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Carbon steel corrosion in clay-rich environment

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ABSTRACT

We investigated the carbon steel corrosion in carbon dioxide clay-rich environment to understand its behavior under geological conditions. The results show the formation of magnetite as the main corrosion product in the first step of the corrosion process, followed by the formation of different corrosion products with complex mixtures of iron-oxide, hydroxycarbonate, hydroxychloride and sulfide phases. These results strongly contrast with similar experiments conducted under H_2 atmosphere where the major corrosion products consisted of iron sulfides. It appears then important to consider all the geochemical parameters including gas composition to better study corrosion of steel buried in geological formations.

1. Introduction

Deep geological disposal remains the preferred option for management of long-lived radioactive waste in several countries including Belgium, Finland, Japan, Republic of Korea, Sweden, Switzerland, USA and France [1–8].

The French radioactive waste management agency (ANDRA) is designing a deep geological repository in Callovo Oxfordian claystone (COx) formation in Eastern France. Current investigations are conducted to optimize and finalize this repository concept with the aim to ensure its long-term safety and its reversibility. The high-level waste (HLW) shall be confined in a glass matrix and then encapsulated into cylindrical carbon steel overpacks. These containers shall be placed into micro-tunnels in the highly impermeable COx layer at a depth of 500 m [6,9,10]. Carbon steel containers must remain leakproof for a few thousand years as a contribution to the multi-barrier containment system for the waste [9,11,12]. The long-term safety assessment of the geological repository has to take into account the degradation of the carbon steel used for the waste overpacks, which is mainly caused by corrosion processes.

One of the most important features of any deep geological repository is that the nature of the environment evolves over time. Generally, the environment evolves in such a way that corrosion becomes less severe and more predictable with time. However, the presence of microorganisms can also affect the environment [6,13]. In a recent study [6], we have shown the presence of sulfate-reducing bacteria (SRB) in the COx claystone and sufficient nutrients and trace elements for bacterial growth. SRB were isolated from argillite under anaerobic conditions and successfully characterized and identified by 16sRNA sequencing. In addition, H_2 is expected to be produced in the disposal site and could be a tremendous source of energy for the growth of anaerobic bacteria, in particular the SRB [6].

Recently, El Mendili et al. [14] investigated the effects of SRB on carbon steel corrosion at 30 °C for 1, 3 and 6 months under anaerobic conditions in the presence of COx claystone and groundwater, with an atmosphere of 5% H_2/N_2, simulating hydrogen production in the site. We showed that the first corrosion products formed on steel surface in these conditions were poorly crystallized iron sulfide and mackinawite, followed then by a fast transformation process into pyrrhotite phase. Finally, our investigations have attempted to demonstrate that in the presence of hydrogen, the corrosion of carbon steel containers under anoxic and sulfidogenic environment sustained by SRB may not be a problem notably due to the formation of a passive layer on the steel surface.

Another possible scenario of deep geological disposal conditions was investigated [15], i.e., the carbon steel corrosion under sequential aerobic and anaerobic microbiologically induced corrosion in the presence of COx claystone and groundwater with an atmosphere of 5% H_2/N_2. The results showed the formation of mixture of lepidocrocite, maghemite and magnetite under aerobic conditions. Upon oxygen consumption and establishment of sulfidogenic conditions, by SRB activity, all these oxides disappeared via transformation into iron sulfide. It was also shown that corrosion rate of steel in anaerobic cultures was higher than that of steel initially corroded in aerobic condition, suggesting a protective

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role of the corrosion product layer formed under sequential aerobic–anaerobic conditions.

Although great care was taken to investigate the influence of major factors on carbon steel corrosion under geological conditions, the mechanism responsible is probably more complex. Indeed, the corrosion of iron and steel surfaces in natural environments often lead to the formation of corrosion layers made of extremely complex mixtures of iron-sulfide, (hydro)oxide, carbonate, and chloride solids [16,17]. According to Anderko and Shuler [18], magnetite and siderite are precursors to a less stable form of iron sulfide such as mackinawite. Mackinawite is a particular form of iron sulfide that is commonly observed in immersion corrosion studies and also easily produced from iron and iron oxides by SRB activity [19]. Mackinawite can then transform into pyrrhotite which is considered to be more thermodynamically favored in anoxic environments, hence pyrrhotite is expected to predominate over long term conditions [18,20–22].

In the present work, we investigate the carbon steel corrosion under carbon dioxide-rich atmosphere in the presence of claystone. The morphology and the nature of corrosion products evolution were analyzed step by step using both scanning electron microscopy (SEM) and confocal micro-Raman spectroscopy and the role of SRB in the mechanism of steel corrosion was then discussed.

