

Passive Layer Degradation of Reinforced Concrete Steels in the Marine Environment: Thermochemical Model

Van Quan Tran, Hoang Long Nguyen, Minh Viet Nguyen, Huu Nam Nguyen, Quang Hung Nguyen

Abstract: This paper is interested in the modeling of the process of depassivation of reinforcement of a saturated concrete exposed to seawater. In particular, it attempts to describe the degradation of the passive layer of reinforcement and the conditions under which it provides more protection. In order to achieve this, a model coupling multi-species transport and Thermochemical is set up. The model takes into account the chemical imbalance involved in the diffusion transport of ions contained in seawater as well as the chemical reactions occurring and its consequences in terms of dissolution at the passive layer. It allows to study the thermodynamic equilibrium of iron oxide in a concrete polluted by sea water and to quantify the duration beyond which the initiation of the corrosion can begin according to the nature of the constituents of the passive layer. It shows, in addition, the kinetics of degradation of the passive layer.

Keywords: Degradation, Passive layer, Reinforcement concrete, Marine environment, Thermochemical model.

I. INTRODUCTION

Chloride induced corrosion is one of the main causes of degradation of reinforced concrete marine structures. It is therefore essential to study it for the understanding of the long-term behavior of materials used in the construction and repair of structures. Initially the steels embedded in the concrete are passivated because of the very basic pH of the concrete. In the presence of Cl^- this passive layer is degraded. Modeling, backed up with a certain number of experiments in situ or in laboratory, must help to understand and evaluate this mechanism of depassivation of steels of reinforced concrete, this mechanism being strongly dependent on the nature of the layer passive. Corrosion is often described as a two-phase process. The first phase, known as "incubation", is a phase during which aggressive agents penetrate into the concrete and help trigger corrosion. The second phase, called "propagation", occurs when corrosion is propagated in the reinforcement. However, the mechanism of corrosion initiation involved in the first phase is still unknown while transport mechanisms are better controlled. In particular, a recent study shows that the durations corresponding to this

phase are extremely variable from one experiment to another[1]. In order to understand the mechanism of "initiation", it seems necessary to distinguish again two phenomena: depassivation and initiation. The depassivation is here defined as the degradation process of the passive layer of the reinforcement, initiation being the set of conditions for which the reinforcement begins to corrode (presence of oxygen in particular). It is this first phenomenon that this work proposes to treat in order to understand its mechanisms using a thermochemical modeling of the degradation of this layer. The nature of the passive layer has been the subject of many studies. The diagram of Pourbaix[2]simplified at 25°C shows that two iron oxides of the passive layer are more stable when the iron is in contact with water: hematite and magnetite ($\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 , respectively). On the other hand, we find experimentally other iron oxide, in particular hydrated oxides such as goethite, lepidocrocite and maghemite ($\alpha\text{-FeOOH}$, $\gamma\text{-FeOOH}$ and $\gamma\text{-Fe}_2\text{O}_3$, respectively) [3]. In fact, the chemical nature of the solution in contact with the steel conditions the nature of the passive layer. In an alkaline solution ($\text{pH} > 8$: 0), like that of the pore solution of concrete, iron can be transformed into one of the hydrated oxides FeOOH [4]–[8] or magnetite [9]maghemite[10]or hematite [11]. All of these products can occur in the pore solution of concrete. (see Table 1).

Table1:Iron oxides identified by the different works

Iron oxides	Experimental solution	Ref
Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$	H_2O , $\text{pH}=7$	[2]
$\gamma\text{-FeOOH}$ Fe_3O_4 $\alpha\text{-Fe}_2\text{O}_3$	H_2O , $\text{pH}=7$	[12]
Fe_3O_4 $\gamma\text{-Fe}_2\text{O}_3$	Alkaline solution, $\text{pH} = 8.4$	[13]
Fe_3O_4 $\gamma\text{-Fe}_2\text{O}_3$ $\alpha\text{-Fe}_2\text{O}_3$	Alkaline solution, $\text{pH} = 12.6$; 13.5	[14]
$\gamma\text{-FeOOH}$ $\alpha\text{-FeOOH}$ Fe_3O_4 $\alpha\text{-Fe}_2\text{O}_3$	Alkaline solution, $\text{pH} = 12.5$; 13.3	[15]
$\alpha\text{-FeOOH}$ Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$	Alkaline solution, $\text{pH} = 13.2$	[16]

