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ABSTRACT Ceocor 2017

Corrosion kinetics behind pipeline IR-free potentials

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Cathodic protection effectiveness is validated based on IR-free potential and current density at a coating defect. In practice both parameters are very difficult to measure properly especially when high resistance coated pipelines are involved.

The IR-free and current density is a result of the thermodynamic and kinetic mechanisms occurring at the steel surface which in turn are dependent on AC and DC polarization level, the environmental conditions, formed deposits on the steel surface and geometry of the coating defect.

Many research has been performed to quantify the corrosion rate of buried steel in laboratory set-ups and on coupons in the field. However the challenge to extrapolate these experimental data to real pipeline corrosion conditions remains difficult because not all mechanisms that occur at the steel surface can be measured, nor can be differentiated from each other to reveal which reaction leads to a given IR-free and corrosion rate.

This article demonstrates results from an advanced computational model that calculates IR-free potential, current density of partial electrochemical reactions, mass and charge transfer, formation of corrosion and calcareous deposits and passive film while keeping into account the diffusion in the soil electrolyte within the coating defect of given geometry. Simulation results will be compared with experimental data found in literature.

Introduction

A conventional way for explaining pipeline corrosion is referring to the Pourbaix diagram that describes the stable phases of iron in aqueous solutions for a given pH and polarization level concentrations (better activity) of the iron species is calculated by the Nernst equation. The Pourbaix diagram however does not take into account changes in temperature and concentration of solvated ions in solution nor the kinetic aspects of the species. In order to understand the corrosion kinetics much more mechanisms must be considered at the same time:

1. the Butler-Volmer equations describe the relationship between the current density and the potential, the kinetic constants and the concentrations of the species;

2. the diffusion coefficient of the species towards and away of the metal surface must be taken into account since they can decrease the reaction rate;

3. the presence of carbonate species have an buffering effect on the pH change and may result in reactions with Ca^{2+} and Mg^{2+} forming for example $CaCO_3$ precipitate which in its turn influences the diffusion of the species;

4. the change in resistivity (or resistance-to-earth) must be updated based on the new composition of the ionic species while the electrochemical reactions take place and also the geometry of the coating defect;

5. potential drop in the soil, inside the coating defect and over the formed passivity layers must be computed

It is obvious that an understanding of the corrosion kinetics in a given environment and for a given polarization level (free corrosion or cathodic protection) is a complex subject.

Soil as a corrosive environment

Soils behave differently than aqueous solutions with that respect that soils have a solid matrix (grain particles) which are fully or partly filled by soil moisture. The presence of the solid matrix has several consequences on the mobility of the species involved in the electrochemical corrosion reactions. The porosity of the soil defines the free space between grain particles and can vary from 0.15 (gravels) to 0.75 (organic clays with high plasticity). The free space can be fully filled with water (saturated conditions) or partly with a (interconnecting) water film around the grain particles (rather dry or field capacity conditions). It is obvious that the diffusion coefficient of the species is largely influenced by the moisture content of the soil. In aqueous solutions such as for Pourbaix diagram and in many experimental work, the diffusion coefficient of the species is relatively high and ranges in the order of 10^{-9} m^2/s. In soils however the (apparent) diffusion coefficient of the majority of the species is one or two orders of magnitude smaller namely between 10^{-10} (saturated conditions) and 10^{-11} (field capacity) m^2/s because of the physical hindrance of the particles which is expressed as the tortuosity of the soil. Oxygen is an exception to the rule. Its apparent diffusion coefficient behaves inversed with the soil moisture content and can have a much larger variation depending on the soil conditions. If the soil is fully saturated and all pores are filled with groundwater, the apparent diffusion coefficient of oxygen is as low as 10^{-11} m/s^2. However if the pores in the soil are partly filled with water, oxygen can easily penetrate in the air space and diffuse in the thin water film around the soil particles and wetted metal surface. Under this condition the apparent diffusion coefficient of oxygen as high as 10^{-5} - 10^{-6} m^2/s as is the case with well aerated sand with low moisture content.
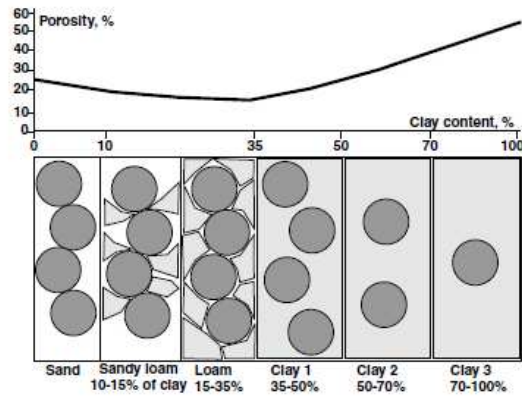
Fig 1 - Porosity of soils as function of clay content [2]

