MODELING PIPELINE STEEL PASSIVATION

Christophe Baeté
Manager Corrosion Engineering
Elsyca n.v.
Vaartdijk 3/603, 3018 Wijgmaal, Belgium
christophe.baete@elsyca.com

Metals that passivate have a low corrosion rate because of the protective film that is formed on the metal surface. Passivity of carbon steel is achieved if the pH at the metal surface is sufficiently high to form a protective layer, as is the case for rebars in concrete and well controlled cathodic protected structures. The protective film however can be destroyed if the electrolyte conditions at the metal surface changes or, if a significant change in polarization potential occurs. As a result uniform or localized corrosion rate increases.

A time-dependent computational model is proposed that calculates the corrosion rates of pipeline steel. The model takes into account the electrolyte chemistry, soil properties, the polarization level of the pipeline, the coating geometry, the electro kinetic Butler-Volmer equations, the formation and destruction of the passive film and the built-up of corrosion products. Simulations are performed for a variety of CP conditions demonstrating the corrosion and passivation behavior of the steel with the corresponding IR-free and current density.

Introduction

The polarization behavior of pipelines is different along their routing since they transverse variety of soils and have a variety of coating sizes. The current demand and polarization level is therefore different. According [1] coating defects in high resistivity soil will have a more electropositive potential than another defect with similar size in a low resistivity soil. A coating defect in a soil with similar resistivity but larger coating defect size will have a more electropositive potential as well. The potential difference along the pipeline will lead to electrochemical stresses by means that the more cathodic coating defects tend to receive current while the more anodic coating defects tend to deliver current and become more electropositive. The potential behavior changes over time because of the seasonal variations

with different soil moisture and aeration conditions. A coating defect under cathodic protection will have a high pH (>9) at each surface. Under sufficient anodic stress conditions the potential tends to shift to more electropositive potentials. The steel oxidizes (corrodes) but because of the high pH the steel passivates and the corrosion is strongly reduced. This is demonstrated in Figure 1.
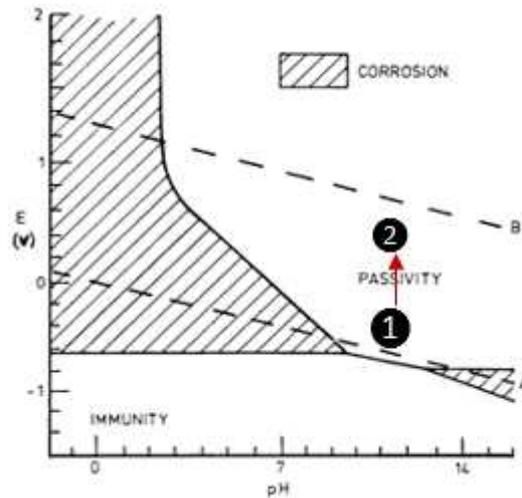

Figure 1 – Passivation under anodic stress

Modeling technology

A computational model is proposed for simulating the polarization behavior of a coating defect on a buried pipeline under cathodic protection in the presence or absence of AC and DC interference.

The following input parameters are applicable:

- hydrodynamic conditions
- (bulk) soil resistivity & pH
- soil particle grain size
- concentration & diff coefficient of the soil species
- soil tortuosity & porosity
- coating thickness
- defect size
- Eon (remote)
- AC voltage (remote)

The perturbation signal can be of any type such as a cathodic protection remote earth ON potential with superimposed AC voltage, or a varying ON potential as occurring during DC stray current. The computational model provides time-dependent results for the following output parameters:

- current density (6 reactions)
- corrosion rate
- IR-free potential
- thickness of passive (Fe_3O_4) and/or rust ($Fe(OH)_2$) film
- spread resistance
- pH front
- $CaCO_3$ formation
- concentration of species

