Study of iron sulphides in long-term iron corrosion processes: Characterisations of archaeological artefacts

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ABSTRACT

Iron sulphides are observed on long term anoxic corrosion profiles of iron artefacts. The archaeological nails studied came from two terrestrial sites (Glinet and Raadhuspladsen) and a subaquatic one (Arles-Rhône 3).

Greigite (Fe_3S_4) and/or mackinawite (FeS_{1-x}) are observed at the outer border of the corrosion product layer. The presence of mackinawite is discussed relatively to the establishment of stable anoxic burial conditions. The nails from the subaquatic site present pyrite globules in the transformed medium. The formation of pyrite (FeS_2) is attributed to the proximity of wood. The iron sulphides formation may also be explained by the presence of sulphate-reducing bacteria in the burial environment.

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1. Introduction

The study of iron sulphide formation in long-term anoxic corrosion processes is a major issue in several contexts as they can inhibit or accelerate corrosion [1–9]. For example, in oil underground facilities, the heterogeneous formation of iron sulphides on pipeline surfaces is suspected to lead to localised corrosion [10,11]. On long-term, these processes would lead to oil leaks and reduce the effectiveness of the oil transport. Moreover, in France it is envisaged to confine high-level radioactive wastes in a glass matrix and store them in a stainless steel canister, which will then be placed in a carbon steel over pack stored in clay (argillite) at 450 m deep [12,13]. Thus, the formation of iron sulphides during corrosion processes could diminish the long-term efficiency of the carbon steel barrier. Last, but not least, it is of particular interest for conservation issues to determine precisely the impact of iron sulphide formation on corrosion kinetics occurring either before or after artefacts' excavation. First in some cases excavation are rendered difficult at present time and the heritage scientists can decide to preserve them in-situ [14–16]. The purpose is then to verify that in the cur-

rent burial conditions of the artefacts, the corrosion rate of these objects are sufficiently low in order to preserve them for several tenth years before being excavated. Yet, in a second issue the presence of iron sulphides is as well of major concerns for the study of corrosion mechanisms after excavations from burial or marine sites. Indeed after excavation, iron pieces corroded in anoxic environments for a long time in these sites are in contact with air again. The drastic changes of the environmental conditions can lead to iron sulphur decomposition and thus to severe degradation of the iron pieces themselves but also of their immediate environment [17–19].

Currently few studies were devoted to iron sulphides presents in archaeological artefacts. Among them are studies led on several iron objects extracted from a waterlogged soil, at the Iron Age site of Fiskerton dating from the 5th–2nd centuries BC (Lincolnshire, UK). They enhanced the presence of greigite, mackinawite and framboidal pyrite in the rust layer [20,21]. Other studies were led on iron samples coming from the archaeological waterlogged site of Glinet (an ancient forge dated from the sixteenth century located in Normandy, France) and enhanced the presence of iron sulphides after long-term anoxic corrosion in soils [13,21]. Especially, Remazeilles et al. [21] highlighted with the help of SEM and of vibrational spectroscopies, that the iron sulphides are distributed locally in the external part of the rust layers surrounding the iron nails. They
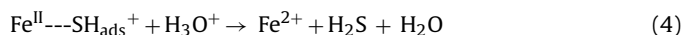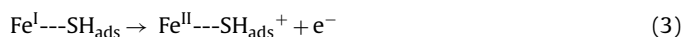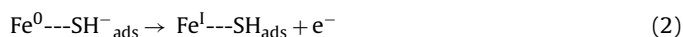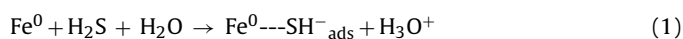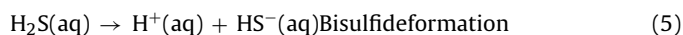
identified in addition that these phases are mackinawite, Fe(III)-containing mackinawite and greigite. This study discussed the iron sulphide formation in the rust layer in terms of microbial sulphate reduction. Unfortunately the study of the physical and chemical conditions leading to the specific iron sulphide formation observed was incomplete and the localisation of greigite relative to mackinawite inside the corrosion layers was not detailed. Finally, not only iron objects but also archaeological wood samples contaminated with iron were studied [15,17,18,21]. In some other environments, Fors et al. [15] studied archaeological wood coming from 7 shipwrecks dating from the 10th, 11th and 17th centuries. The results of XANES analyses highlighted the presence in lignin-rich parts of the wood of organic sulphur compounds as thiols and disulphides, or iron(II) sulphides and pyrite when a sufficient amount of iron(II) is present. Nevertheless, only one of the studied samples was close to a corroded nail. Besides the author has noticed that the more the samples are far away from any corroded iron piece, the less iron sulphides are observed within the wood. But very few analyses were conducted on iron sulphides in these archaeological woods to identify them locally in this study.