Oxygen is the dominant cathodic reaction in the corrosion process. It determines the corrosion rate and the corrosion potential of steel. However because of limitations in diffusion its ability to increase the pH is limited and cathodic protection requires in most cases more negative potentials to achieve the electrolysis of water with the formation of hydrogen gas and hydroxyls (except in very acid soils)

Modeling corrosion kinetics

A time-dependent numeral model was presented during the Ceocor conference a few years ago [3]. While the solver was meant for AC corrosion simulations further extensions to the software have recently been implemented for taking more complex systems.

The computational model consists of an axisymmetric domain of a circular defect with user-defined surface area and coating thickness.

The ions considered in the computational domain are given in Table 1. Sodium and chlorides are used to maintain electro-neutrality of the solution and their concentration is determined as function of the specific resistivity of the soil electrolyte. The soil species can diffuse into the soil and the concentration gradient can be established as function of the electrochemical and chemical processes taking place.

Na^+	Cl^-	H_2	OH^-	H_2O	O_2	Fe^{2+}	H_2CO_3	HCO_3^-	CO_3^{2-}	Ca^{2+}

Table 1 – ionic species for computational model

The software takes into account 6 different electrochemical reactions as shown in Table 2. The current density of each reaction is calculated for each time step (e.g. millisecond) of the induced remote earth voltage signal or polarization level. The current density is calculated for each partial reaction using the Butler-Volmer equation.

Nr	Name	Stochiometry
1	H_2 evolution / re-oxidation	$2H_2O + 2e^- = H_2 + 2OH^-$
2	O_2 reduction / formation	$2H_2O + O_2 + 4e^- = 4OH^-$
3	ferro – ferri conversion	$3H_2O + Fe_2O_3 + 2e^- = 2OH^- + 2Fe(OH)_2$
4	magnetite reduction to iron hydroxide	$4H_2O + Fe_3O_4 + 2e^- = 2OH^- + 3Fe(OH)_2$
5	iron oxidation	$Fe^{2+} + 2e^- = Fe$
6	magnetite formation	$4H_2O + Fe_3O_4 + 8e^- = 8OH^- + 3Fe$

Table 2 - electrode reactions stochiometry

The concentration of the species involved in the reactions is updated according to their diffusion rate in the soil. As such the concentration profile of species is determined from which the evolution of the ion concentrations, pH front, the soil resistivity and spread resistance over time and space is simulated. The diffusion coefficient of the species in the soil is normal constant in the absence of scaling ions such as Ca^{2+}. In the presence of scaling ions, the diffusion coefficient of the species is reduced when the saturation index is reached. The concentration of Ca^{2+} and CO_3^{2-} in the computational domain can vary depending on the ruling pH front. In other words, the $CaCO_3$ and thus resulting diffusion coefficients are time and space dependent. If the saturation index is exceeded the volume of the local precipitated $CaCO_3$ is calculated. The diffusion coefficients are then reduced as function of the $CaCO_3$ fraction that fills the soil pores.

