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Galvanic corrosion of carbon steel in anoxic conditions at 80 °C associated with a heterogeneous magnetite (Fe_3O_4)/mackinawite (FeS) layer

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Anodic polarization of carbon steel electrodes in deaerated 0.01 mol L^{-1} NaCl + 0.01 mol L^{-1} $NaHCO_3$ + 0.001/0.01 mol L^{-1} Na_2S solutions (with pH ~ 7.5) led to heterogeneous layers made of magnetite and mackinawite. A locally accelerated dissolution of the steel was observed in any case and the most corroded areas were covered with a layer enriched with mackinawite. This suggests that part of the electrode surface was blocked, covered with a magnetite rich layer where water reduction was favored. The effects of the galvanic coupling between a magnetite electrode and a bare carbon steel electrode covered with a ~5 mm thick argillites layer were then studied in a 0.01 mol L^{-1} NaCl + 0.01 mol L^{-1} $NaHCO_3$ solution at room temperature and 80 °C. Electrochemical measurements demonstrated that a relatively high galvanic current initially flowed between the magnetite electrode (cathode) and the steel electrode (anode). However, this current decreased with time down to negligible values. Micro-Raman spectroscopy analysis revealed that a magnetite layer was formed on the steel electrode, thus suppressing the initial difference between anode and cathode. When the same experiment was performed with the steel electrode set under an argillites layer enriched with Na_2S, the galvanic current density remained constant at a significant value (~20 µA cm^{-2}) during the 11 days of experiment. It led to the formation of a layer composed of mackinawite (and chukanovite) on the steel electrode. This result confirms that heterogeneous magnetite/mackinawite layers can favor galvanic corrosion even in anoxic conditions.

1. Introduction

This study relates to the problem of long-term disposal of nuclear waste. In France, it is envisaged to store high-level radioactive waste at a depth of ~500 m in a deep geological disposal, drilled in very stiff (indurated) clay (Callovo-Oxfordian COx claystone so called "argillites") formation [1]. A schematic representation of the multi-barrier concept is shown in Fig. 1. The waste will be trapped in a glass-matrix set inside a stainless steel container, itself placed in a carbon steel overpack. Carbon steel casing will be inserted inside the horizontal tunnels (sub-horizontal boreholes) drilled in argillites and a specific cement grout (pH ~10) will be used to fill the gap between the carbon steel casing and argillites. The overpacks, equipped with pads, will finally be slid into the carbon steel casing. A temperature as high as 80–90 °C is expected at the overpack surface because of the intense radioactivity. Once the repository closed, all the oxygen (O_2) trapped in the system is expected to be consumed more or less rapidly by the corrosion of carbon steel or by other chemical processes occurring in argillites. Anoxic conditions will prevail afterwards.

As shown in Fig. 1, the base of the carbon steel casing will be in contact with argillites while the rest of the casing will be in contact with cement grout. It is also expected that in various places the sides of the casing may also be in contact with argillites. As a consequence, one of the possible risks of localized corrosion of the carbon steel casing is the galvanic coupling that might happen

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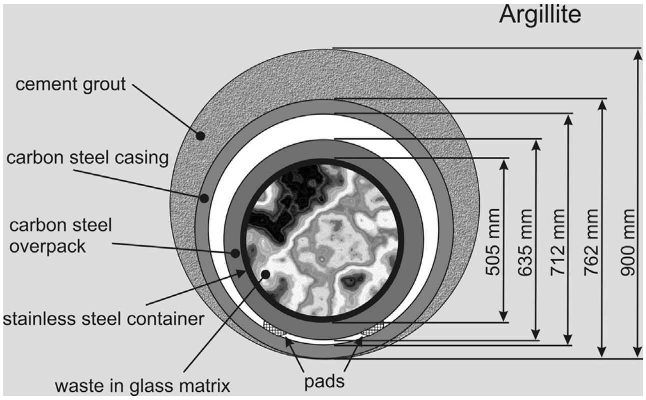

Fig. 1. The envisioned multi-barrier concept for the French disposal of high level nuclear waste: cross-sectional view.

between two zones of the metal in contact with different environments, i.e. COx claystone and cement grout. The persistence of the galvanic effect, initially due to the heterogeneity of the medium, should be governed by the nature of the corrosion products that progressively cover the metal surface on the anodic and cathodic zones. For instance, it was recently observed that localized corrosion of carbon steel in seawater was a self-sustaining process that could persist for a long time (6–8 years) [2]. It could be demonstrated that the corrosion products forming in the cathodic zones increased the cathodic character of the metal underneath while the products forming in the anodic zones increased the anodic character of the metal underneath [2]. Besides, using a carbon steel electrode pre-corroded in argillites at 80 °C, it could be demonstrated that a heterogeneous corrosion product layer could itself induce corrosion cells [3].

In argillites, the corrosion of carbon steel mainly leads to carbonated compounds such as siderite $FeCO_3$ and chukanovite $Fe_2(OH)_2CO_3$ [3–10]. However, due to the heterogeneity of this natural medium, other corrosion products were also observed, in particular magnetite Fe_3O_4 and mackinawite FeS [3,7,9,10]. The formation of mackinawite was attributed to sulfide species issuing from pyrite (FeS_2) particles present in argillites at the vicinity of the steel surface [7]. In the cement grout, magnetite Fe_3O_4 is expected to be the main corrosion product of carbon steel because of alkaline conditions and low carbonate concentrations [11].