The iron sulphides usually observed in long-term anoxic corrosion systems are well-crystallised or Fe^{III}-containing mackinawite ($Fe^{II}S^{-II}_{1-x}$), greigite ($Fe^{II}Fe^{III}_2S^{-II}_4$) and pyrite ($Fe^{II}S^{-I}_2$).

The denomination "mackinawite" usually refers to the stoichiometric compound FeS, sometimes described as $Fe_{1+x}S$ because of substitution reactions. The main mechanism conducting to mackinawite formation involves dissolved Fe^{2+} and H_2S and/or HS^-. Dissolved Fe^{2+} could be produced by the following multi-step surface reactions [22]:

$$Fe^0 + H_2S + H_2O \rightarrow Fe^0\text{---}SH^-_{ads} + H_3O^+ \qquad (1)$$

$$Fe^0\text{---}SH^-_{ads} \rightarrow Fe^I\text{---}SH_{ads} + e^- \qquad (2)$$

$$Fe^I\text{---}SH_{ads} \rightarrow Fe^{II}\text{---}SH_{ads}^+ + e^- \qquad (3)$$

$$Fe^{II}\text{---}SH_{ads}^+ + H_3O^+ \rightarrow Fe^{2+} + H_2S + H_2O \qquad (4)$$
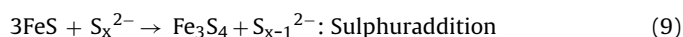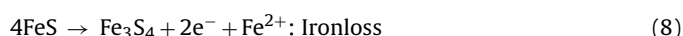
Then two competing reactions involving either hydrogen sulphide or the bisulfide lead to mackinawite formation [23]. Several mechanisms have been proposed by various authors [4,23–26]. The most common mechanism proposed in aqueous solution is:

$$H_2S(aq) \rightarrow H^+(aq) + HS^-(aq) \quad \text{Bisulfide formation} \qquad (5)$$

$$HS^-(aq) \rightarrow H^+(aq) + S^{2-}(aq) \quad \text{Bisulfide dissociation} \qquad (6)$$

$$Fe^{2+} + S^{2-} \rightarrow FeS \quad \text{Iron sulphide formation} \qquad (7)$$
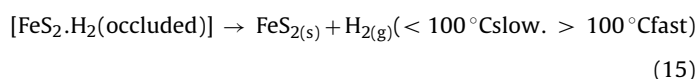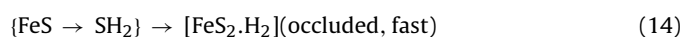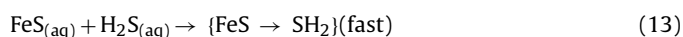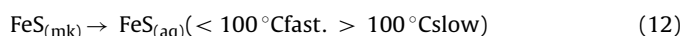
Nevertheless, depending on reaction time and conditions, three different physico-chemical states of mackinawite could result from the previous mechanism of formation. Firstly, the initial precipitate obtained by reaction of dissolved Fe^{2+} and H_2S and/or HS^- is called "nanocrystalline mackinawite" [21,25]. It is a poorly crystallised state of mackinawite. Then, the crystallisation led to the transformation of the nanocrystalline state to the well-crystallised one [21,25]. And finally, in slightly oxidizing conditions Fe^{II} is partially substituted by Fe^{III}. This state is called "Fe^{III}-containing mackinawite" and its composition is supposed to be: $Fe^{II}_{1-3x}Fe^{III}_{2x}S$ [21,25]. However, the crystallographic structure could withstand no more than 20% of substitution [27].

