

Discussion on AC Corrosion Mechanism and Risk Assessment for Cathodically Protected Pipelines

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ABSTRACT

Although a lot of AC corrosion failure cases have been reported on cathodically protected pipelines, the mechanism of AC corrosion process is still not completely understood and there has been a lack of technical consensus on AC corrosion mechanism under cathodic protection, especially for high CP level. AC corrosion simulation experiments under different CP levels were conducted and during the AC corrosion process, AC corrosion rates, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), corrosion morphologies, corrosion products and environmental parameters near specimen were measured and analyzed. The effect of hydrogen evolution reaction on AC corrosion process under high CP level was discussed based on electrical equivalent circuit model at steel/electrolyte interface, dynamic electrochemical reaction process and the change of local environmental parameter close to specimen surface.

Key words: AC corrosion, cathodic protection, corrosion mechanism, hydrogen evolution reaction, metal/electrolyte interface

INTRODUCTION

A series of AC corrosion failures initiated field and laboratory investigations that indicated induced AC corrosion could occur on coated steel pipelines even when industry accepted CP protection criteria are met.¹⁻⁸ In the past 30 years, AC corrosion has been recognized as a threat to the integrity of buried

pipelines sharing the right-of-way with high voltage AC transmission lines. The reported AC corrosion failure cases showed that the AC corrosion has typical characteristics: 1) typical morphological characteristics: a distinct tubercle of “stone-hard soil” was often observed to grow from the coating defect, pitting-like attack with a rounded bottom; 2) soil resistivity near corrosion location was significantly lower than the specific resistivity of the surrounding soil; 3) high CP level; 4) the pH at corrosion location was high; 2) the main AC corrosion product in soil was magnetite with mixture of carbonate. Although there have been extensive studies investigating the AC-induced corrosion of steel,⁹⁻¹³ AC corrosion, instead, continues to be a controversial subject, and many aspects of it still need to be clarified, especially the mechanism of AC corrosion under high level of CP and how to choose CP parameters under the AC interference.

Different opinions have been proposed attempting to explain the mechanism of AC corrosion under the combination effect of AC interference and high level of CP protection. Nielsen et al. proposed “Alkalization Mechanism”, which demonstrated that the excessive CP could result in a considerably high pH value (i.e., 14 or even higher) of the soil around the coating defect. The combined action of potential vibration caused by the AC and adequately high pH induces corrosion attacks by entering the corrosion area (ferrate stabilization) at high pH value according to Pourbaix diagram.¹¹ Panossian conducted a study attempting to verify the alkalization mechanism experimentally and his results indicated that the kinetic of ferrate formation is very low and the AC corrosion must not be attributed to ferrate formation.¹² Panossian proposed that AC corrosion was a consequence of oscillation of metal/electrolyte interface, which depending on the electrolyte pH, put the system alternatively within the active and immune domains or alternatively within passive and immune domains. However, Panossian’s experiment results didn’t show significant corrosion in excessively alkaline solutions (pH is near to or higher than 14), and only the electropolishing phenomenon was observed in high pH condition, which could not give explanation for the high AC corrosion rate in the field cases under high CP level and high pH environment. Nielsen introduced the concept of “spread resistance” in the Randle’s electrical circuit model and proposed autocatalytic mechanism of AC corrosion on cathodically protected pipelines.^{9,13} The spread resistance is governed by the size of the coating defect, the soil resistivity at the coating defect, the chemistry of the soil, and the cathodic protection current density flowing through the coating defect, which contributes to the AC current density accompanying with the AC voltage. The AC current density may lead to DC depolarization, therefore, increasing the level of cathodic protection may be attempted in order to maintain a certain cathodic protection potential, which further decreases the spread resistance at the coating defect due to the production of ions such as OH⁻, thereby the AC current density increased. This will further depolarize DC, decreasing the spread resistance, etc. This scenario results in an autocatalytic cycle leading to AC corrosion. For the autocatalytic mechanism of AC corrosion, the increasing AC current density is an important factor attributing to high AC corrosion rate. However, Büchler conducted tests in quartz sand soaked with 1M NaOH at pH 14. The AC current densities of 500A/m² and 1200 A/m² were imposed under no or limited cathodic protection current. Over a test period of 3 months, no significant corrosion was observed. While in the presence of cathodic current densities more negative than 1A/m², high corrosion rates of up to 1 mm/y were found in both 1M and 0.1 M NaOH.¹⁴ Thereby, he concluded that neither the highly alkaline environment created by the cathodic protection nor the high AC current densities caused by the low spread resistance can primarily be responsible for the occurrence of AC corrosion. The cathodic protection current has an inherent effect on the corrosion process that is not associated with the changes in the conductivity and pH at the metal surface. For the high AC corrosion rate under high level of CP, Büchler gave the explanation that passive film would form under high CP current density and with the application of AC, the oxidation state of the rust layer changes with the AC cyclic. As long as the charge passing through the metal surface is consumed for changing the oxidation state of the rust layer, the passive film remains untouched. In contrast, if the cathodic charge is too large to be consumed for the reduction of the rust layer, the passive film will be electrochemically reduced. If the cathodic charge is too large to be consumed for the reduction of the rust layer, the passive film will be electrochemically reduced. A higher cathodic DC current results in a more efficient cathodic dissolution