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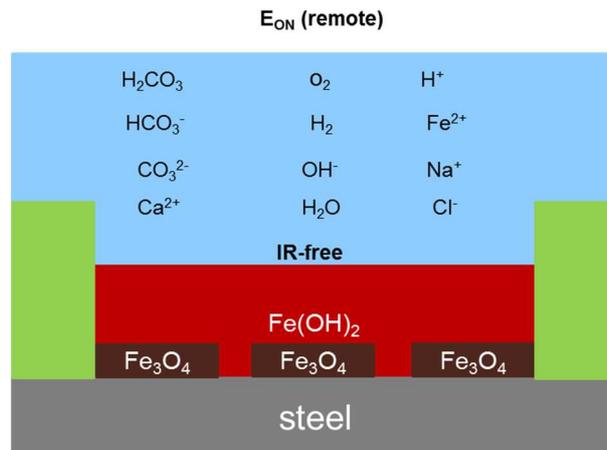- updated concentration and diffusion coefficient of the species

Figure 2 – Schematic representation of computational model

Boundary conditions

Simulations were performed in a coarse texture soil under different soil moisture content and in the presence or absence of scaling agent calcium. The coating defect has a surface area of 1 cm^2 and has a thickness of 50 μm only (almost flush). Two different cathodic protection potentials were considered namely -1.060 and -1.200V_{CSE} respectively. The signal was kept constant for 10 minutes. Table 1 gives a summary of the different parameters.

Param	Value
Soil porosity	0.48
Grain radius	500μm
Soil tortuosity	1.5
Calc porosity	0.05
Calc tortuosity	1.5
Soil pH	7.5 (initial bulk concentration)
Soil ρ	50 Ωm
Soil water saturation	20, 40, 60, 80 and 100%
O_2 conc	3 ppm
Ca^{2+} conc	0 and 80 ppm
HCO_3^- conc	60 ppm
Eon, remote	-1.060 and -1.200V_{CSE}

Table 1 – overview of the input parameter values for modeling

Simulation results

At first instance simulations were performed in the absence of calcium ions. As such no calcium carbonate precipitation can take place but the pH is partly controlled by the presence of HCO_3. Figure 3 shows the cathodic protection current density and IR-free protection potential for different soil moisture contents in the case of an applied CP remote earth potential of -1.060 and -1.200 V_{CSE} respectively. The CP current requirement is the highest at soil water saturation of 60% and tends to decrease at higher and lower water saturation levels. The IR-free potential becomes more electropositive when the soil water content

decreases. A similar behavior is found for a higher cathodic protection level of -1. 200VCSE.The behavior at full saturation level of 100% is an outlier that cannot be explained yet.
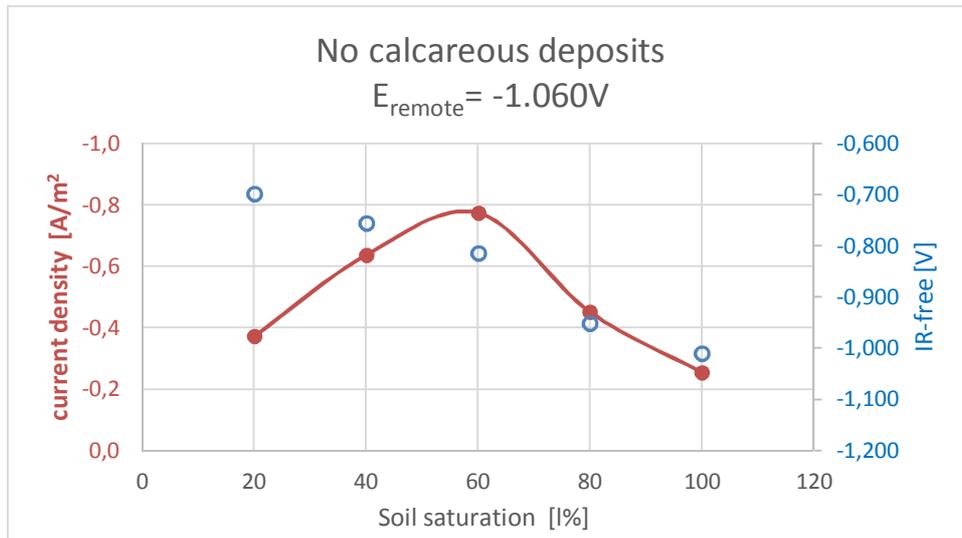

