

MARINE CORROSION OF IRON: MATHEMATICAL MODELLING OF THE PROCESSES AND MEASUREMENT OF LOST MASS

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RESUMEN

Hemos derivado el modelo matemático de Melchers para la difusión de oxígeno a través de la capa de herrumbre formada en la superficie de aceros sometidos a procesos de inmersión total, mediante un principio más fundamental: la ley de Planck-Nernst. Para esto se ha despreciado las corrientes convectivas así como la migración de las moléculas de oxígeno. También, además de considerar un flujo unidimensional, se asume que el consumo de oxígeno, debido a reacciones químicas con el hierro, únicamente ocurre en la interfase metal-herrumbre. Por último, se ha determinado experimentalmente un valor para el parámetro α que aparece en el modelo de Melchor, el cual es una medida de la cantidad de hierro convertida en herrumbre adherente.

Palabras clave: Modelo de Melchers, herrumbres, ley de Planck-Nernst, ecuación de difusión

ABSTRACT

We have derived the Melchers' mathematical model of the oxygen diffusion across the rust layer formed on the surface of the steels submitted to total immersion, by a most fundamental principle: the Planck-Nernst law. To achieve it, we have neglected the convection and migration of the oxygen molecules, and we have assumed both that this problem is 1-D and that oxygen consumption, due to chemical reactions, can only occur at the interface between the metallic surface and the rust. Furthermore, we have experimentally determined an α value for Melchers's model, which accounts for the amount of iron coming from the steel which is converted into adherent rust.

Keywords: Melchers' model, Planck-Nernst law, rust, diffusion equation

1. Introduction

Corrosion may be defined as the destruction of a material by action of the surrounding environment. Material resistance to corrosion depends of many variables as material properties itself, environment characteristics and other ones [1-6]. Important aspects in the corrosion of a material are the mass transport characteristics, which occurs by convection, migration and diffusion. In a recent paper, Melchers [6] proposed a new phenomenological theory for

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modeling general marine immersion corrosion, which was successfully applied to previously reported observations. However, he does not start from more fundamental equations, like the Planck-Nernst law. We believed that this step could be very important, because it gives a more general overview of the corrosion process. Other corrosion process can be derived from fundamental equations too. On the other hand, in his equations Melchers proposed several parameters which need to be determined experimentally.

2. Mathematical modelling

This model is restricted to that part of the corrosion processes of steels submitted to total immersion processes which is controlled by the diffusion of the oxygen through the rust layer. Neglecting the convective motion of specie k (in our case oxygen molecules) and considering small concentrations, the transport of this specie is described by the Planck-Nernst law [4]:

$$\vec{j}_k = -D^*_k \vec{\nabla} C_k + \left(-\frac{z_k F D^*_k}{RT} C_k \right) \vec{\nabla} \phi \tag{1}$$

where \vec{j}_k is the mass flux of specie k , C_k represents the concentration, D^*_k represents the effective diffusivity constant of oxygen in the rust layer, F the Faraday constant, R the ideal gas constant, T the absolute temperature and ϕ the electric potential in the electrolyte. Migration and diffusion are considered here. The transport of each species satisfies the mass transport equation:

$$\frac{\partial C_k}{\partial t} + \vec{\nabla} \cdot \vec{j}_k = S_k \tag{2}$$

where S_k is a source term that takes into account the production and/or consumption of oxygen. Assuming S_k equal to zero (which can be justified if we assume that oxygen consumption, due to chemical reactions, can only occur at the interface of the metallic surface and the rust), and considering only the 1-D problem on x -axes, and by replacing eq.(1) into eq. (2), we obtain:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x} \left[\left(-\frac{z F D^*}{RT} \frac{\partial \phi}{\partial x} \right) C - D^* \frac{\partial C}{\partial x} \right] = 0 \tag{3}$$

This is a migration-diffusion equation. Now, let's only consider the diffusion process. Then $\phi = 0$ and the eq. (3) is reduced to:

$$\frac{\partial C}{\partial t} - \frac{\partial}{\partial x} \left[D^* \frac{\partial C}{\partial x} \right] = 0 \tag{4}$$

Let's suppose that $D^* = w(x)D$, where $w(x)$ is a dimensionless mathematical function representing the rust layer porosity, and D the diffusivity constant of oxygen in the water, which is independent of position x . Thus eq. (4) can be written as:

$$\frac{\partial C}{\partial t} - D \frac{\partial}{\partial x} \left[w(x) \frac{\partial C}{\partial x} \right] = 0 \tag{5}$$

This equation is the starting point from which Melchers [6] performs the analysis of the oxygen diffusion through the rust layers. Melchers [6] considered a stationary regime for eq. (5). Then, he used the appropriate boundary conditions and calculated the corrosion rate as:

$$\frac{dc}{dt} = \left[\frac{E}{3/\alpha(Et + F)^{2/3}} \right] \quad (6)$$

where c measures the iron corroded in mm, E and F are constants that depend on the on the sea water electrolyte temperature, and α represents the amount of iron actually converting into AR. According to Melcher's [6] the α term is usually less than one, because some iron can be washed away or do not convert into AR. However, this term has not been measured, to the best of our knowledge. In the rest of the paper, we will concentrate upon the determination of this value.

