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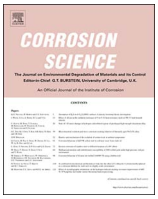

Role of previously formed corrosion product layers on sulfide-assisted corrosion of iron archaeological artefacts in soil

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ABSTRACT

Iron archaeological nails (16th century) were used as representative of the mild steel structures envisaged for the storage of nuclear waste. The influence of sulfide species on the corrosion behavior of the nails was investigated via the thorough description of the modifications undergone by the corrosion products surrounding the metal after re-immersion in deaerated sulfide solution. The only observed modification was the formation of FeS at the corrosion product layer/soil interface. The corrosion product layer, mainly composed of $FeCO_3$, acts as protective barrier, the reactivity of $FeCO_3$ preventing sulfide species to reach the metal and influence the corrosion process.

1. Introduction

Iron archaeological artefacts can be used to gather information on the corrosion of mild steel over long time periods and predict, for instance, long term corrosion behavior in nuclear waste systems [1,2]. To some extent, it is possible to select a site that contains samples as similar as possible as the system of interest. For instance, the archaeological nails of the Glinet site, studied for several years, can be considered as typical of samples of mild steel in anoxic carbonated soils [3–13]. The corrosion product layers formed on these 400 years old artefacts have been thoroughly characterized via numerous analytical techniques, including micro-probes and even nano-probes [9,10]. They are mainly composed of carbonated compounds, i.e. siderite $FeCO_3$ and chukanovite $Fe_2(OH)_2CO_3$, that form a dense and compact layer, several 100 μm thick, around the metal. Chukanovite is generally found in an inner stratum closer to the metal than siderite. In addition, an external layer of magnetite Fe_3O_4 was sometimes observed, the remnant of the mill scale initially present on the nail before its burial. It has been observed that this external magnetite layer could sometimes be in contact with the metal. Magnetite is an electronic conductor and thus establishes a short-cut in the electronic conduction path between the metal and the corrosion medium [11]. Iron sulfides FeS were also observed in some cases [3,12,13]. A microbiological study demonstrated that sulfate-reducing bacteria SRB were present in the corrosion product layers and more likely responsible for FeS formation [13]. The FeS phases were however only present in the outer part of the corrosion product layer [13], which indicates that the detected SRB were more likely also located there, i.e. separated from the metal by the densest and most compact inner part of the corrosion product layer. A similar conclusion was drawn after the detailed study of the corrosion product layers covering carbon steel coupons reacted in clay porewater seeping in a test chamber in situ in the Callovo-Oxfordian formation envisioned for the nuclear waste storage [14,15]. Finally, the characterization of the interface between the metal and the carbonated-compounds based layer at a nanometric scale has revealed the presence of a several 100 nm thick layer of iron oxides (magnetite and maghemite) in contact with the metal [10,16].

In several countries, mild steel will be used for the geological disposal of high-level nuclear waste [17–19]. In France, the waste is planned to be stored at a depth of ∼450 m in a deep geological repository, drilled in very stiff (indurated) clay (Callovo-Oxfordian COx claystone so called "argillites") formation [18]. Mild steel will be used in particular for the overpack around the stainless steel canister that will contain the vitrified waste. Once the repository closed, the oxygen trapped inside the system is expected to be consumed more or less rapidly by the corrosion of mild steel or by other chemical processes occurring in argillite so that anoxic conditions will prevail during the lifetime of the mild steel overpack. The argillite contains about 17 wt.% of calcite [20,21] that will provide carbonate dissolved species so that mild steel will be in an anoxic carbonated environment. As a result, the

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information gathered from the studies of the archaeological nails of the Glinet site is considered to be relevant to describe the long term behavior of the mild steel overpacks.

Pyrite FeS_2 is also one of the components of argillite, even though a minor one that represents only 1 wt.% of the rock [20,21]. It was however expected to be a potential source of sulfide species, thus able to influence the corrosion process and favor the formation of iron sulfide FeS on the steel surface, which was recently confirmed [22,23]. Moreover, the growth of SRB cannot be completely discarded. It may occur once the temperature at the overpack surface, expected to be initially as high as 90 °C due to the intense radioactivity of the waste, has decreased to values around 30–40 °C, a temperature range more favorable for the growth of most SRB species. The possible influence of sulfide species massively produced at the vicinity of a steel surface already covered by a thick and dense layer of carbonated corrosion products is then a question of utmost importance. Can this sulfide production affect deeply the corrosion process? Can the dense and thick corrosion product layer have a protective role against sulfide?

The present study addresses these questions. Iron archaeological nails excavated from the Glinet site were used as representative of the surface of the mild steel overpacks after centuries of corrosion in the anoxic carbonated environment issued from the argillite. They were immersed for two months at room temperature in sulfide-containing anoxic electrolytes. Their corrosion product layers were thoroughly characterized afterwards by µ-Raman spectroscopy and scanning electron microscopy (SEM) observation coupled with chemical analysis via electron dispersive spectroscopy (EDS). The modifications induced by immersion in sulfide–containing electrolytes were compared to those observed after immersion of other nails in sulfide-free electrolytes.

