

A modelling of the mechanisms occurring during the atmospheric corrosion of iron

L. Maréchal¹, S. Perrin¹, S. Hoerlé¹, F. Mazaudier¹, P. Dillmann²

¹Laboratoire d'Etude de la Corrosion Aqueuse DEN/DPC/SCCME, CEA Saclay 91191 Gif Sur Yvette, France

²Laboratoire Pierre Süe, CEA/CNRS, DSM/DRECAM/SCM, CEA Saclay 91191 Gif Sur Yvette, France
laurent.marechal@cea.fr

Abstract – In order to predict the long-term corrosion of metallic containers in storage conditions, a modelling of atmospheric corrosion of iron is proposed. This modelling takes into account the mechanisms which occur during the three stages of a wet-dry cycle. During the wetting stage, the reduction of lepidocrocite (β -FeOOH), a constituent of the rust layer, is considered to be the rate-limiting step of the corrosion. During the second stage of the cycle, the wet period, the reduction of dissolved oxygen on the lepidocrocite, previously reduced, is controlling the mechanism. The amount of oxidized metal depends on the quantity of reduced lepidocrocite and also on the oxygen diffusion in the electrolyte and the rust layer. At the end of the cycle, the blocking of the anodic sites is considered to describe the extinction of electrochemical corrosion during the drying. It appears that each stage of the cycle depends mainly on the chemical and morphological properties of the rust layer.

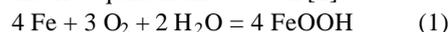
INTRODUCTION

Nuclear waste containers could be stored for very long term interim (about 300 years). As condensation on the metallic containers in such environmental conditions cannot be completely prevented, the containers surfaces may then be exposed to cyclic wet and dry periods (atmospheric corrosion). This condensation is mainly due to ambient temperature and humidity fluctuations. The first candidate materials considered for the containers of high level waste are low alloy steels because of their relatively low sensitivity to localized corrosion. The atmospheric corrosion behaviour of such steels has generally well been predicted for short periods of a few tens of years by the well-known bilogarithmic laws [1]. Nevertheless, for most longer time periods of few hundred years, which could be the length in very long term nuclear waste containers storage, this type of predictions are probably more uncertain. The main reason of this lack of reliability is the complex mechanisms involving the rust layer during atmospheric corrosion cycles and the subsequent modifications of the protective properties of the rust scale. A mechanistic modelling of these phenomena then appears to be necessary to establish more relevant and robust prediction of corrosion allowance in the behaviour of materials such as iron or low alloy steels. In order to obtain a long-term prediction of the containers damage, predictive equations are required. This study presents the modelling of

the three different stages occurring during iron atmospheric corrosion. The results are discussed by taking into account in the modelling the characterizations of rust layer observed on archeological objects.

IRON ATMOSPHERIC CORROSION

The atmospheric corrosion is an electrochemical process needing aqueous conditions for its occurrence. For iron, or low alloy steels, atmospheric corrosion can be summarized by the stoichiometric equilibrium between [2]:



In fact, the rust layer is characterized by a more complex structure with several iron oxide and iron oxi-hydroxide. The main feature of atmospheric, compared to aqueous bulk corrosion, is the succession of wet-dry cycles. The cycles are divided in three following stages: wetting, wet stage and drying. These stages are characterized by their state of wetness and by their different electrochemical and chemical behaviours. Actually, during the cycle, an aqueous layer, which acts as an electrolyte, is formed in indoor conditions by water condensation. The time of wetness, which defines the duration of the electrochemical process, is strongly dependent on many parameters which include the water vapour content of the atmosphere, i.e. the relative humidity at a given temperature (Figure 1).

Each stage of the wet-dry cycle is explained, by modelling the physico-chemical processes, in the

following sections and a damage is given by taking into account the rust layer characteristics observed on archeological objects.

