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Abiotically or microbially mediated transformations of magnetite by sulphide species: The unforeseen role of nitrate-reducing bacteria

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ABSTRACT

In the anoxic conditions of nuclear waste deep geological repository, the main iron corrosion products formed at the surface of the carbon steel overpacks are siderite ($\text{Fe}^{\text{II}}\text{CO}_3$) and magnetite ($\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$) that form a rather protective layer. The originality of this work is the consideration of the bacterial metabolism of nitrate-reducing bacteria (NRB), often overlooked in corrosion processes. *Klebsiella mobilis* was used as a model of NRB and incubated with ferrous carbonates/magnetite corrosion bilayers under anoxic conditions. As a consequence of a combination of biotic and abiotic processes magnetite was reduced to mackinawite ($\text{Fe}^{\text{II}}\text{S}$) and subsequently transformed to greigite ($\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{S}_4$).

1. Introduction

A major problem facing the nuclear industry involves radioactive waste. France plans to store vitrified, high-level nuclear waste in stainless steel containers with a carbon steel overpack at a depth of 500 m in a claystone formation (Callovo-Oxfordian formation, Bure, Lorraine) in order to prevent the migration of radionuclides [1]. In the short term, corrosion processes of the carbon steel overpack disposed in a deep clayey environment would be based on purely electrochemical mechanisms with well-established corrosion kinetics. In the anoxic conditions of nuclear waste repository, the production of a significant amount of dihydrogen (H_2) is expected from the water radiolysis and from the anaerobic corrosion of elemental iron [2,3]. H_2 can be involved in the biocorrosion process where it can be used as an electron source for bacteria [4,5]. Passively penetrating through microbial membranes, H_2 represents an ideal inorganic electron donor to support energetic conversions of a wide range of hydrogenotrophic bacteria [6].

The formation at the steel surface of a rather protective layer, mainly composed of siderite ($\text{Fe}^{\text{II}}\text{CO}_3$), chukanovite ($\text{Fe}_2^{\text{II}}(\text{OH})_2\text{CO}_3$) and magnetite ($\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$) is expected [7–9]. The presence of such

protective layer on the metal surface leads to low corrosion rates and actually ensures a sufficient lifetime for the technical system. The local transformation of part of this layer, for instance by bacterial activity, may reduce its protective efficiency and increase significantly the corrosion rate. It may also lead to localized corrosion phenomena, in particular if iron sulphides are generated. It is well known that FeS compounds are electronic conductors able to act as cathode [e.g. 10]. Local formation of FeS may then create corrosion cells *via* galvanic coupling between the zones of the metal covered by FeS and those covered by other corrosion products. The influence of the heterogeneity of the corrosion product layer was recently addressed, in the scope of marine corrosion of carbon steel, and showed to be a crucial point [11]. Such galvanic effects were also observed with a steel electrode covered by a heterogeneous layer generated in a clayey environment [12]. This demonstrates that the properties of the corrosion product layer are of utmost importance as far as long term corrosion is concerned.

The influence of microorganisms on the transformation of iron corrosion products remains substantially under-studied to date with a need of deeper knowledge of biocorrosion mechanisms. Since the middle of the last century, the scientific community endeavoured to

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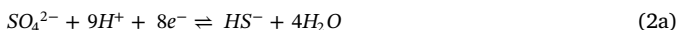
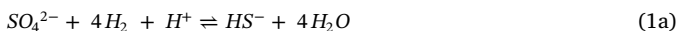
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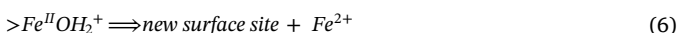
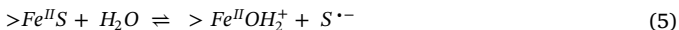
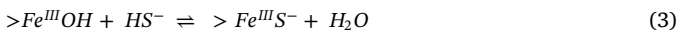
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define the corrosion mechanisms influenced by the activity of sulphate-reducing bacteria (SRB) and thiosulfate-reducing bacteria (TRB) [13]. These two metabolic groups involved in microbiologically influenced corrosion can catalyse anodic reaction (e.g. anode sulphidation) and accelerate corrosion processes through galvanic effects induced by the precipitation of FeS on the steel surface [13]. The formation of sulphide is not only observed during sulphate respiration by SRB (Eq. (1a)) and TRB (Eq. (1b)), but also during the assimilatory reduction of sulphate (Eq. (2a)) to fulfil their needs in sulphured amines (cysteine (Eq. (2b)), methionine), and thiols.



The presence of sulphide can lead to the reductive dissolution of Fe^{III} species from iron corrosion products like ferrihydrite, lepidocrocite, magnetite, hematite, and goethite [14]. The reaction mechanism is well described as a surface-controlled process and occurs in four steps [15]: (i) Fe^{III} species at the surface of iron (oxyhydr)oxide minerals rapidly form a surface complex with sulphide (Eq. (3)), (ii) before transferring electron from S to Fe (Eq. (4)); (iii) the resulting $\text{Fe}^{\text{II}}\text{S}$ is hydrolysed (Eq. (5)) and leads to the release of the $\text{S}^{\cdot-}$ radical (which rapidly reduces additional Fe^{III} species to generate sulphur species with high oxidation number); (iv) the surface complex $\text{Fe}^{\text{II}}\text{OH}_2^+$ is released to solution (Eq. (6)) and leaves a new surface site to perpetuate the sulphide reductive dissolution of Fe^{III} species.