Under free corroding conditions the oxygen reduction (reactions 2) and iron oxidation (reaction 5) occur. As a consequence of the oxygen reduction, hydroxyls are formed. A precipitation reaction of iron hydroxide recombination ($Fe^{2+} + 2\ OH^- = Fe(OH)_2$) must take place otherwise the pH will increase and a passive film will spontaneously be formed according reaction 6 which is never the case under free corroding and aerated conditions.

Furthermore, the growth of the rust layer $Fe(OH)_2$ and passive film Fe_3O_4 must be considered. It should be noted that at sufficiently negative potentials the passive film or magnetite can be reduced (reaction 4) to form the corrosion product $Fe(OH)_2$. The redox condition of the corrosion product can be converted according to reaction 3. This ferri-ferro conversion represents the pseudo-capacitive component of the AC corrosion mechanism. Both the rust and passive film layer have a voltage drop that depends on their thickness. The thickness of these layers and the voltage across them must be calculated as well. It is known that the corrosion rate may reduce over time by the formed corrosion products or passive film layer. Reaction 5 is the free corrosion reaction at moderate pH in absence of complete coverage of magnetite film while reaction 6 only occurs when the pH is sufficiently high (pH~10). Once the passive film is completely formed, reaction 5 is inhibited.

The mechanisms describe above (diffusion, precipitation, passive film and corrosion product formation) all have their influence on the current density computed for the partial reactions in Table 2. Hence the corrosion rate is calculated by Faraday's law from the iron oxidation reactions 5 and 6 in Table 2.

Example

The polarization behavior of a 1 cm^2 steel probe was measured [4] in sand saturated with scaling ions as given in Table 3. The scan rate was 30mV/min and started at a cathodic potential of -2000mV versus Cu/CuSO$_4$. The specific resistivity was 17 ohmm.

Figure 2 shows the measured curve with ON and OFF values. The simulated curve is shown in Figure 3. It can be seen that at anodic potentials the current density is constant during a scan of approximately 750 mV. This is explained by the fact that a passive film (Fe_3O_4) is easily formed because of the significant increase in the pH at the metal surface during the cathodic scan on one hand, and because of the precipitation of $CaCO_3$ on the other hand which decreases the diffusion of hydroxyls

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towards the soil. During passivation however the hydroxyls are partly consumed (Table 2 reaction 6) and are diffusing away into the soil after which the pH decreases slightly as shown in Figure 4. The thickness of the passive film Fe_3O_4 is expressed as the parameter theta. Theta equals one means that the entire surface of the steel is covered with one monolayer (few nanometer thick) of Fe_3O_4. A theta is less than 1 means that the passive film is not existing or is not fully covering. For values above 1 different layers are built up and the surface is fully passivated. At sufficient anodic potentials the current density increases which corresponds to the generation of oxygen gas (Table 2 reaction 2).

Ion	Diff [m²/s]	Conc [mol/m³]
Na+	2.33E-10	17
Cl-	3.56E-10	17
H_2	1.00E-10	0
OH-	9.25E-10	8.00E-04
H2O	1.00E-08	55000
O_2	2.00E-09	0.2
Fe^{2+}	1.26E-10	0
H_2CO_3	3.00E-10	0
HCO_3-	2.07E-10	2.5
CO_3^{2-}	1.62E-10	0
Ca^{2+}	1.39E-10	10