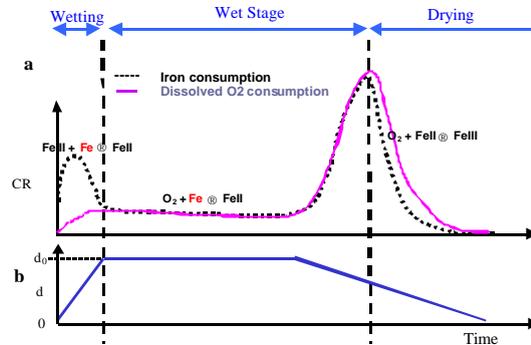
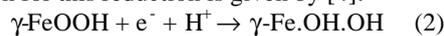


Fig. 1. The Wet-Dry cycle. At the back the schematic variations of electrolyte thickness (d) during the cycle. At the top the corresponding variations of Iron (dotted line) and Oxygen (solid line) consumption rates (CR) as measured by Stratmann [3].

WETTING STAGE

During the first stage, wetting stage, as the electrolyte is growing at the sample surface, the anodic dissolution of iron is beginning. This anodic dissolution, as there is no oxygen consumption (Figure 1), is only due to the reduction of one of the active phase of the rust layer: the lepidocrocite, γ -FeOOH. The proposed reaction for this reduction is given by [4]:



The lepidocrocite reduction requires electrons and can only occur at the metal/rust interface with the reduction front propagating through the rust layer as γ -Fe.OH.OH is an electronic conductor (Figure 2). The reaction (2) also needs H^+ ions from the electrolyte and only a few monolayers on the γ -FeOOH crystals surface inside the rust layer react. The species γ -Fe.OH.OH is also an ionic conductor that permits rather rapid movement of H^+ ions and, as the only mobile species involved are H^+ ions, the reduction reaction may be reversible [4]. The reduction reaction goes on over all the γ -FeOOH reducible surface and reduced γ -FeOOH finally coats the rust layer (Figure 2). The corrosion behaviour during the wetting stage is controlled by the reduction of γ -FeOOH. Considering the reaction as the rate-limiting step, the expression of the reduction current is:

$$i_g = F.k.[H^+].s_{FeOOH} \quad (3)$$

where F is the Faraday constant, k is the rate constant of the reactions, $[H^+]$ is the proton concentration in the electrolyte (as H^+ diffusion inside the rust layer is not considered) and s_{FeOOH} is the concentration of the surface sites (Fe[III] sites) where the reduction reaction takes place in a γ -FeOOH plan.

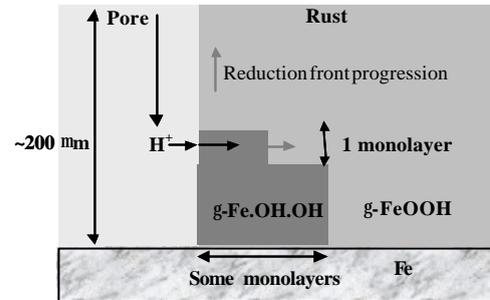


Fig. 2. Schematic representation of the phenomena occurring during wetting.

The expression of the damage of this stage is possible to obtain by integration of the expression of the reduction current deduced from (3) :

$$p_g = \frac{b.n.e.S}{2.V_{mFeOOH}}.V_{mFe} \quad (4)$$

where n is the number of reduced monolayer of γ -FeOOH, e the thickness of one γ -FeOOH layer, S is the area of the pores per surface unit, V_{mFeOOH} the molar volume of γ -FeOOH, V_{mFe} the molar volume of iron and b is the fraction of γ -FeOOH in the rust layer.

The maximum damage, considering that all the lepidocrocite in the rust layer is reduced during this stage, is $0.5 \mu\text{m}/\text{cycle}$. This result corresponds to a corrosion rate of 50 microns per year (by considering 50 cycles per year [5]), due only to the γ -FeOOH reduction. This value, even if it's in the same damage order of magnitude of the experimental results [6], is still too important as only one of the cycle phases is considered. The relation (4) is somehow an overestimation as it considers the worst case. In reality, it seems that there is a heterogeneous distribution of γ -FeOOH in the rust layer. As a consequence, all the surface γ -FeOOH is not in electrical contact with the metal and thus will not be reduced (γ -FeOOH is more likely to be distributed in small islands than in a continuous coating).