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The thickness of the passive layer has also been the subject of a number of experimental works. Scanning electron microscopy, Raman spectroscopy and X-ray



diffraction (XRD) make it possible to determine its thickness more precisely[17]. However, the complexity of structure and composition of this passive layer makes that the results obtained by the different authors diverge. A first study of Noda et al. [13] estimates this thickness between 5 nm and 20 nm while other authors [17], [18] estimate this thickness to a few nanometers. Thanks to the X-ray reflection technique, Pan et al. [12] find that the thickness is about 1.4 nm. As a result, we will use values ranging from 1 nm to 20 nm in our study. Nevertheless, the models of behavior of these passive layers exposed to the chemical aggressions miss. The conditions of depassivation are, therefore, poorly defined. The aim of this study is to model the process of degradation of passive layers and the conditions in which they no longer fulfill their roles. For that, it is necessary to take into account the reactive transport of the ions contained in the sea water. Indeed, a balance between the pore solution and the reinforcements settles down during the setting of the concrete, the reinforcement being "protected by a passive film and the basicity of the pore solution. When the ions enter the pore solution, the equilibrium is broken, especially near the reinforcement. In order to take into account this imbalance and its consequently, it is necessary to model the reactive transport of the ions contained in the seawater and the chemical reactions that occur in the reinforcement. The first part of this study describes the 1D model implemented. The second presents a number of results relating to oxides that can degrade in the presence of chloride ions in particular. The third offers elements of interpretation. The last one concludes.

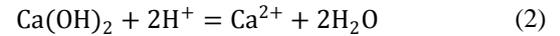
II. SIMULATION

A. Thermochemical approach

Thermochemical is initially the part of chemistry that studies the thermal phenomena accompanying chemical reactions. It has, however, largely developed and allows, by applying the second principle of thermodynamics, to define the meaning of chemical reactions and the composition of the system after reaction. It has been used for a long time in hydro-geology to study the pollution of soils and waters by heavy metals for example. In the case of steels, Liang et al. [19] carried out a study on the corrosion of iron activated by contaminated uranium water. A study by Bourrié et al. [20] focuses on the oxidation of iron in hydromorphic soils. In civil engineering, this technique is less used. However, there are some studies in the literature: cement hydration model [21]–[24] study of the influence of chloride on the hydration of cement [25] study of the long-term durability of concrete barriers used for the storage of radioactive waste [26]. It nevertheless seems to be adapted to our problems and to the modeling of the degradation of the passive layer in concrete. In order to perform these thermochemical calculations, we use TOUGHREACT software [27]. It is a software for coupling Thermochemical and multi-species and multi-phasic transport by an iterative sequential method. It thus makes it possible to deduce the precipitation / dissolution of the mineral phases under thermodynamic equilibrium. The principle consists in calculating a saturation index IS for a given solid phase, defined by the equation:

$$IS = \log \left(\frac{Q}{K} \right)$$

where Q is the product of the ionic activities involved and K is the solubility product of the solid. If IS = 0, the solution is at equilibrium. If IS < 0, the solution is under saturated, the solid can dissolve. If IS > 0, the solution is supersaturated, the solid can precipitate. In the case of portlandite, for example, the chemical reaction in thermochemical database Thermoddem [28] is written as:



The product of the ionic activities is then calculated according to the formula:

$$Q = \frac{\{Ca^{2+}\}}{\{H^+\}^2} \quad (3)$$

Where {Ca²⁺} and {H⁺} are respectively the activities of Ca²⁺ and H⁺, the ionic activity of a species being the product of its concentration (mol/kg of H₂O) and its coefficient activity γ itself expressing itself in the following way:

$$\{Ca^{2+}\} = \gamma_{Ca^{2+}} [Ca^{2+}] \quad (4)$$

The coefficient of activity γ is calculated by the Debye-Hückel model (see [27] for example). In the TOUGHREACT code, the speciation and the reaction equilibrium are determined from a thermodynamic equilibrium database (there exists a number such as Thermoddem of the BRGM [28]). The K solubilities of the various oxides previously listed are found in these databases. Table 2 lists them at 25°C

Table 2: Composition and thermodynamic properties at 25°C of the mineral phases considered in the modeling