Figure 3a – CP level under -1.060V$_{cse}$ remote earth potential for different soil moisture content and no calcareous precipitate
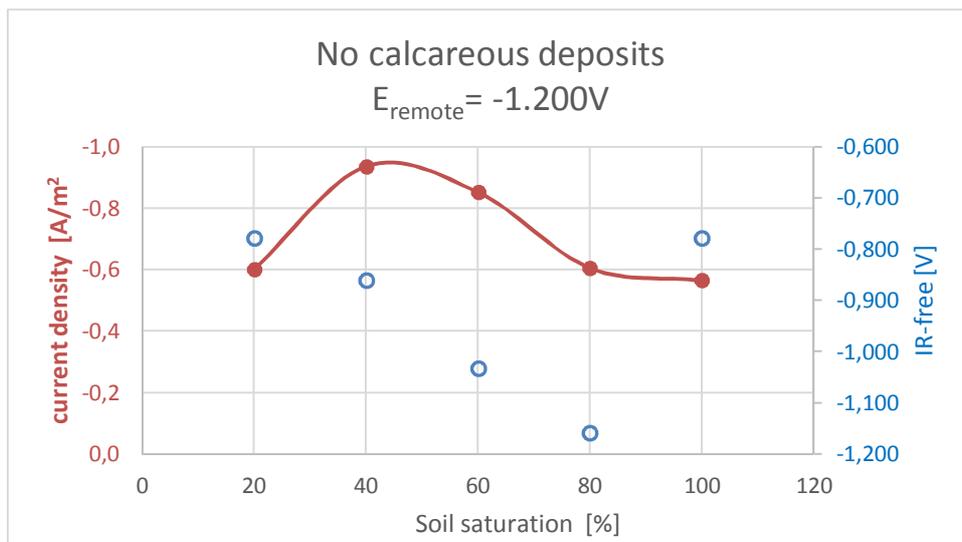

Figure 3b – CP level under -1.200V$_{cse}$ remote earth potential for different soil moisture content and no calcareous precipitate

In the case calcium ions are considered the CP behavior changes. $CaCO_3$ can be formed under cathodic protection if the pH is sufficiently high. This can clearly be seen when a potential of -1.060V$_{cse}$ is applied. The IR-free potential remains quasi constant for the different water saturation levels of the soil. At higher CP level of -1.200V$_{cse}$ the IR-free potential becomes more electronegative with increasing water content.
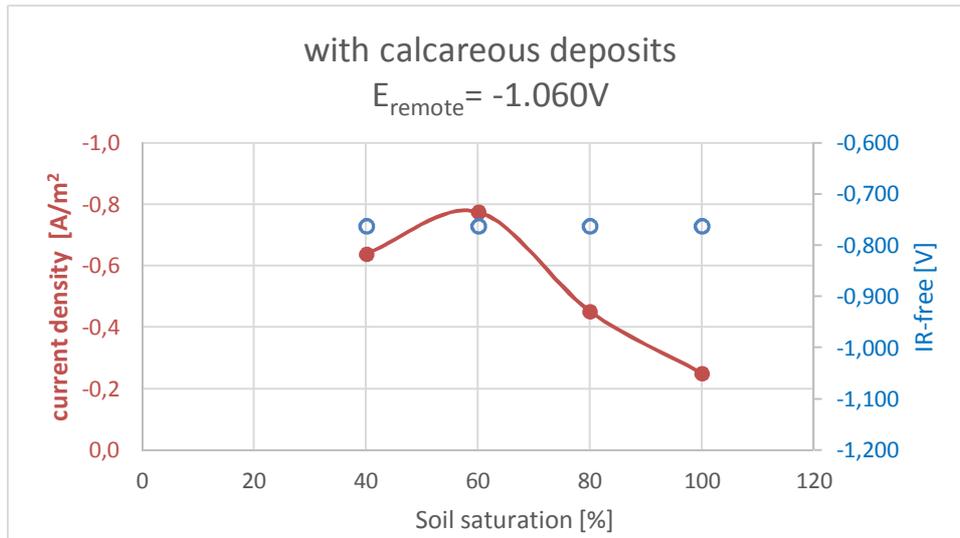
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Figure 4a – CP level under -1.060V_cse remote earth potential for different soil moisture content and with calcareous precipitate
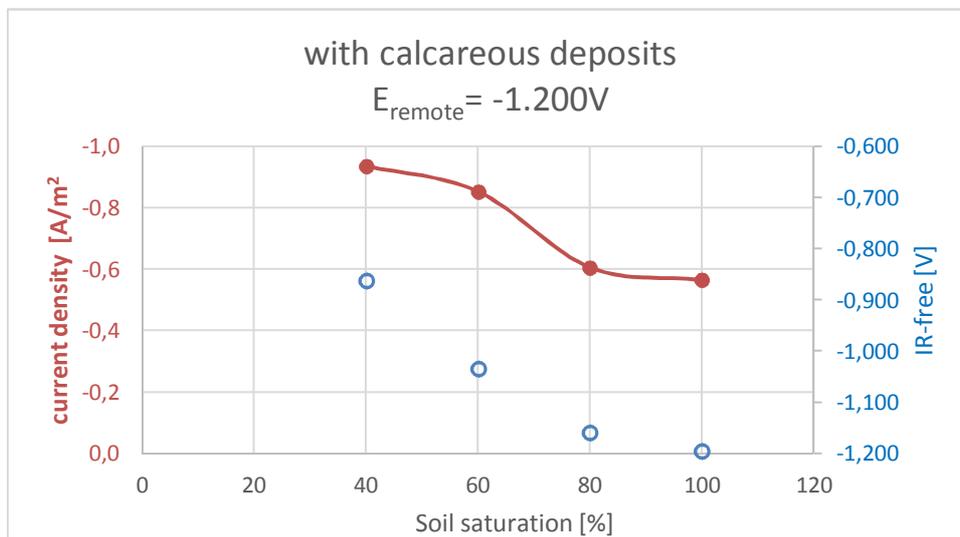

