 2 months under cathodic protection. Their residual corrosion rates were deduced from voltammetry and weight loss measurements. In aerated soils, the current density due to O_2 reduction, $j_{K,O2}$, was modelled with a mixed activation–diffusion controlled kinetic. The anodic part j_A of the current density j, computed as $j_A = j - j_{K,O2}$, obeyed Tafel law. Its extrapolation to the protection potential gave a corrosion rate (~7 μm yr^{-1}) consistent with that obtained from weight loss measurements. With a deficient protection, corrosion rates remained at ~80 μm yr^{-1}, a value given by both methods.

1. Introduction

Buried carbon steel pipelines are protected against external corrosion by the combination of organic coating and cathodic protection (CP). CP is used to mitigate corrosion at the defects of the coating and the applied current only flows through the uncoated parts of the pipeline. According to the EN 12954: 2001 standard [1], an efficient CP goes along with a residual corrosion rate lower or equal to 10 μm yr^{-1}. However, the relationship between the polarisation level and the actual residual steel corrosion rate is still questionable. The present laboratory study, part of a project initiated by GDF SUEZ and TOTAL, aims at an improved guidance on cathodic protection criteria by developing tools and methods directly applicable on the field to estimate the "necessary and sufficient" conditions to guarantee a negligible corrosion rate.

The behaviour of carbon steel in soils was extensively studied and the influence of various parameters such as degree of aeration, pH, moisture, ionic species, electrical resistivity or microbiological activity was already described [e.g. 2–17]. Various studies were devoted to the connection between cathodic protection criteria and soil characteristics [e.g. 18–22] and the EN 12954: 2001 standard [1] specifies reference values of the protection potentials to be applied according to soil conditions. In a recent work, the residual corrosion rate of steel under CP was estimated from voltammetry experiments, using a first type of soil as an example [23]. The method is based on the possibility to deduce the anodic current from the overall current by subtracting the cathodic part estimated via a cathodic Tafel straight line [24]. A detailed analysis of the polarisation curves can then lead to an estimation of instantaneous residual corrosion rates (τ_{rc}) of steel coupons under cathodic protection. In the weakly aerated clay sand soil considered in the first preliminary study, the reduction of oxygen played a minor role. It has been shown possible to get a reliable estimate of the residual corrosion rate from voltammetry experiments as the average of instantaneous calculated τ_{rc} gave a value consistent with the average one from weight loss measurements [23]. The instantaneous residual corrosion rate τ_{rc} could be followed with time. With an applied cathodic protection potential (corrected from ohmic drop) of $E_{IR\ free} = -0.95\ V_{Cu/CuSO4}$ (value recommended by the EN 12954: 2001 standard [1] for anoxic conditions), τ_{rc} decreased rapidly during the first 20 days to reach ~10 μm yr^{-1}. In these almost anoxic conditions, the approximation of the cathodic part of the curve by a cathodic Tafel line was reliable.

The aim of the present study was then to investigate the potentiality of this approach by varying soil characteristics and CP conditions. First, another soil was considered for this new study. Secondly, a specific experimental procedure was designed to ensure a sufficient aeration of the soil and prevent anoxic conditions

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http://dx.doi.org/10.1016/j.corsci.2013.03.038

to prevail at the steel/soil interface. In these conditions, O_2 reduction should play a major role and the cathodic part of the curve should not obey the Tafel law. The cathodic component of the overall current must then be modelled differently as the reaction is more likely under mixed activation–diffusion control. Finally, the methodology was tested with coupons under deficient CP conditions, i.e. inadequate protection potentials were applied. As in previous work [23], the relevance of the electrochemical method was estimated by comparison with results given by weight loss measurements.

2. Materials and methods

2.1. Materials

The X70 carbon steel commonly used for pipelines was considered for this study. Its average chemical composition was (in wt%): 98.06% Fe, 0.09% C, 1.53% Mn, 0.29% Si, 0.013% P, 0.002% S and 0.02% V. Cylindrical coupons (diameter: 30 mm, thickness: 2 mm) were cut in the purchased sheets. Each coupon was grit blasted and degreased prior to its mounting in a Teflon® sample-holder so that only one plane circular side of the coupons, with an active area of 5 cm^2, was exposed to the soil.