2. Materials and methods

2.1. Preparation of archaeological samples

Three iron nails coming from the archaeological site of Glinet (France, Seine Maritime) were used. The site corresponds to an ancient forge and is dated from the 16th century. The nails were used to maintain the wood timbers of the workshops during the operating time of the industrial site. This period lasted along the 16th century and the site was then abandoned. The wooden structure collapsed and was buried. We can then consider that the corrosion process started around 1600 so that the age of the corrosion product layers covering the nails is 400 years.

The nails were excavated from an anoxic zone of soil and immediately stored in ethanol, without having been cleaned, until their sampling for analysis. They correspond to a set of nails analyzed previously by various techniques [3–13]. They are composed of wrought iron with carbon content between less than 0.02 wt.% to 0.1 wt.%, grain size between 10 µm and 40 µm and a high amount of inclusions [3].

So that the open circuit potential (OCP) of the metal could be measured during the immersion test, the archaeological nails were prepared as follows: first, they were cut in two with a diamond wire saw. Nujol was used as lubricant to provide an oily protective film for the surface exposed to air during the cutting. Fig. 1 displays a photograph of each nail before it was cut in two. The black rectangle shows the half of the nail (tip side in each case) that was used for the experiment. A copper wire was weld to the metal section revealed by the cutting and this part of the nail (~1 cm long) was embedded in epoxy resin. The prepared samples were then introduced in a glove box (Jacomex P[box]-T4) filled with argon (residual oxygen content ≤1 ppm). The resin was left to dry inside the Glove Box. The samples were finally immersed for two months, each in a beaker containing 300 mL of electrolyte.

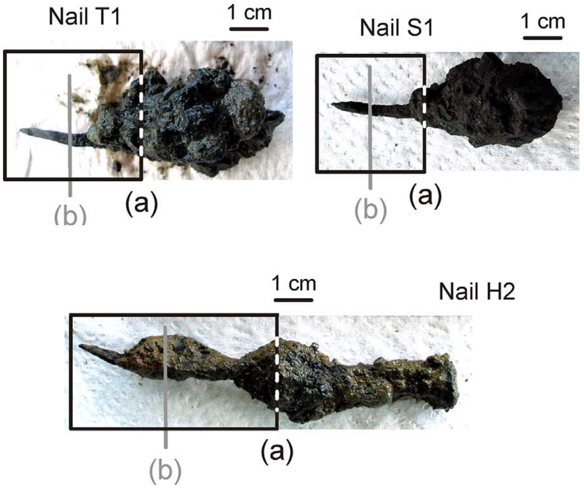

Fig. 1. Pictures of the nails used for the study showing the locations of the cuts made for electrical connections (a) and analysis of cross-sections after the 2 month immersion (b).

Table 1
Solutions considered for the immersion tests.

	[NaCl]/mol L^{-1}	[$NaHCO_3$]/mol L^{-1}	[Na_2S]/mol L^{-1}	[Na_2S]/[$NaHCO_3$]
Nail T1	15×10^{-3}	2×10^{-3}	0	0
Nail S1	15×10^{-3}	2×10^{-3}	1×10^{-4}	1/20
Nail H2	15×10^{-3}	2×10^{-3}	1×10^{-3}	1/2

2.2. Immersion tests and solutions used

Three solutions were considered for the immersion test as summarized in Table 1. One solution was free of sulfide species and consisted of a mixture of NaCl ($0.015\ mol\ L^{-1}$) and $NaHCO_3$ ($0.002\ mol\ L^{-1}$). This solution was chosen as representative of an aggressive carbonated media, with a chloride concentration much larger than the carbonate concentration. It does not represent the soil electrolyte of the Glinet site. For instance, the typical carbonate concentration in Glinet is approximately ten times higher than that considered here [5,24]. According to thermodynamic data, this carbonate concentration is however sufficient to ensure (in the absence of O_2) the stability of both chukanovite and siderite [25]. Nail T1 was immersed in this solution (T is for "test solution"). The other solutions were characterized by the same NaCl and $NaHCO_3$ concentrations but also contained Na_2S. Two Na_2S concentrations were considered, a small one of $10^{-4}\ mol\ L^{-1}$ and a higher one of $10^{-3}\ mol\ L^{-1}$. The sulfide to carbonate concentration ratios of these two solutions were then equal to 1/20 and 1/2, respectively. Nail S1 was immersed in the solution with small Na_2S concentration, nail H2 in the solution with higher Na_2S concentration. In each case, the pH of the solution was set at 7 by addition of a small amount of hydrochloric acid. This pH value was chosen because the pH of the electrolyte present in the argillite formation envisioned for the storage of nuclear waste in France is close to neutrality [26].

Each nail was immersed in a beaker containing 300 mL of solution, inside the glove box at room temperature ($T = 21 \pm 2$ °C). The electrolyte was not stirred so as to be as close as possible to the real situation, i.e. a metal in contact with the electrolyte filling the pores of a soil. The open circuit potential (OCP) of the metal was measured with respect to a saturated calomel electrode (SCE, $E = +0.244$ V vs SHE at 25 °C) using a high impedance voltmeter. At the beginning of the experiment, a measurement was performed each hour because the OCP varied rapidly. The interval between two measurements was increased with time as the OCP tended to stabilize.