To prevent the destructive effect of sulphide species on iron alloys, miscellaneous methods have been developed in the past few years, for another context than radioactive waste repository, such as the use of biocides and the biocompetitive exclusion [16]. This approach entails selecting and stimulating the growth of indigenous bacteria by controlling the addition of chemical compounds acting as nutrients or electron acceptors, in particular nitrate and/or nitrite [17,18]. The addition of nitrate/nitrite at low concentrations (< 1 mM) leads to a decrease of sulphide according to several potential mechanisms (Fig. 1a–c) [16,17,19–22]: (i) a stimulation of nitrate-reducing bacteria (NRB) at the expense of SRB and TRB in competition for the same organic electron donor (Fig. 1a); (ii) a switch of sulphate reduction by promoting dissimilatory reduction of nitrate (Fig. 1b); (iii) a removal of sulphide through the lithotrophic activity of nitrate-reducing, sulphide-oxidizing bacteria (NR-SOB) (Fig. 1c). Concomitantly, this nitrate/nitrite supplementation involves an increase of NRB population. Moreover, such nitrate level concentration (< 1 mM) could be present in underground [23]. To date, few studies have reported the effect of NRB on the biocorrosion of iron and carbon steel in the literature [24–30]. The originality of this work is the consideration of the bacterial metabolism of NRB often overlooked in corrosion processes, as opposed to those taken into account for several years (e.g. SRB and TRB). Indeed, the microbial group of NRB could influence the stability of the rather protective corrosion product film composed of a bilayer of ferrous carbonates (mainly constituted of siderite and chukanovite) and magnetite expected to form on carbon steel in the anoxic conditions of nuclear waste repository. For instance, the oxidation of Fe^{II} -bearing minerals to mixed $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$ and/or Fe^{III} phases has recently been documented in the presence of biologically produced nitrite from the respiration of nitrate by NRB [31,32] or in the presence of chemically

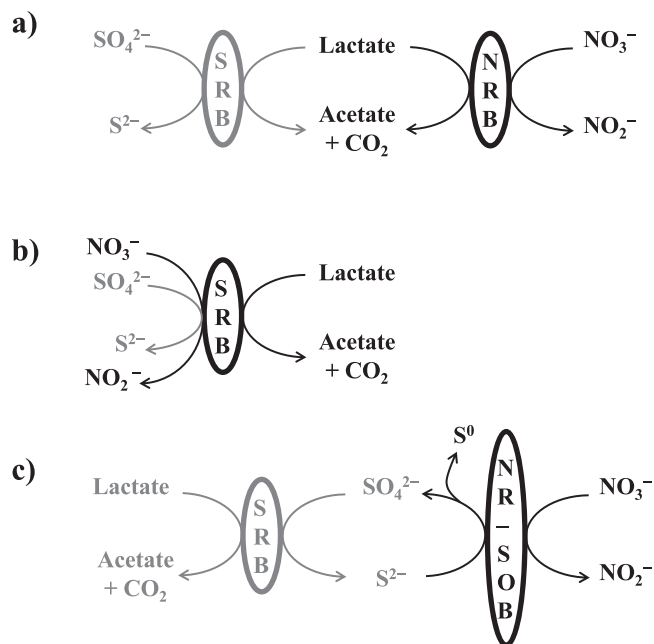


Fig. 1. Effect of nitrate on the biogeochemical cycle of sulphur: (a) a competition between sulphate-reducing bacteria (SRB) and nitrate-reducing bacteria (NRB) for the same organic electron donor (i.e. lactate) leading to an inhibition of sulphate reduction to sulphide; (b) nitrate is the preferred electron acceptor for SRB, and thus, sulphate is not reduced; (c) oxidation of sulphide to sulphate and sulphur by nitrate-reducing, sulphide-oxidizing bacteria (NR-SOB).

provided nitrite species [33].

In order to evaluate the role of NRB on the transformations of ferrous carbonates/magnetite corrosion bilayers, *Klebsiella mobilis* was used in the present study as a model of nitrate-reducing (non-denitrifying) bacteria. Since this bacterium is unable to enzymatically oxidize Fe^{II} species, all oxidation of Fe^{II} species will be the result of chemical reactions with oxidized species (e.g. nitrate, nitrite). Corrosion bilayers of ferrous carbonates/magnetite synthesized by anodic polarization at applied current density were incubated with *K. mobilis* in the presence of dihydrogen and lactate (as electron donors), and nitrate (as sole electron acceptor). At the issue of the incubation with *K. mobilis*, the corrosion product layers were characterized by Raman spectroscopy, X-ray diffraction (XRD) scanning and Mössbauer spectroscopy, which revealed that iron sulphides had formed. To unravel microbial processes involved during this biocorrosion study, abiotic experiments were performed with Na_2S solutions added instead of *K. mobilis*. The resulting corrosion product layers were characterized by optical microscopy, μ -Raman spectroscopy, and scanning electron microscopy.

2. Materials and methods

2.1. Generation of ferrous carbonates/magnetite bilayers at the surface of a carbon steel coupon using galvanostatic anodic polarization

The electrochemical method previously described by Romaine et al. [34,12] was used for the formation of ferrous carbonates/magnetite bilayers on carbon steel coupons under claystone layers. It was shown that the composition of the artificial layers generated by such accelerated procedure was similar to that obtained at OCP [12], and expected for the natural one. The main difference between artificial and natural layers is assumed to be porosity as the accelerated growth more likely promotes the formation of larger and more numerous pores. The working electrodes were S235JR carbon steel disks with a diameter of 16 mm. The steel composition (weight %) was: 98.2% Fe, 0.122% C, 0.206% Si, 0.641% Mn, 0.016% P, 0.031% S, 0.118% Cr, 0.02% Mo,

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