of the passive film, a higher reformation during the anodic half wave, and a higher corrosion rate.¹⁵ Besides, Stalder proposed that AC corrosion may be affected by the chemical composition of the environment and he pointed out that the effect of high pH value on AC corrosion of pipeline was closely related to the ratio between earth-alkaline (i.e., Mg^{2+} , Ca^{2+}) and alkaline (i.e. K^+ , Na^+) cations in soil around coating holidays. If earth-alkaline cations were abundant around coating holidays, a protective corrosion products film (i.e., $Mg(OH)_2$, $CaCO_3$) would form by the reaction of earth-alkaline cations with OH^- . As a result, the corrosion of pipeline was controlled. Otherwise, the high pH value would lead to the dramatic decrease of spread resistance and hence in an accelerated corrosion rate.¹⁶ While laboratory experimental results showed when the CP polarized potential was equal to or more positive than -1.12 V (CSE), the corrosion rates of specimens in earth-alkaline cations containing environment were less than that in alkaline cations containing environment under the same CP polarized potentials and AC current densities, which reversed when the CP polarized potential was equal to or more negative than -1.19 V (CSE) and at this time, the corrosion rates of specimen in earth-alkaline cations containing environment increased significantly when the AC current density was larger than 100 A/m².¹⁷

From the above it could be seen that although there have been different mechanisms trying to explain AC corrosion process, there has been a lack of technical consensus on the AC corrosion mechanism under high level of CP and the effect of chemical composition of environment on AC corrosion behavior.

In this work, AC corrosion simulation experiments under different CP levels and environments were conducted and weight loss corrosion rates, corrosion morphologies, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and environmental parameters close to specimen surface were measured and analyzed. The effect of hydrogen evolution reaction on AC corrosion process under high CP level was discussed based on electrical equivalent circuit model at steel/electrolyte interface, dynamic electrochemical reaction process and the change of local environment close to specimen surface during AC interference.

EXPERIMENTAL PROCEDURE

Experimental Equipment

The schematic diagram of experimental equipment was shown in Figure1. It could be seen that the electrical circuits included AC interference circuit and CP circuit. The AC interference circuit included an AC power, capacitor C (50 V, 1000 μ F), switch S1, working electrode (WE), salt bridge, corrosive media, counter electrode of mixed metal oxide anode (MMO), resistor R1 (10 Ω , 10 W), fuse and rheostat (RX1). AC current of 50 Hz in frequency was applied on WE through the AC circuit. The capacitor C was used to protect the AC signal from interference of DC signal and the rheostat was used to adjust the AC current density to the pre-set value. The function of resistor of R1 was used to get AC current.

The CP circuit was consisted of a DC power, inductor (10 H), switch S2, working electrode (WE), salt bridge, corrosive media, counter electrode (MMO), resistor R2 (10 Ω , 25 W), fuse and rheostat (RX2). The DC power was used to provide DC current and it could work in two modes: constant potential and constant current. The inductor was introduced to prevent AC current flowing into CP circuit and the CP current was adjusted by rheostat. The function of resistor of R2 was used to get DC current.

Salt bridge was used to avoid the influence of the reaction products of counter electrode (MMO) on the environment around working electrode (WE) in solution environment.

