Transient numerical model for crevice corrosion of pipelines under disbonded coating with cathodic protection

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ABSTRACT

Cathodic protection can strongly affect the chemical and electrochemical characteristics of the solution under a disbonded coating. In this work, a transient mathematical model was developed to evaluate the effectiveness of cathodic protection on the pipeline steel under a disbonded coating, and the mechanism of cathodic protection for preventing crevice corrosion was discussed. The model includes the temporal evolution of the potential of the steel, pH, oxygen concentration, and conductivity of the solution within a crevice. The implicit finite difference method was used to solve the complex set of mass-transfer equations that describe the system. The chemical and electrochemical processes inside the crevice were numerically analyzed, and the results were compared with those obtained from the experimental data. The results showed that the dissolved oxygen inside the crevice is rapidly consumed, thereby inhibiting oxygen corrosion; the alkaline environment, which is generated by oxygen reduction, results in the formation of a passivation environment. The cathodic current gradually flows into the crevice by overcoming the solution resistance, and the steel is completely electrochemically protected. As the local-solution environment changes as a function of time and distance, various mechanisms may synergistically act to protect the metal inside the crevice from corrosion.

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1. Introduction

A common procedure to protect buried steel pipelines is to combine coating with cathodic protection. Coating provides a barrier between the steel and the environment, protecting the pipeline from corrosion. However, the mechanical damage that occurs during pipeline installation may result in defects. The loss of adhesion of the coating to the pipeline around these defects may occur with time [1,2]. Pipeline steels are known to be susceptible to two forms of stress corrosion cracking (SCC), commonly known as high-pH SCC and near-neutral-pH SCC; both these types of corrosion tend to initiate at the defects formed during pipeline installation [3]. Zhu et al. revealed that SCC is closely related to the local electrolyte environment under the disbonded coating [4]. Coating serves as a shield for the cathodic current, resulting in a potential gradient on the pipeline surface; thus, the steels fall into the sensitive potential-pH scope of SCC [5–8]. To avoid these effects, a cathodic protection system should be designed to maximize the cathodic-protection degree of the steel without hydrogen evolution.

It is well known that cathodic protection can inhibit metal corrosion [9–11]. However, theoretical research on the cathodic protection potential distribution and mass-transfer process under a disbonded coating is limited, especially on the relation of these properties with time and

space; as a result, the mechanism of the cathodic-protection effect on the chemical and electrochemical environment is still a matter of debate [12–15]. The distribution of potential and current under a disbonded coating depends on the transport of ionic species and on the dynamics of chemical reactions occurring inside the crevice [16–19]. Several experimental results about the distribution of the current and potential have been reported [20–23], and mathematical models that make use of the Laplace equation have been proposed [1,16,17,24–27]. However, these models provide only limited information about the transient-mass transfer that resulted from the effects of cathodic protection on crevice corrosion. The electrochemical processes (e.g., current and potential distribution, electrochemical reactions, ionic migration, and gas diffusion) occurring with and without cathodic protection are very different from each other [18,28,29]. These processes are strongly influenced by time and space parameters, which lead to a more complex crevice corrosion behaviour [30]. Therefore, the mathematical models proposed so far are typically simplified [31]. The procedure that leads to a mathematical solution in the steady-state simulation model was greatly simplified by neglecting the effect of time parameters. An accurate mathematical description of the corrosion process is not trivial, and the complexity of the equations makes them difficult to solve. These factors have strongly limited the number of proposed transient models that can describe the distribution of potential, current, and mass transfer in the crevice [32].Therefore, it is necessary to analyze the development process of the local-solution environment with the cathodic

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protection in time and space, as well as to investigate the mechanism of the cathodic protection that can prevent metal corrosion under a disbonded coating.

The main aim of this study is thus to numerically simulate the transient state for crevice corrosion of the pipeline steel with cathodic protection potential. The effectiveness of the presented model is validated through experimental data obtained in our previous work [9]. The results discussed in this contribution provide a theoretical description of the chemical and electrochemical transient conditions of the local environment under a disbonded coating, which cannot be easily measured, such as material concentration and conductivity. The mechanism of cathodic protection that prevents crevice corrosion is also discussed.

2. Theory

The crevice geometry used in the model proposed in this work is schematically shown in Fig. 1. The soil extract enters the coating at the defect; this may result in a loss of adhesion and may form a crevice between the coating and the pipeline, i.e., the loss of adhesion typically occurs around the defect. To simplify the mathematical model and for the sake of symmetry, a rectangular-plane crevice was used as a research object with gap δ and crevice depth L.