WET STAGE

When a large part of the available γ -FeOOH is already reduced to the conducting γ -Fe.OH.OH, it coats the surface developed by the rust layer porosity. If a connection between the underlying metal exists then the reduced γ -Fe.OH.OH on the surface of the pores can act as a cathodic area. Oxygen can then be reduced on that surface. Cathodic and anodic areas are decoupled, the oxidation of iron taking place on the small metal area in contact with the electrolyte at the bottom of the pores and the reduction reaction on the large cathodic area formed by the reduced γ -FeOOH. The actual mechanism of oxygen reduction is somewhat complicated and has not yet been clearly resolved in the presence of iron oxides [7]. For modelling purpose, the detailed mechanisms will not be considered, but only the overall reduction reaction. In the modelling, it is considered that atmospheric oxygen is dissolved at the atmosphere/electrolyte interface. Dissolved oxygen is then supposed to diffuse first through the electrolyte and then through the porosity of the rust layer on an average distance l (Figure 3).

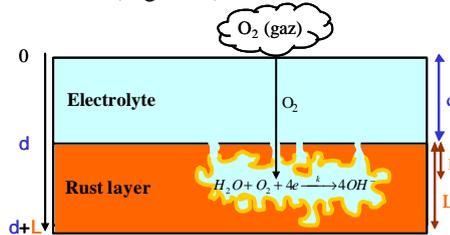
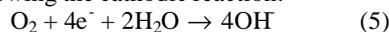


Fig. 3. Schematic representation of the oxygen reduction modelling. The electrolyte and the rust layer thicknesses are d and L respectively and l is the oxygen average diffusion distance through the rust layer porosity.

Oxygen is then reduced on the γ -Fe.OH.OH surface following the cathodic reaction:



Reaction (5) leads to an oxygen consumption which depletes oxygen concentration in the pores of the rust layer. The modelling is established as follows. Only diffusion of dissolved oxygen, first through the electrolyte and then through the pores, where there is an oxygen sink (the consumption of O_2 by reaction (5)), is considered. Assuming that e (porosity), t (tortuosity) and D_o (oxygen diffusion coefficient) are independent of space variables and that the stationary state is reached, the expression of the damage, due to the oxygen

reduction on reduced γ -FeOOH surfaces in the rust layer, is given by the expression :

$$p_o = \frac{e}{t} \cdot \frac{D_o C_o}{e \cdot d + l + I} \cdot 2V_{mFe} \left(1 - \exp\left(-\frac{(L-l)}{I}\right) \right) \Delta t \quad (6)$$

where V_{mFe} is the molar volume of iron, Dt is the duration of the wet stage, d is the electrolyte thickness, L the rust layer thickness and I is characterized by :

$$I = \sqrt{\frac{e \cdot D_o}{t \cdot b \cdot s_a \cdot k}} \quad (7)$$

where s_a is the surface of the pores per volume unit. The damage due to this reduction is mainly dependant of the average diffusion distance of oxygen through the rust layer porosity (Figure 4). If the reduction is considered to occur at the rust layer/electrolyte surface, the damage is equal to $0.9 \mu\text{m}/\text{cycle}$.

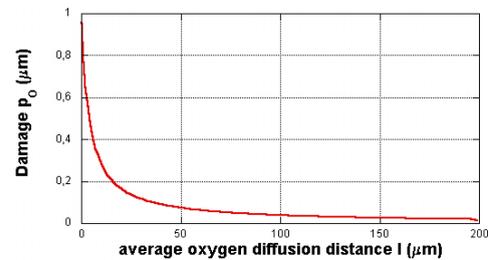


Fig. 4. Wet phase damage due to the oxygen reduction on lepidocrocite in function of the average oxygen diffusion distance l in the rust layer.

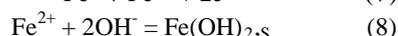
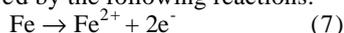
Nevertheless, if oxygen should diffuse in the pores of the rust layer on $20 \mu\text{m}$ depth, the damage will be equal to $0.15 \mu\text{m}$, a value which is closer to the experimental values deduced from the characterization of archeological objects [6].

DRYING STAGE

At the beginning of the drying stage, the decrease of the electrolyte thickness (less than ten micrometers) leads to such an increase of the oxygen diffusion limiting current that it is no longer the rate of the cathodic reaction, but the rate of the anodic reaction that determines the corrosion rate. Thus, the first phase of the drying stage is characterized by an increase of the oxidation of iron due to the oxygen reduction on lepidocrocite (Fig. 1). This first drying phase damage can be expressed from the equation (6)

by taking into account that the thickness d is a function of drying duration.