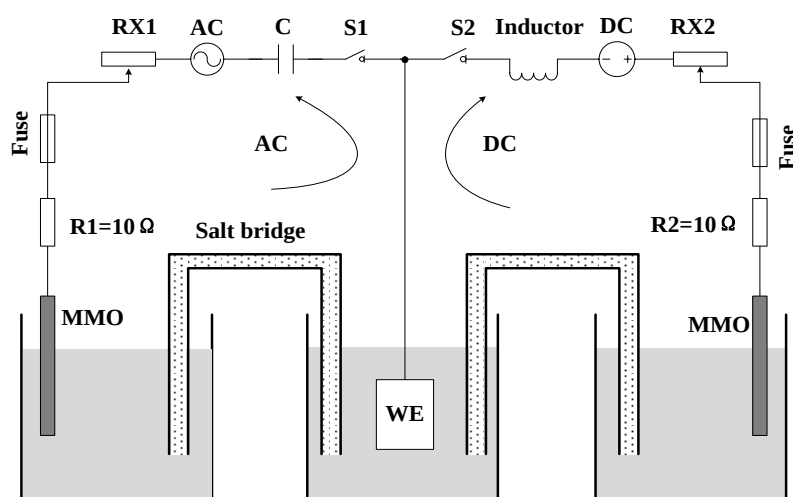


Figure 1: Schematic diagram of experimental equipment

Experimental Materials and Media

Specimens fabricated from X70 pipeline steel were used and the chemical composition in wt% was as follows: C 0.061, Si 0.24, Mn 1.53, P 0.011, S 0.0009, and Fe balance. The X70 steel specimens of 10mm × 10mm × 6mm in size were adopted and all the surfaces were polished with sand paper to 800 grit. The specimens were then washed with deionized water and cleaned by ultrasonic with anhydrous ethanol for 10 minutes. Finally, these specimens were dried for further experiments. The specimens used for the weight loss test were weighed by an Electronic Balance, and were embedded in paraffin wax after wires were bonded to the backside of the specimen with conductive copper glue.

Three kinds of soil simulated environments were applied in the experiments. One is the solution of 4g/L Na₂SO₄, and the other two were mixture of quartz sand and solution, which could simulate the diffusion characteristics of soil better than solution. The composition and properties of the adopted soil simulated environments were shown in Table 1.

Table 1: Composition and properties of three soil simulated environments

No.	Name of the soil simulated environment	Composition	pH
1	Soil simulated solution	4g/L Na ₂ SO ₄	6.4
2	Soil simulated environment with alkaline cations	Quartz sand +solution (8.95g/L Na ₂ SO ₄ +2.66g/L CaCl ₂ +1.47g/L MgCl ₂ +73.07g/L NaCl+0.140 g/L NaHCO ₃)	6.5
3	Soil simulated environment with earth-alkaline cations	Quartz sand +solution (42.56g/L CaCl ₂ +23.52 g/L MgCl ₂ +2.21g/L NaCl+0.140 g/L NaHCO ₃)	6.8

The soil simulated solution was made from analytic grade reagents and deionized water (18 MΩ-cm in resistivity). The soil simulated environments with alkaline and earth-alkaline cations were made by mixing quartz sand and solution according to the volume ratio of 13:6 and the purity of quartz is 99.9%.

Corrosion Weight Loss Test

The corrosion weight loss test of X70 steel under different levels of CP and different AC current densities in three types of soil simulated environments were carried out by using the equipment shown in Figure 1, with an immersion time of 168 hours. At the end of the experiment, the specimens were removed immediately, and the corrosion morphology of the surface was photographed by using an optical camera. The corrosion products were then cleaned and the weight loss was measured with an Electronic Balance and the corrosion rate was calculated according to formula (1). To ensure reproducibility of the results, three specimens were tested in each experiment performed.

$$v_d = 8.76 \times \frac{\Delta w}{St\rho} \times 10^4 \quad (1)$$

Where: Δw is the weight loss, S is the exposed area, t is immersed time, ρ is the density of steel.

Electrochemical Measurement

1) Electrochemical impedance spectroscopy (EIS) measurement

In order to explore the effect of AC current passing through the steel/electrolyte interface under CP, EIS measurements under different levels of CP were performed using CH Instruments electrochemical workstation system. During the measurements, the frequency range used was from 100 kHz to 0.01Hz, and the voltage amplitude was ± 10 mV rms. A classical three electrodes electrochemical cell was used. Pipeline steel specimens with working area of 1 cm^2 were used as working electrode. A platinum column was used as the counter electrode. All the potentials were measured versus a saturated calomel electrode (SCE). A steady state was particularly important to get relevant quantities for impedance measurements. Therefore, sufficiently long time is necessary for the specimen under applied potential reaching a steady state. From the observed current transients in this study, a 3-hour delay was necessarily needed for the steel electrode to achieve a steady current before performing the EIS measurements.

2) Cyclic voltammetry measurement

In order to explore the electrochemical reaction process during the oscillation of AC interference under different CP potentials, the cyclic voltammetry (CV) measurements were performed by using the same circuit as that in EIS measurements. After the immersion of 24h under a certain CP potential, the cyclic voltammetry (CV) measurements were performed on a three-electrode system through electrochemical work station. During the CV measurements, the scanning potential range was set from $-2.0 V_{\text{SCE}}$ to $1.5 V_{\text{SCE}}$ to simulate the effects of AC interference on CP potentials. Due to the limitation of the used equipment, it was not possible to run experiments with scan rates sufficiently high in order to simulate 50 Hz AC currents which were commonly used in China. Based on the previous studies, a medium scan rate of 100 mV/s was used in the CV measurements.

Local environment parameters measurement

A lot of failure cases and researches have shown that the local environment close to the coating holiday of buried pipeline could experience great change during AC interference in soil environment. In order to investigate the variation of local environment around the specimen during the combination effect of AC and CP in soil simulated environment, the spread resistance of specimen under different CP potentials and AC current densities were analyzed. Firstly, the AC voltage and AC current density of the specimen were measured and the spread resistance could be got by dividing AC voltage with AC current density.