All experiments were performed in a natural sand soil extracted from the field in the Landes region (South-West of France). This soil was characterised as received and the results are summarised in Table 1. The analysis was performed according to various relevant standards, namely NF X31-107: 2003 for the determination of the proportions of minerals [25], ISO 10390: 2005 for the determination of pH [26], ISO 14235: 1998 for the determination of the organic carbon content [27], ISO 11048: 1995 for the chloride and sulphate contents in aqueous extract [28], NF T 90-019: 1984 for Na^+ and K^+ contents in aqueous extract [29]. A specific methodology was used for the determination of Ca^{2+} and Mg^{2+} contents in aqueous extract. It appeared that the soil was mainly composed of sand, the pH of the aqueous extract was neutral (7.0 ± 0.1) and the chloride content was low (7.8 mg L^{-1}). The calcium concentration was not negligible and reached ∼25 mg L^{-1}.

The soil samples used for experiments were prepared by incorporating and mixing a solution of 5 g L^{-1} Na_2SO_4 dissolved in demineralised water to pre-weighted and pre-dried samples of the soil. All experiments were performed at room temperature (19–23 °C).

An electrochemical cell was specifically designed for the present study so as to favour the aeration of the soil (Fig. 1). It consists of a 15 L cylindrical Plexiglas vessel (30 cm high, 25 cm diameter). Eight holes are managed in the cell top cap for four working electrodes (X70 steel coupons), one reference electrode and one auxiliary electrode. An opening is set in the side of the cell in order to sample a small part of the soil from time to time to determine the soil resistivity. The cell itself is set above a tank containing the 5 g L^{-1} Na_2SO_4 solution and a peristaltic pump drives the electrolyte from the bottom of the tank up to the lid of the cell. The solution then falls onto the soil through numerous holes drilled in the lid. A layer of gravel is set at the bottom of the cell under the soil to favour the draining of the liquid and prevent the soil to fill in the holes. The four steel coupons are buried close to the soil/air interface, at a depth of ∼2 cm. The soil is not compacted so as to favour the transport of the aerated electrolyte. The water content of the soil, measured at the end of the experiments, was about 40% of the saturation level. The resistivity of the soil in these conditions was measured at 50 ± 8 Ω m.

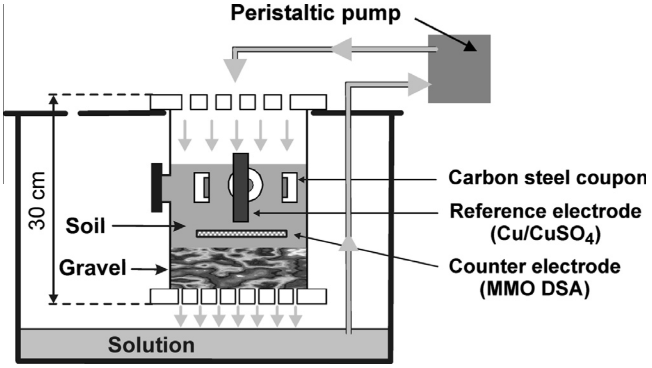

Fig. 1. Schematic representation of the electrochemical cell designed for the study of the behaviour of steel coupons in aerated soils. Only three of the four coupons are represented for clarity.

The counter electrode was a Mixed Metal Oxide Dimensional Stable Anode (MMO DSA) that is a titanium grid coated with tantalum and iridium oxides (Ta_2O_5 and IrO_2). Reference electrodes were copper–copper sulphate electrodes $Cu/CuSO_4$ (+0.316 V/SHE at 25 °C) commonly used in the field. In the following sections of the article, electrochemical potentials are expressed with respect to this reference electrode.

Experiments were also performed in weakly aerated conditions comparable to those considered in previous study [23]. In this case, the cell was completely filled with the humidified soil and hermetically sealed. The system allowing the electrolyte circulation was of course set aside. The water content of the soil was set at about 25% of the saturation level. The coupons were buried at a depth of ∼20 cm. The resistivity of the soil in these weakly aerated conditions was higher than that measured in aerated conditions with an average value of 84 ± 15 Ω m.

2.2. Electrochemistry

All electrochemical measurements were performed in the cell described above (Fig. 1), with circulation of the electrolyte for aerated conditions, without circulation of the electrolyte for weakly aerated conditions.

First, Electrochemical Impedance Spectroscopy (EIS) was used to determine the electrical resistance of the soil (R_s) between the reference electrode and each of the four steel coupons set in the cell. The experiments were performed with a GAMRY femtostat

Table 1
Main features of the Landes soil as received from the field.

Type of minerals (wt%)			pH	Organic carbon content (mg per g of dry matter)
Clay	Silt	Sand		
3.5	8.1	88.4	7.0 ± 0.1	7.7

Concentration (mg L^{-1}) of various ions in aqueous extract (accuracy: ±5%)

Cl^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
7.8	27.3	22.4	12.9	24.8	2.0