The second stage of the drying stage is much more complex. The electrolyte thickness decrease leads to an increase of the corrosion products concentration and then to the blocking of the anodic sites. This passivation-like phenomenon is represented by considering that the corrosion products are deposited on the anodic sites, which leads to the blocking of the dissolution sites and thus to the decrease of the oxidation current. The anodic sites blocking process is rendered by the following reactions:



where reaction (7) is the iron dissolution (Figure 5). Reaction (8) reproduces the blocking of the anodic sites with a deposit of iron hydroxide. It is neither real precipitation nor adsorption, but a modelling way to consider the blocking of the anodic sites when diffusion can no longer remove quickly enough the corrosion products due to a very rapid oxidation reaction (because potential becomes very anodic during the drying).

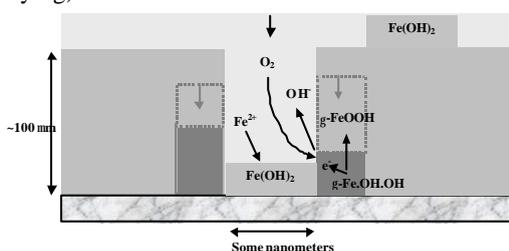


Fig. 5. Schematic representation of the phenomena occurring during drying

As concerning the modelling assumptions, the blocking of anodic sites by a ferrous hydroxide deposit is only a simulation of the actual process, far more complex. An expression of the anodic current has been determined by considering the anodic sites blocking [8]. The modelling considers only the stage of the drying that comes with electrolyte at the surface. The re-oxidation of the rust layer at the end of the drying that allows the γ -FeOOH to regenerate for the next cycle is then not modelled. It is the end of the wet-dry cycle, as described by the modelling.

CONCLUSIONS

A modelling of the complex processes occurring during an atmospheric corrosion wet-dry cycle of

iron is proposed in this paper. This modelling is based on mechanistic considerations, so as to provide a more reliable support for long term predictions of atmospheric corrosion on iron based nuclear waste containers than empirical extrapolations give. The guiding principle of the modelling is to focus on the different electrochemical reactions associated with the different stages of the wet-dry cycle, namely γ -FeOOH, oxygen reduction and anodic sites blocking. This modelling gives acceptable order of magnitude for the damages in a given wet-dry cycle. However, the modelling does not take into consideration some complex aspects of the rust layer such as the spatial distribution of the different phases. Indeed, it seems that a part of the lepidocrocite, which could be distributed in the form of isolated island, is not accessible for reduction during the wetting stage. Nevertheless, the modelling reveals to be a fruitful tool for investigating the mechanisms involved in atmospheric corrosion. To go further in long-term atmospheric corrosion modelling, it seems necessary now to go further in the rust layer characterizations and a more dynamic approach, which is in way, by ageing archeological objects in climatic chamber will give strong information related to a well known wet-dry cycle.

REFERENCES

1. M. POURBAIX, "The linear bilogarithmic law for atmospheric corrosion" in *Atmospheric corrosion*, W. H. Ailor Ed., John Wiley & Sons, pp. 107-121 (1982).
2. D. LANDOLT, "Traité des matériaux : Corrosion et chimie de surface des matériaux", Presses polytechniques et universitaires romandes, Lausanne (1993).
3. M. STRATMANN, *Berichte der Bunsengesellschaft für Physikalische Chemie*, **94**, pp. 629-639 (1990).
4. M. STRATMANN, K. BOHNENKAMP, H. J. ENGELL, *Corrosion Science*, **23** (9), pp. 969-985 (1983).
5. M. BAKLOUTI, N. MIDOUX, F. MAZAUDIER, D. FERON, *Journal of Hazardous Materials*, **B85**, pp. 273-290 (2001).
6. P. DILLMANN, V. VIGNEAU, F. MAZAUDIER, C. BLANC, S. HOERLE, *EFC Series*, **36**, 316 (2002).
7. V. JOVANCICEVIC, J. O. M. BOCKRIS, *Journal of the Electrochemical Society*, **133**, pp. 1797-1807 (1986).
8. S. HÉRLÉ, F. MAZAUDIER, *EFC Series* **36**, 179 (2002)