Mineral	Formula	LogK
Portlandite	Ca(OH) ₂ + 2H ⁺ = Ca ²⁺ + 2H ₂ O	22.8
Jennite	Ca ₉ H ₆ Si ₆ O ₁₈ (OH) ₁₂ ·2H ₂ O + 18H ⁺ = 9Ca ²⁺ + 6H ₄ SiO ₄ + 8H ₂ O	147.3
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O + 12H ⁺ = 2Al ³⁺ + 6Ca ²⁺ + 3SO ₄ ²⁻ + 38H ₂ O	57.0
Monosulfoaluminate	Ca ₄ Al ₂ (SO ₄) ₂ (OH) ₁₂ ·6H ₂ O + 12H ⁺ = 2Al ³⁺ + 4Ca ²⁺ + SO ₄ ²⁻ + 18H ₂ O	73.1
Hydrotalcite	Mg ₆ Al ₂ (OH) ₁₄ ·3H ₂ O + 14H ⁺ = 2Al ³⁺ + 4Mg ²⁺ + 17H ₂ O	73.8
Hematite	α-Fe ₂ O ₃ + 6H ⁺ = 2Fe ³⁺ + 3H ₂ O	-1.4
Magnetite	Fe ₃ O ₄ + 8H ⁺ = 2Fe ³⁺ + Fe ²⁺ + 4H ₂ O	3.4
Maghemite	γ-Fe ₂ O ₃ + 6H ⁺ = 2Fe ³⁺ + 3H ₂ O	6.4
Goethite	α-FeOOH + 3H ⁺ = Fe ³⁺ + 2H ₂ O	0.5
Lepidocrocite	γ-FeOOH + 3H ⁺ = Fe ³⁺ + 2H ₂ O	1.37
Green rust	Fe(OH) ₂ ·Cl _{0.3} + 2.7H ⁺ = Fe ³⁺ + 2.7H ₂ O + 0.3Cl ⁻	-3.04

B. Transport of species

Our object is to study only the mechanism of depassivation of the passive layer. Concrete will be considered to be completely saturated with water. As a consequence, only the ionic diffusion is taken into account. It is modeled by the Fick law expressed in the case of a unidirectional transfer:

$$\phi \frac{\partial C_j}{\partial t} = -D_e \frac{\partial^2 C_j}{\partial x^2} \quad (5)$$

Where C_j and D_e are respectively the concentration of species j in the pore solution (mol/kg of H₂O) and the effective diffusion coefficient in concrete (m²s⁻¹). In our model, we use a single effective diffusion



coefficient at 25°C for all species in concrete. Its value is equal to $2.5 \times 10^{-12} \text{ m}^2\text{s}^{-1}$ [26], [29].

III. MODEL GEOMETRY, INITIAL AND BOUNDARY CONDITIONS

In order to reduce the calculation time, we consider the 1D model with a coating thickness of 15 mm. We choose a mesh with 100 elements. The first element, representing seawater, has a very large volume to ensure a constant concentration of chemical species. The composition of seawater is given in Table 3. The following 98 elements represent concrete. The last element consists of mixing the constituents of the concrete and an iron oxide of the passive layer of the reinforcement, so we have 5 calculations of thermodynamic equilibrium of the iron oxide in a concrete polluted by water these calculations corresponding to the 5 iron oxides identified in the passive layer (see Table 1). The volume fraction f (equation 6) is calculated from the thickness of the passive layer, thickness ranging from 1 to 20 nm.

$$f = \frac{V_{\text{oxide}}}{V_{\text{solid}}} \quad (6)$$

The modeled concrete is a concrete made with Portland cement CEM I of ratio E/C = 0.45. Hydration process is considered complete. The initial composition of the mineral phases of the concrete which comes from the work of Trotignon et al. [26], [29] is given in Table 2 of their works.

Table3: Concentration of the main species of seawater [30]

Ions	Concentration (mol/kg of H ₂ O)
Na ⁺	0.469
K ⁺	0.012
Ca ²⁺	0.010
Mg ²⁺	0.053
HCO ₃ ⁻	0.002
SO ₄ ²⁻	0.028
Cl ⁻	0.546
pH=8.22	

IV. RESULTS AND DISCUSSION

A. Results

1) Thermodynamic equilibrium of iron oxide in a concrete exposed to seawater

The literature gave us the iron oxides present in the passive layer. A thermodynamic equilibrium is obtained between each of these iron oxides, the initial mineral phases of the concrete and the seawater which progresses in the material. In ambient conditions (T = 25°C, P = 1 atm), our investigation shows that hematite, magnetite and goethite are stable. On the other hand, maghemite and lepidocrocite dissolve in the solution after a few days (see Figure 1).