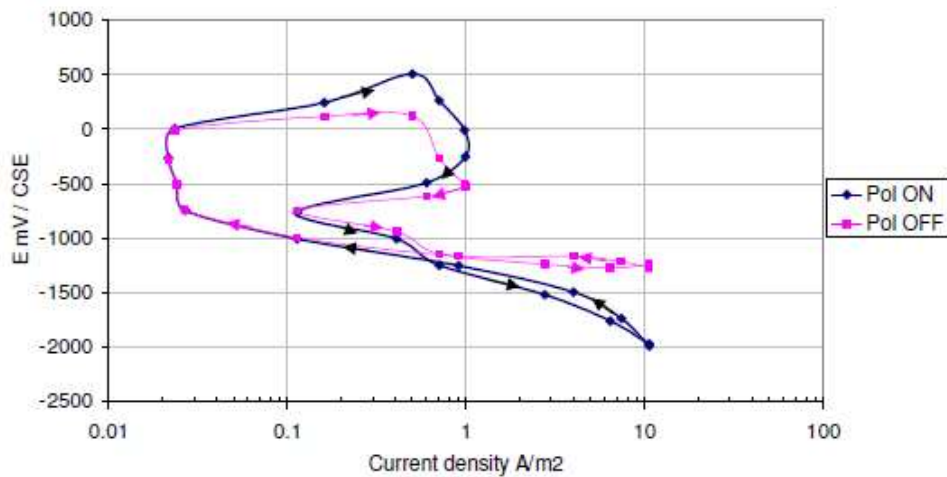**Table 3 - electrolyte composition of sat' sand w/ scaling effect**

Figure 2 – measure polarization curve in sat' sand w/ scaling effect
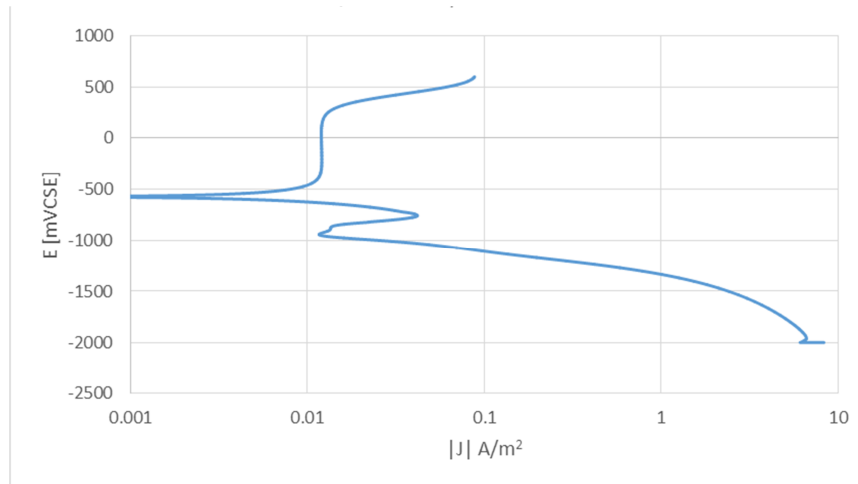
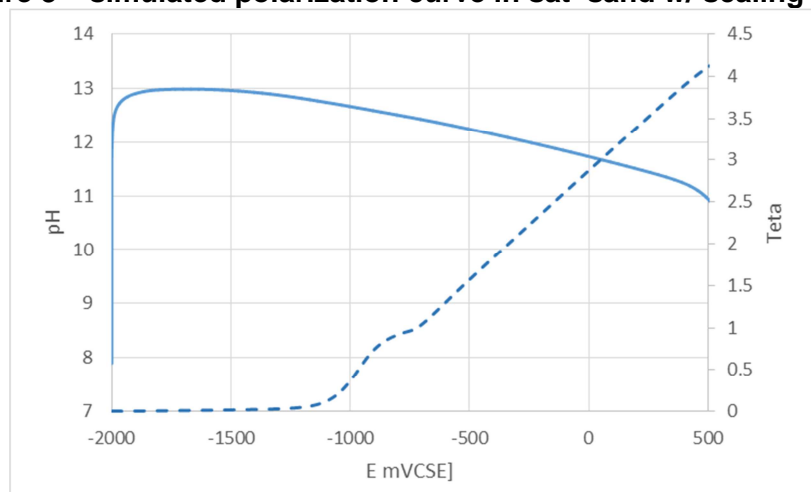**Figure 3 – simulated polarization curve in sat' sand w/ scaling effect**

Figure 4 – evolution of pH and thickness of the passive film (theta=1 equal one monolayer of Fe_3O_4

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