Figure 4b – CP level under -1.200V_cse remote earth potential for different soil moisture content and with calcareous precipitate

Discussion

The water content of the soil plays a role in the CP behavior of the steel at the coating defect. The maximum current demand occurs between 40 and 60 % saturation level. The pores in the soil are partly filled with water and air. The water is present as a film around the particles. Under this condition the current demand is the highest since free oxygen is available in the air fraction and the diffusion path through the water film is the shortest. The corrosion rate is at its maximum. Oxygen concentration at the metal surface also determines the increase in pH during cathodic protection and thus controls the formation of a passive film. In the case that the surface is fully covered by a protective Fe_3O_4 layer the corrosion rate is significantly reduced. In the case sufficient cathodic protection is applied the steel does not tend to oxidize and remains in the immunity region.

In Figure 5 the IR-free potential and pH from the various simulation results are plotted against each other in the Pourbaix diagram. The surface area of the circles is proportional to the corrosion rate which is maximum 25μm/yr in this case. There are mainly two group of

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results. One group shows a high pH (>11) at the metal surface being either in passive or in immunity region. These group represents most of the simulations done in absence of calcium. The second group represents the simulations resulting in a low pH (~7.5) at the metal surface. They occur in the corrosion region of the Pourbaix diagram. Figure 6 plots the thickness of the passive film Fe_3O_4 against the corrosion rate. The corrosion rate increases if the passive film is not fully closed (teta <1) except for three outliers. Figure 7 shows the IR-free potential for the various conditions of the passive film. The more complete the film (still not fully closed) the more electropositive the IR-free potential. Comparing Figure 6 with Figure 5 it can be concluded that the highest IR-free potential values correspond with a low corrosion rate.
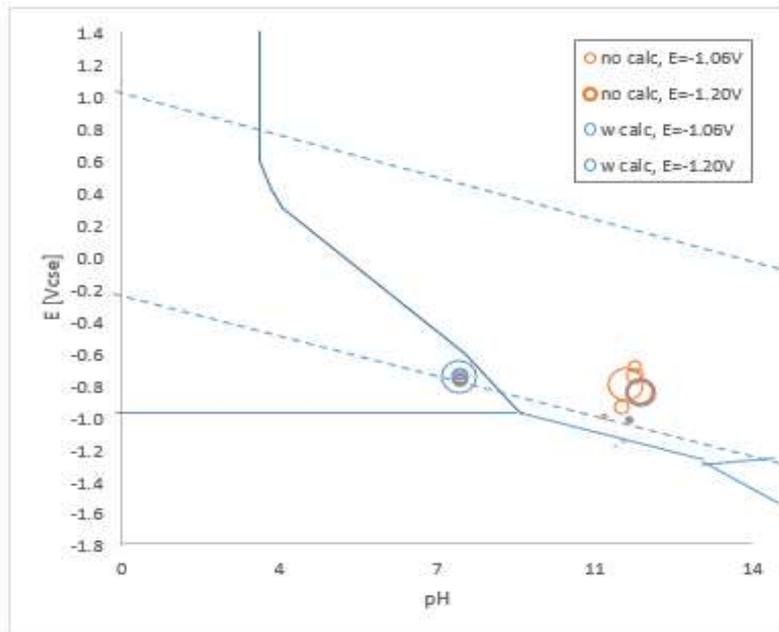