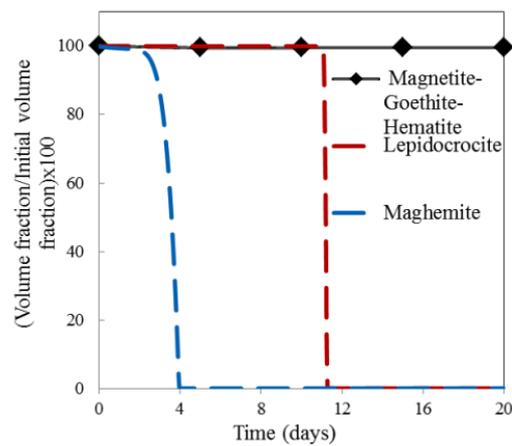
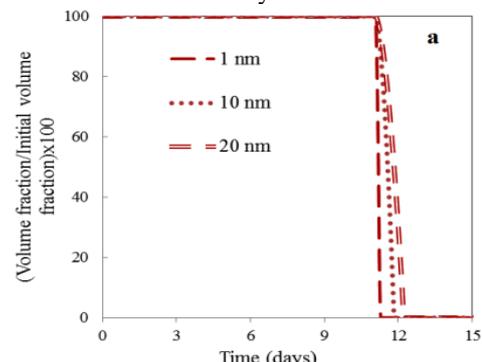


Fig. 1: Thermochemical equilibrium of each oxide in the pore solution in the presence of seawater

The results presented in Figure 1 show that in the passive layer, only maghemite and lepidocrocite are problematic. In reality, the structure of the passive layer is complex and contains several oxide phases (see introduction). In addition, there is no reason for the volume fractions of the iron oxides to be the same along the reinforcement which could explain the pitting corrosion [14]. Nevertheless, the dissolution of maghemite and lepidocrocite plays a very important role. A specific study on these oxides is thus proposed in the following paragraph.

2) Investigation of passive layer degradation of maghemite or lepidocrocite

In this section, the passive layer is considered to consist solely of lepidocrocite or maghemite. A sensitivity study to the thickness e of the passive layer is carried out. Passive layer thicknesses are 1 nm, 10 nm, 20 nm, respectively. The results give two different degradation mechanisms depending on the nature of the oxide studied. The degradation of Lepidocrocite gives a critical threshold effect (see Figure 2a). Indeed, whatever the thickness of the passive layer, the dissolution of lepidocrocite begins at the same time (11 days in the context of this study). In addition, if we denote the volume fraction and consider that $\Delta f/\Delta t$ is the degradation rate of the passive layer, we find that the change in speed of degradation is sudden and starts at 11 days (see Figure 2b.) whatever the thickness of the layer.



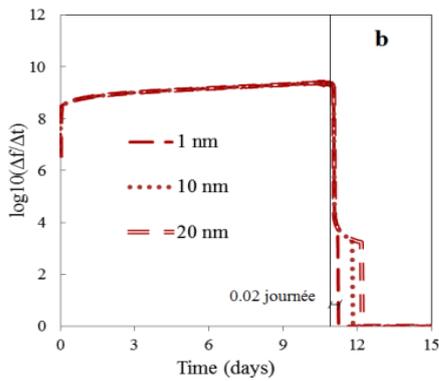


Fig. 2: (a) Degradation of the passive lepidocrocite layer. (b) Degradation rate of the passive layer of lepidocrocite

