



A mathematical model for modeling the formation of calcareous deposits on cathodically protected steel in seawater

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ABSTRACT

A 1D mathematical model, which aims at modeling the formation of calcareous deposits on the surface of cathodically polarized steel in seawater, was developed in this paper. The current model is related to mass transport phenomenon, electrochemical reactions, precipitation reactions and homogenous reactions. The model is also capable of tracking the growth interface of the calcareous deposits via the arbitrary Lagrangian–Eulerian method. The current model predicted time-dependent changes of the physical properties of calcareous deposits, including thickness, deposit porosity, coverage rate and electric resistance, and the numerical results are in good agreement with existing experiments.

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1. Introduction

Cathodic protection (CP) is an effective and commonly used means for preventing offshore metallic facilities from corrosion which is caused by seawater. Under CP, the electrochemical reactions [1–4] that occur on the surface of metallic structures are the reduction of oxygen for applied protection potentials varying from -0.8 to -1.2 V vs. SCE



and the reduction of water leading to hydrogen evolution for more negative cathodic potentials.



Both reactions can generate OH^- ions near the surface of metallic structures resulting in the formation of calcareous deposits on the metal surface. Moreover, the existing experiments show that the calcareous deposits are mixtures of CaCO_3 and $\text{Mg}(\text{OH})_2$ [5]. The mechanism for the formation of calcareous deposits [6] is believed to be



The formed compact calcareous deposits act as a physical barrier impede solute diffusion (e.g. oxygen), and thus the current density which is needed to keep CP decreases with the increase of time. Hence, understanding the formation kinetics and the physical–chemical properties of such layers is essential to improve cathodic protection monitoring.

So far, there are numerous papers [1–3,7–15] devoted to studying how the factors such as CP, physics and chemistry of seawater, and surface preparation influence the formation of calcareous deposits through experiments in seawater. However, there are few papers studying this phenomenon via numerical method. The first available model on simulating the formation of calcareous deposits was presented by Sadasivan [16]. In his master's thesis, a 1D model was developed to simulate this phenomenon by considering diffusion as the mass transport mechanism. Moreover, the Tafel equation and the limiting current density were used to present hydrogen evolution and oxygen reduction in his model, respectively. Subsequently, Dexter and Lin [17] presented a steady state model to calculate the pH at metal surface under a cathodic polarization in quiescent saline waters in the presence of both calcareous deposits and biofilms. In 1993, Yan et al. [5,18] published two papers on mathematical modeling of the formation of calcareous deposits on cathodically protected steel rotating disk in artificial seawater. The model was used to study the influences of parameters such as applied potential, rotation speed, temperature, salinity and depth on the formation of calcareous deposits and their ability to change the cathodic current density in CP systems. Deslouis et al. [12] only considered $\text{Mg}(\text{OH})_2$ deposition and presented a model which is capable of evaluating of the thickness of deposits at short and long time scales.

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Nomenclature

a	anode
c	cathode
$c_{i,0}$	concentration of species i on the electrode surface (mol/m ³)
$c_{i,bulk}$	concentration of species i in bulk solution (mol/m ³)
$c_{i,interface}$	concentration of species i at interface (mol/m ³)
$c_{i,ref}$	reference concentration of species i (mol/m ³)
D_i	diffusion coefficient of species i (m ² /s)
$D_{i,e}$	effective diffusion coefficient of species i (m ² /s)
E	electric field strength (V/m)
F	Faraday's constant (96,487 C/mol)
i_{0j}	exchange current density of electrochemical reaction j (A/m ²)
\mathbf{J}	current density vector (A/m ²)
j_j	current density of electrochemical reaction j (A/m ²)
k	proportionality constant
\bar{k}	forward reaction constant for the homogenous reaction (m ³ /(mol s))
\bar{k}	backward reaction constant for the homogenous reaction (1/s)
k_{CaCO_3}	reaction rate constant for the precipitation reaction of CaCO ₃ (mol/(m ² s))
$k_{CaCO_3, interface}$	surface reaction rate constant for the precipitation reaction of CaCO ₃ (mol/(m ³ s))
K_{eq}	equilibrium constant for the homogenous reaction (m ³ /mol)
$k_{Mg(OH)_2}$	reaction rate constant for the precipitation reaction of Mg(OH) ₂ (m ⁷ /(mol ² s))
$k_{Mg(OH)_2, interface}$	surface reaction rate constant for the precipitation reaction of Mg(OH) ₂ (m ⁶ /(mol ² s))
$k_{sp,Mg(OH)_2}$	apparent solubility product constant of Mg(OH) ₂ (mol ² /m ⁶)
$k_{sp,CaCO_3}$	apparent solubility product constant of CaCO ₃ (mol ³ /m ⁹)
l	thickness of calcareous deposits (m)
L	thickness of diffusion layer (m)
m	cementation exponent
m'	reaction order of precipitation reaction of CaCO ₃
M_i	molecular weight of species i (kg/mol)
n	saturation coefficient
\mathbf{N}_i	molar flux of species i (mol m ² /s)
n_j	number of electrons in reaction j
p_{ij}	anodic reaction order of species i in reaction j
q_{ij}	cathodic reaction order of species i in reaction j
R	universal gas constant (8.3145 J/(K mol))
R_i	reaction rate of species i (mol/(m ³ s))
$R_{i,e}$	effective reaction rate of species i (mol/(m ³ s))
$R_{i,interface}$	surface reaction rate of species i (mol/(m ² s))
s_L	fluid saturation
T	temperature (K)
u_{mi}	mobility (mol m ² /(J s))
$u_{mi,e}$	effective mobility (mol m ² /(J s))
\mathbf{v}	growth velocity of calcareous deposits (m/s)
V	volume of porous deposit layer (m ³)
V_c	solution volume in the porous deposit (m ³)
V_p	volume of porous deposit (m ³)
V_s	volume of deposit (m ³)
V_u	volume of diffusion layer (m ³)
$\chi_{CaCO_3/Mg(OH)_2}$	molar ratio of CaCO ₃ to Mg(OH) ₂
Z_f	surface resistance (Ω m ²)
Z_f	porosity resistance (Ω m ²)
Z_i	charge number of species i