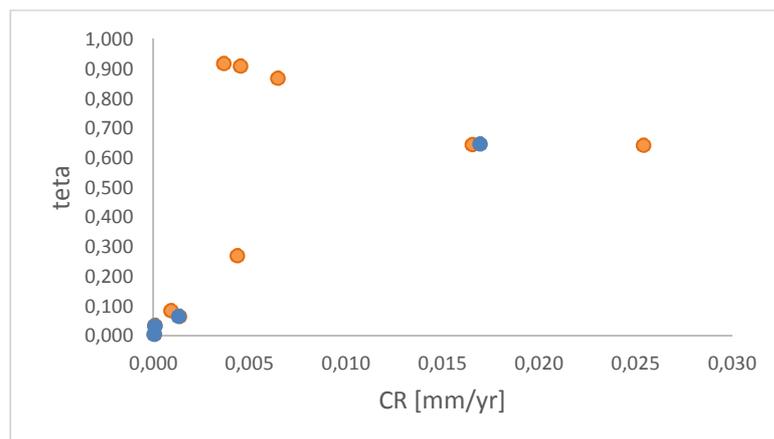**Figure 5 – representation of simulation results in the Pourbaix pH diagram**

Figure 6 – thickness of passive film layer Fe_3O_4 versus corrosion rate
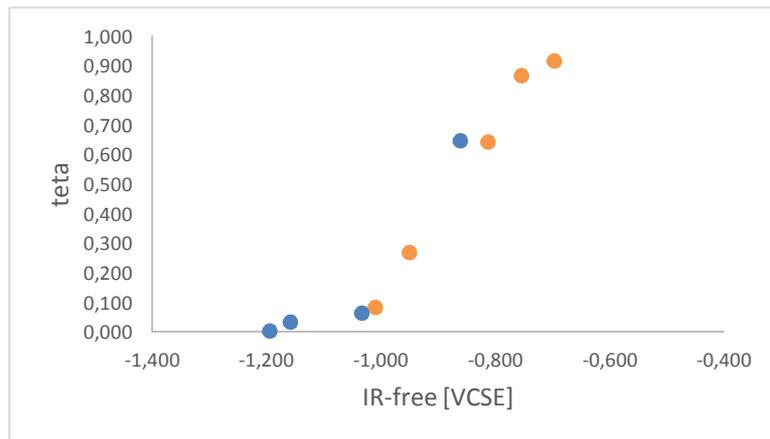
Figure 7 – thickness of passive film layer Fe$_3$O$_4$ versus IR-free potential

Conclusions

The passivity of pipeline steel in soil was investigated for three different water saturation levels and calcium concentration of the soil under two different CP levels of -1.060 and -1.200V$_{CSE}$ respectively. Advanced modeling technology was applied which enables to reveal the corrosion mechanisms, the protection level and the formation of the passive film for the different soil conditions and CP levels.

From the simulation results it can be concluded that the highest current demand occurs at a saturation level between 40-60%. The corrosion rate depends on the condition of the passive film which on its turn depends on the pH at the metal surface. Under moderate CP the formation of the passive film occurs and the corrosion rate tend to increase as long as the surface is not fully covered by magnetite Fe$_3$O$_4$. Meanwhile the IR-free potential becomes more electropositive.

The formation of calcium carbonate precipitation significantly affects the passivity of steel since the pH at the surface tends to be rather neutral.

More (long term) experiments under various conditions are planned for investigating the various conditions that provide IR-free potentials and corrosion rates in the different regions of the Pourbaix diagram.

References

[1] Guide des Techniques de Mesures en Protection Cathodique, CeoCor, Janvier 1994