3. Experimental results

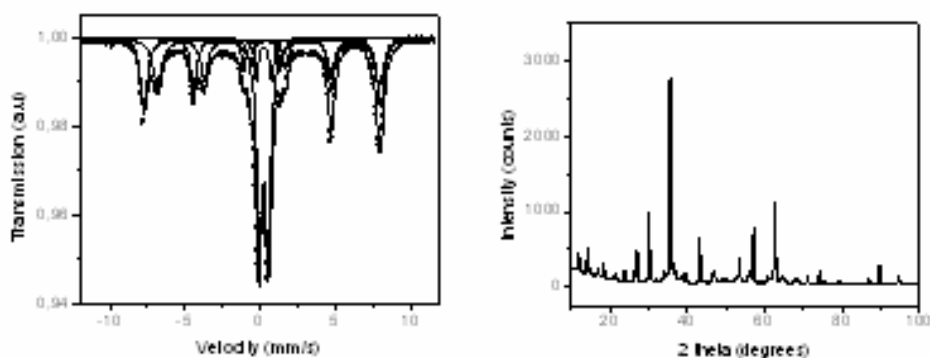


Figure No.1. Left: Typical room temperature Mössbauer spectrum of scraped AR coming from weathering steels. The spectrum was adjusted with three lorentzian magnetic sextets and one lorentzian quadrupolar doublet. Right: XRD pattern corresponding to same sample. The solid line represents a fit using Rietveld refinement analysis.

Weathering steel (WS) and carbon steels (CS) were exposed to total immersion in solutions with 0.6 M NaCl concentration [7]. The adherent (AR) and not-adherent (NAR) corrosion products were examined by room temperature and 77 K Mössbauer spectrometry, infrared spectroscopy and XRD diffraction using Rietveld refinement analysis. The NAR for both steels was composed of lepidocrocite, the most abundant phase, superparamagnetic goethite, and akaganeite showing that these components do not adhere to the surface of the steel due to the high chloride concentrations. The AR for both steels was composed of akaganeite, spinel phase (magnetite/maghemite), lepidocrocite, and magnetic and superparamagnetic goethites exhibiting a wide distribution of particle sizes. The relative abundance of the components in the rusts, for both steels, were very similar indicating that the deterioration processes were also similar and that a rust layer forms which exhibits little protective properties.

Taking into account the chemical composition of the steels [7], iron is 98.8% in CS and 97.8% in WS, and following the procedures for determining the total mass loss according to ISO 8407

[8], the values obtained for the iron mass loss in A36 and A588 steels are of 5.51 g and 3.93 g, respectively. Because we are interested in the fraction of these iron ions that form part of the rust phases, we should take into account that the mass of the collected rust contains not only that of the iron ions coming from the steel, but also the mass of the oxygen and the hydrogen ions coming from the corrosive environment. The relative weight abundance in percentage of each iron phase in each type of rust has also been determined. After simple calculations, we found that only about 21% and 22% of the corroded iron converts completely into adherent rust for CS and WS, respectively. Moreover, about 45% and 47% of the corrosion products are lost from the metal surface and about 34% and 31% of the iron ions do not convert for CS and WS, respectively. This means that most of the rust is NAR. This work allows the assessment of amount of iron conversion α to be estimated at 0.21. This numerical value is new, to the best of our knowledge, in the literature. These results are very important for the evaluation of the behavior of weathering steels in high levels of chlorides environments such as the seawater.

4. Conclusions

The Melchers' mathematical modeling of the oxygen diffusion across the rust layer in total immersion corrosion of steels was derived from the Planck-Nernst law. For that purpose we have considered 1-D transport of oxygen molecules in which only diffusion phenomena occurs, and that there is no source of oxygen consumption and production in the rust layer. On the other hand, in the experimental part of this work, the AR differentiated as scraped and hit, and NAR formed on Cs and WS exposed to chloride solutions in total immersion tests were examined by means of different techniques, with the purpose to determine the α -parameter. The NAR for both steels was composed of lepidocrocite, the most abundant, akaganeite, and goethite, whereas the AR in both steels contains additionally a spinel phase (magnetite/maghemite), which is the most abundant. For both steels around 21% of the corroded iron converts completely into adherent rust.

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