When the proportion of Fe^{III} relative to Fe^{II} reaches 67% [21], there is a solid-state transformation of Fe^{III}-containing mackinawite into greigite ($Fe^{II}Fe^{III}_2S_4$) [23,24,28–33]. This transformation occurs via an iron loss or a sulphur addition (dissolved zero valent sulphur in the form of polysulphide) pathway in slightly oxidising conditions [34,35]:

$$4FeS \rightarrow Fe_3S_4 + 2e^- + Fe^{2+}: \text{Iron loss} \qquad (8)$$

$$3FeS + S_x^{2-} \rightarrow Fe_3S_4 + S_{x-1}^{2-}: \text{Sulphur addition} \qquad (9)$$

Besides, in anoxic conditions, the formation of greigite is favoured by acidic conditions since protons are oxidative agents, temperature around $70\,^\circ$C and Fe/S concentration ratio of ¾ [23,28,36–38].

Concerning the formation of pyrite, numerous studies have been conducted. It has been shown that without external influence, the pyrite nucleation is kinetically limited by the lack of iron sulphide precursors [23,39]. The pyrite formation, indeed, is inhibited by a high nucleation barrier [40]. But active $FeS_{(mk)}$ surfaces could initiate the pyritization. Various mechanisms are proposed to explain the formation of pyrite from $FeS_{(mk)}$ precursors. Firstly we can cite the solid-state transformation of greigite by an excess of zero valent sulphur species [24,34,37,41]. Greigite is then an intermediate in the pathway from mackinawite to pyrite. If the mackinawite and/or greigite surface is oxidised the transformation reaction is accelerated [24,42]. Wilkin and Barnes [43] detailed the solid-state pathway leading to the formation of framboidal pyrite. According to their study the first step is the nucleation and growth of an iron monosulphide. Then this initial iron monosulphide reacts with zero valent sulphur species to form greigite. Afterward, greigite microcrystals aggregate. Finally, aggregated greigite forms framboidal pyrite via the addition of sulphur, $Fe_3S_4 + 2S^\circ \rightarrow 3\ FeS_2$ (10), or through loss of Fe, $Fe_3S_4 + 2H^+ \rightarrow 2\ FeS_2 + Fe^{2+} + H_2$ (11) [44]. Once formed, the framboidal pyrite could constitute continuous growth sites for pyrite. Secondly, a dissolution-precipitation process from an iron sulphide precursor, greigite or mackinawite, is another possible pathway. According to Rickard and Luther [23,45], the surface reactions involved in the dissolution-precipitation pathway are:

$$FeS_{(mk)} \rightarrow FeS_{(aq)}(< 100\,^\circ C\,\text{fast.} > 100\,^\circ C\,\text{slow}) \qquad (12)$$

$$FeS_{(aq)} + H_2S_{(aq)} \rightarrow \{FeS \rightarrow SH_2\}(\text{fast}) \qquad (13)$$

$$\{FeS \rightarrow SH_2\} \rightarrow [FeS_2.H_2](\text{occluded, fast}) \qquad (14)$$

$$[FeS_2.H_2(\text{occluded})] \rightarrow FeS_{2(s)} + H_{2(g)}(< 100\,^\circ C\,\text{slow.} > 100\,^\circ C\,\text{fast})$$

$$(15)$$

Other authors associate the pyrite formation to the presence of micro-organisms or organic matters as sulphate-reducing bacteria or algae [15,46–51]. In this case, greigite and mackinawite would not necessarily be direct precursors for pyritization.

Thus, depending on the environmental conditions, the formation of iron sulphides could be explained by various reaction pathways, some of which are purely inorganic whereas others involve bacterial activity. To better understand the formation of iron sulphides in archaeological samples, it is then important to investigate the environmental conditions leading to some iron sulphides rather than others in several archaeological sites of different times. In addition, precise characterisations are needed in order to determine the iron sulphide localisation in the corrosion product layer and their relative distribution. Therefore, this study is devoted to the characterisation by complementary analytical techniques of iron sulphides located in the corrosion product layers of archaeological nails issued from several anoxic archaeological sites.

2. Materials and methods

2.1. Samples

Archaeological iron nails buried for several centuries in soils presenting anoxic conditions are studied by complementary analytical techniques: μRaman spectroscopy and FESEM-EDS. They come from one subaquatic and two terrestrial sites described in Table 1.