2. Experimental section

2.1. Materials

The Callovo-Oxfordian (COx) claystone from the Bure site (east of France) contains three main mineralogical phases: a dominant argillaceous phases 40–50% clay (50–70% interstratified illite/smectite), a carbonate phase (~22–30%, essentially calcite with a few percent of dolomite) and a quartz phase (18–32%) [23]. These three main phases are accompanied by other minor phases including pyrite, feldspar, and organic matter, in mass quantities of less than a few percent. The clay used for our experiments was sampled under oxygen-free conditions, sealed in plastic/aluminium bags, and transferred to the laboratory. Powder samples were prepared for batch experiments in a glove box filled with nitrogen gas. A simplified groundwater composition was calculated by BRGM (French Geological Survey) and beaucaire et al. [24,25], from analyses of samples coming from the site of the Meuse/Haute-Marne laboratory (France). The simulated groundwater was prepared in the laboratory at 25 °C with the following reagents: $NaHCO_3$, Na_2SO_4, $Na_2SiO_3–9H_2O$, NaCl, KCl, $CaCl_2–2H_2O$, $MgCl_2–6H_2O$, $SrCl–6H_2O$. All the reactants except metasilicate ($Na_2SiO_3–9H_2O$) were weighed out and grinded, then placed in a 2-liter flask containing 1.5 L of ultrapure water. The flask was closed and the solution is then brought into equilibrium (pH stabilization) under magnetic stirring for 24 h until the reagents were completely dissolved. The solution was bubbled with a mixture of 89.5% Ar + 5% H_2 + 5.5% CO_2 until the pH reached about 6.5. Metasilicate was then added and the solution volume in the flask was adjusted to 2 L. After clarification, the solution was again degassed to pH 7.2. The final groundwater composition is detailed in Table 1. Lactate (1 ppm) was added at the beginning of the experiments to simulate the SRB activity as indicated by El Hajj et al. [11].

2.2. Steel preparation

The P235GH carbon steel was used because it has a number of obvious benefits as a canister material, including good combination of strength and ductility, good corrosion properties in the expected repository environment, extensive experience with fabricating and sealing large cylindrical objects, and the relative abundance and cost of the material. The steel coupons were cut into 10 × 10 × 0.5 mm and both surfaces were polished with a Buehler polisher using a PSA discs (Pressure Sensitive Adhesive discs) to a surface roughness of 3 μm. According to the ASTM standard method for corrosion measurement (ASTM, 1966), the steel coupons were then cleaned with HCl (15%) and sodium carbonate (5%) before experiments. For each experiment four steel coupons were used, two coupons for weight loss measurements and two for structural characterizations.

Table 1
Synthetic water composition in equilibrium with the COx claystone (pH = 7.2).

Elements	Measured concentration (mmol/L)	Theoretical concentration (mmol/L) [25]
Na^+	44.9	45.6
K^+	1	1.03
Mg^{2+}	6.4	6.67
Ca^{2+}	7.3	7.36
Cl^-	42.1	41.0
SO_4^{2-}	15.5	15.6

2.3. Experimental procedure

Each batch experiment was conducted with 100 ml of groundwater mixed with 20 g of claystone and 4 steel coupons in a serum bottle. Before addition of the steel coupons to the groundwater and the clay contained in the serum bottle, anaerobic conditions were achieved first by degassing the medium using a vacuum pump, then placing the bottles in a glove box filled with nitrogen gas, and finally by continuously bubbling a 3% Ar/CO_2 gas at 0.5 bar in the solution for 30 min. At this stage the groundwater/clay system is considered to be air-free but small traces of oxygen cannot be excluded. Then, the steel coupons were added horizontally inside the clay in the bottom of each bottle, and bottles were sealed. Finally, the whole system (bottle containing clay, groundwater and steel) was bubbled with 1 bar CO_2 at 30 °C for 10 min and the pressure was kept at 1 bar during the time exposure (1, 3 and 6 months). The final addition of CO_2 gas is meant to better simulate the geochemical conditions in the COx claystone formation.

2.4. Weight loss and corrosion rate

For all experiments, the steel corrosion rate was determined according to the ASTM standard method for corrosion measurement. The corrosion products are stripped using the chemical HCl (15%) and isopropanol with 5 mg/l of hexamethylenetetramine to determine the mass loss.

The corrosion rate could be calculated using the following formula:

$$\text{Corrosion rate}\ \mu\text{m/y}:\ \frac{3650 \times \text{weight loss(mg)}}{\text{Density}(\text{g/cm}^3) \times \text{Area}(\text{cm}^2) \times \text{Time(days)}}$$

With a density of 7.85 g/cm^3 for steel

2.5. Solution analysis

At the end of reaction time, an aliquot of the solution was syringe-filtered using a 0.2 μm polypropylene filter (Whatman). The solution was then analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Perkin-Elmer) to quantitatively determine the iron concentration. The microbial activity was monitored by studying sulfide production by sulfate reduction into sulfide. Sulfate was measured by ion chromatography (DIONEX ICS 2500)