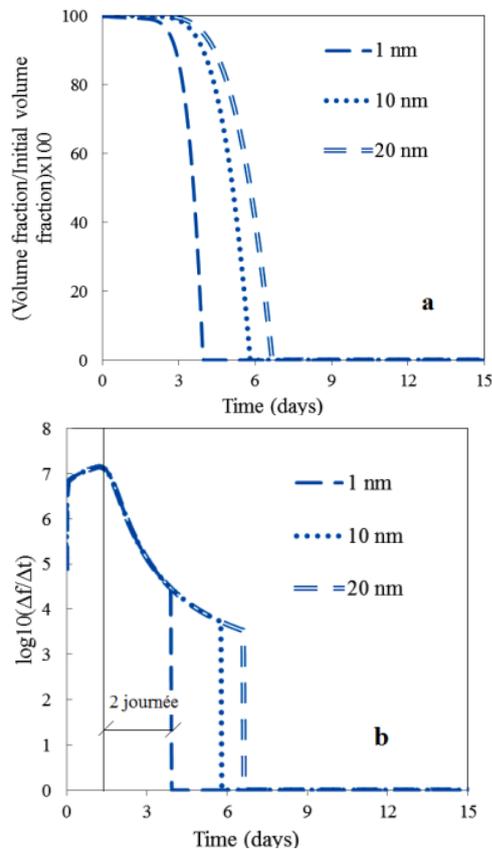


Fig. 3: (a) Degradation of the passive layer of maghemite. (b) Degrowth rate of the passive layer of maghemite

With regard to maghemite, the threshold effect is less obvious and it does not depend on the thickness (see Figure 3a, b). The degradation seems to begin at the beginning of the exposure: more exactly, it increases strongly after 1.5 days of exposure whatever the thickness of the layer. Unlike lepidocrocite, the change in rate of degradation of the maghemite layer is not abrupt (see Figure 3b). Finally, for the same thickness 1 nm of lepidocrocite or maghemite, the kinetics of dissolution is slower for maghemite (0.02 day versus 2.0 days for lepidocrocite).

B. Discussion

1) *Passive layer degradation process*

During the propagation of seawater, the chlorides play a role in fixing the Fe³⁺ ions in the pore solution to form rust containing chlorides according to the following formula:



2.7H⁺

Even in the absence of oxygen, the process of depassivation can be triggered since the reaction between the Cl⁻ ions and the Fe³⁺ ions cause an imbalance of the solution with respect to the iron oxides present on the reinforcement. which is consistent with the work of Sagoe-Crentsil and Glasser [31]. The consumption of Fe³⁺ in solution therefore tends to dissolve the iron oxides in order to restore equilibrium.

2) *Some proposals for a priori treatment of reinforcement*

This paper showed that the risk of depassivation of a concrete reinforcement in the presence of sea water seemed to come from the dissolution of two iron oxides: maghemite and lepidocrocite. The other oxides, generally encountered in the passive layers of reinforcement, seem to be more stable. It would be interesting to wonder about the treatments to be done to limit the quantity of these two oxides. A number of studies have shown that it is possible to transform maghemite into hematite by heat treatment by raising the temperature of the reinforcement to a temperature between 370°C and 600°C [32]. It is obvious that from an industrial or ecological point of view, it seems difficult to apply this treatment. Regarding lepidocrocite, it can be transformed into goethite when immersed in an alkaline solution. The immersion of a reinforcement in concrete seems to be a good mechanical choice but also vis-à-vis the protection against corrosion! Nevertheless, one study shows that this transformation at room temperature is not complete [4]. There is always a certain amount of lepidocrocite. However, it seems interesting to extend this type of investigation to identify suitable reinforcement packaging.

Table4: Interconversion between iron oxides[11]

Precursor	Product	Type of transformation	Preferred medium
Lepidocrocite	Hematite	Thermal dehydroxylation	Gaz
	Goethite	Dissolution/Precipitation	Alkaline solution
	Magnetite	Reduced reaction	Alkaline solution with Fe ²⁺
Maghemite	Hematite	Thermal conversion	Air

V. CONCLUSION

A 1D transport / thermochemical coupling model is proposed to study the depassivation of reinforcement in concrete exposed to seawater. At a temperature of 25°C, some oxides present in the passive layer (magnetite, hematite and goethite) remain stable despite the presence of chloride ions and dissolved oxygen. Others, such as lepidocrocite and maghemite, which are found in the outer layer of the passive layer, dissolve in the presence of chloride ions in order to restore the chemical equilibrium broken by the presence of chloride ions. The dissolution of these last two oxides can thus be initiated, including in the absence of oxygen. The time before which lepidocrocite and maghemite dissolve does not seem to be dependent on the initial quantity of these oxides.

(7) These first simulations make it possible to understand the



conditions under which certain oxides can dissolve in the presence of chloride ions. Nevertheless, the modeling of the whole process of depassivation of the reinforcement is not solved. In particular, it seems necessary to take into account the diffusion of the chemical species in the remaining oxide layer. Finally, the non-uniform nature of chloride corrosion is not taken into account because of the 1D nature of the modeling. Taking into account a passive layer thickness variation seems to be an interesting way to continue investigations.

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