2.1. Assumptions of model equations

This study focused on the chemical and electrochemical characteristics of the local solution under the disbonded coating with the application of a moderate cathodic protection potential. The imposed cathodic protection potential results in the consumption of all the oxygen entering from the holiday opening. To simplify the mathematical model, the following additional assumptions were considered besides the basic assumptions of the infinite dilution theory [33]:

(1) The crevice is filled with an electrolyte solution, and the bulk solution outside the defect is saturated with air. The temperature of the solution and the atmospheric pressure are 25 °C and 101.3 kPa, respectively;

(2) The volume of the bulk solution is infinite, and the material concentration of the bulk solution is hardly affected by the electrochemical reactions occurring in the crevice;

(3) Only the following oxygen reduction is considered as the cathodic reaction during the cathodic protection:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-; \tag{1}$$

(4) In order to compare the experimental data [9] with those obtained with our model, the solution used in this work is an aerated, dilute sodium sulfate solution; thus, four chemical components should be considered: OH^-, SO_4^{2-}, Na^+, and O_2 (named as component $i = 1, 2, 3, O$, respectively);

(5) The solution inside the crevice is stagnated, and the mass transfer takes place via migration and diffusion;

(6) The solution satisfies the Newman electroneutrality principle [33]:

$$\sum z_i C_i = 0 \tag{2}$$

where C_i is the molar concentration of species i (mol·cm^{-3}); and z_i is the charge number;

(7) The thickness of the electric double layer on the metal surface is sufficiently small to be neglected;

(8) The model takes only one dimension into account, because the crevice gap δ is too small compared with the size of the crevice depth L.

2.2. Model equations

2.2.1. Mass flux and balance equations

The mass migrates under the electrical field, diffuses under the concentration gradient, and convects with the liquid flow. The mass flux N_i of species i is given by the following expression [33]:

$$N_i = -z_i u_i F C_i \frac{\partial \varphi}{\partial x} - D_i \frac{\partial C_i}{\partial x} + V C_i \tag{3}$$

where N_i is the flux of component i (mol·cm^{-2}·s^{-1}); u_i is the ionic mobility of species i (m·V^{-1}); F is the Faraday constant (96,500 C·mol^{-1}); φ is the local potential of the steel inside the crevice (V); D_i is the diffusivity (cm^2·s^{-1}); and V is the convection velocity of species i (m·s^{-1}). Thus, on the right side of the equation, a first migration term, a second diffusion term, and a third convection term are present.

The convection velocity V is zero for a quiescent solution. Therefore, the mass flux inside the crevice can be written as follows:

$$N_i = -z_i u_i F C_i \frac{\partial \varphi}{\partial x} - D_i \frac{\partial C_i}{\partial x}. \tag{4}$$

The u_i term in the dilute solution is related to its diffusivity by the following expression:

$$u_i = \frac{D_i}{RT} \tag{5}$$

where R is the gas-law constant (8.314 J·mol^{-1}·K^{-1}), and T is the absolute temperature (298 K).

Combining Eqs. (4) and (5) gives:

$$N_i = -\frac{z_i F}{RT} D_i C_i \frac{\partial \varphi}{\partial x} - D_i \frac{\partial C_i}{\partial x}. \tag{6}$$
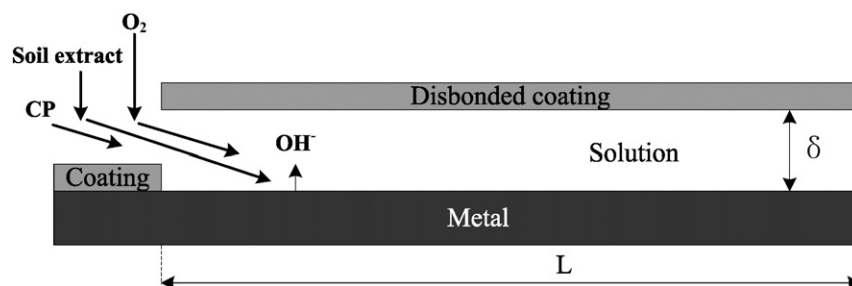

Fig. 1. Schematic view of disbonded coating. L and δ are the total depth and gap of the crevice, respectively.