Greek letters

α_j	transfer coefficient for reaction j
η_j	overpotential for reaction j (V)
ℓ	current density (A/m ²)
ϕ	potential (V)
ρ	charge density (C/m ³)
ρ_i	density of species i (kg/m ³)
ϑ	relative permittivity
ε	coverage rate
θ	deposit porosity
θ_0	initial deposit porosity
σ	electric conductivity (S/m)
σ_e	effective electric conductivity (S/m)
σ_e^*	effective conductivity in calcareous deposits (S/m)
ν_{ij}	stoichiometric coefficient for the species i in reaction j
τ	tortuosity of porous layer

Based on these existing models and current development in simulation, we believe that a more advanced model can be developed. An overall view of recently published papers, which aim to simulate the electrochemical phenomena, shows that there are two main ways to introduce the electrochemical reactions into mathematical models: (1) application of Butler–Volmer equation [19–22] or Tafel equation [23,24]

$$j_j = i_{0j} \left\{ \prod_i \left(\frac{c_{i,0}}{c_{i,ref}} \right)^{p_{ij}} \exp \left[\frac{\alpha_{aj} F}{RT} \eta_j \right] - \prod_i \left(\frac{c_{i,0}}{c_{i,ref}} \right)^{q_{ij}} \exp \left[\frac{\alpha_{cj} F}{RT} \eta_j \right] \right\} \quad (6)$$

$$j_j = i_{0j} \frac{c_{i,0}}{c_{i,ref}} \exp \left[\frac{\alpha_{aj} F}{RT} \eta_j \right] \quad (7)$$

(2) employment of polarization data obtained from potentiodynamic scan experiments [25]. For both above-mentioned methods, if the following expression:

$$\ell = f(\phi) \quad (8)$$

is used to stand for the polarization behavior, then the schematic of a fictitious computational domain along with the governing equations and the boundary conditions for most electrochemical reactions involved in simulation can be shown in Fig. 1.

Published papers [26–30] also show that these two methods can afford satisfactory numerical results for simple or simplified systems. However, the physical, chemical and biological phenomena, taking place on the cathodic surface in seawater is time-dependent and quite complex [31,32]. Hence, both methods would run out when come to simulate such a phenomenon existing in long-running systems. Nevertheless, measurement errors and defects for potentiodynamic scan experiments are unavoidable. Fig. 2 gives a schematic of the obtained polarization curve via potentiodynamic scan experiment. Clearly, the obtained polarization data only include information of the points located on the “dash dot line”. And that means lots of useful information about the electrochemical behavior of tested material would be missed (e.g. information of point A, B, C, etc.). Moreover, a number of factors will introduce other errors into the measurement results [33], such as the interfacial capacitance at the electrode/solution interface, irreversible changes to the interfacial structure caused by long-time polarization, the scan rate and mode used in potentiodynamic scan experiments, immersion time, and so on. Obviously, without a unified test standard for potentiodynamic scan experiments, the obtained polarization data vary from person to person even for the same system. Hence, it is open to objection that whether or

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