Magnetite is an electronic (semi)conductor characterized by a low resistivity [12]. It can play the role of cathode, i.e. the reduction of water or dissolved oxygen can take place on the surface of magnetite particles electrically connected to the metal. Various studies showed that galvanic corrosion could occur between bare steel and steel covered with magnetite in different conditions [13–17] and even in deaerated environments [18]. The reduction reaction mainly takes place on the magnetite layer as magnetite is more noble (i.e. has a higher potential) than steel. A similar process would also occur between a zone of the steel surface covered with magnetite and a zone covered with a porous layer of isolating compounds.

Other corrosion products are electronic conductors and in particular iron sulfides [19]. Actually, the occurrence of localized corrosion in oil and gas industry is often associated with the formation of heterogeneous FeS layers. The areas covered with iron sulfides may then act as cathode, the other part of the steel surface acting as anode [20]. Similarly, the conductivity of FeS plays a key role in the corrosion phenomena associated with electroactive sulfate-reducing bacteria because the electrons can go on flowing from the metal to the bacteria through the FeS layer [21].

The aim of the present study was to assess the risk associated with galvanic effects occurring between magnetite covered zones and other areas of a carbon steel surface. More particularly, the study was focused on the influence of sulfide species on such galvanic effects. The electrochemical behavior of carbon steel electrodes covered with heterogeneous corrosion product layers composed of magnetite and mackinawite was studied first. These layers were obtained by anodic polarization at 80 °C in deaerated $0.01\ mol\ L^{-1}$ NaCl + $0.01\ mol\ L^{-1}$ $NaHCO_3$ + $0.001/0.01\ mol\ L^{-1}$ Na_2S solutions of pH = 7–8.

Secondly, the behavior of the galvanic couple formed with a carbon steel electrode and a magnetite electrode was investigated. Both electrodes were covered with a ~5 mm thick layer of argillites before to be immersed in $0.01\ mol\ L^{-1}$ NaCl + $0.01\ mol\ L^{-1}$ $NaHCO_3$ solutions at room temperature (RT) and 80 °C. The galvanic current was followed with time and the corrosion product layer formed on the steel electrode was thoroughly characterized by μ-Raman spectroscopy. Finally, a similar experiment was realized with the carbon steel electrode covered with an argillites layer enriched with Na_2S.

2. Materials and methods

2.1. Materials and electrolytes

The working electrodes were S235JR ferritic-pearlitic carbon steel disks with an active area of $1.76\ cm^2$ (anodic polarization experiments) or $2\ cm^2$ (galvanic coupling experiments). The nominal composition of S235JR steel (weight %) is: 98.2% Fe, 0.122% C, 0.206% Si, 0.641% Mn, 0.016% P, 0.031% S, 0.118% Cr, 0.02% Mo, 0.105% Ni and 0.451% Cu. The surface was polished with silicon carbide (grade 600, particle size 25 μm), rinsed with deionized water and carefully dried just before the beginning of the experiment.

Magnetite as a corrosion product is often non stoichiometric and has a chemical formula $Fe_{3-x}O_4$ due to an excess of Fe(III) cations. It may have electrical properties that differ from those of a stoichiometric magnetite (i.e. Fe_3O_4) that would result from a completely different process of formation (e.g. mineralogical process or high temperature oxidation process). The magnetite electrode, shown in Fig. 2, was then prepared using a fragment of the corrosion product layer formed on a carbon steel infrastructure of the Nantes-Saint Nazaire seaport (Atlantic Coast, France). The fragment was characterized by μ-Raman spectroscopy (and X-ray diffraction, results not presented) following the procedure described in Section 2.3

Raman spectroscopy analysis demonstrated that this fragment of corrosion product layer was mainly composed of magnetite

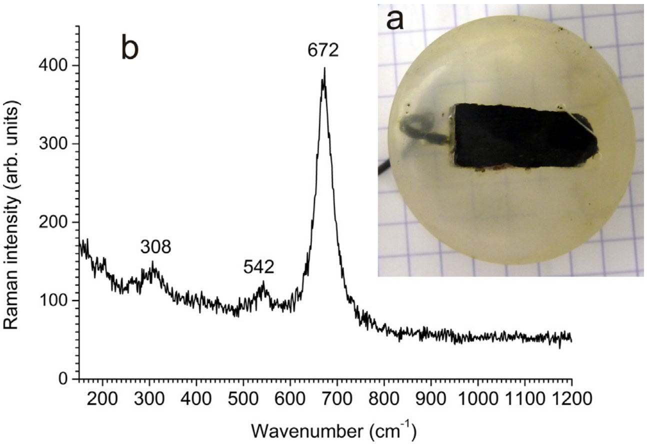

Fig. 2. (a) Photograph of the magnetite electrode and (b) typical Raman spectrum obtained during analysis of its surface.