Corrosion at the carbon steel-clay borehole water interface under anoxic alkaline and fluctuating temperature conditions

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ABSTRACT

Coupons of carbon steel were corroded in situ in anoxic clay porewater under slightly alkaline conditions. Sample damage was less than 1 µm for 9 months at 85 °C only, and corrosion interfaces were covered by a thin, protective layer of Fe-silicate. The damage was more significant for samples exposed to room temperature transients (up to 38 µm for two years), and the long-term surface differentiated in cathodic (Fe-silicate covered) areas and anodic crevices filled with siderite, chukanovite, β-Fe$_2$(OH)$_3$Cl, and covered by tubercles. Sulfide compounds were detected, and were related to the metabolism of sulfate-reducing prokaryotes detected by microbiological techniques.

1. Introduction

High-level nuclear waste (HLW) is a legacy of the use of nuclear power for peaceful or military purposes, and must now be properly disposed of to shield the future generations from its harmful effects. Over the years, consensus has emerged to consider disposal in deep underground repositories as the safest solution [1–3]. For example, the French project called CIGEO (for "Centre Industriel de stockage GEOlogique") has been articulated along the setup of several engineering and natural barriers, mitigating the migration and transfer of radionuclides at the Earth surface. Thus, HLW as a nuclear glass cooled in stainless steel containers would be encapsulated in low-alloy carbon steel (C-steel) overpacks and introduced in C-steel casings within horizontal microtunnels drilled in the Callovo-Oxfordian (COx) clay of the Paris Basin [4,5]. The casing would allow the nuclear waste to be retrieved from the repository, should new technologies of nuclear waste handling be developed in the future. In 2005, the design involved the presence of voids between the overpack and the casing and between the casing and the clay formation. These voids were to be gradually refilled by porewater seeping from the clay formation, leading to corrosion of casings and overpacks in successively distinct environments (i.e. in contact with clay, porewater, or vapour phase at equilibrium with porewater). Under such conditions, general corrosion is expected to predominate over long term for C-steel [6–10], however, pitting could not be entirely ruled out, even though pits would remain metastable and tend to close up [7]. Hence considerations on the long-term integrity of the HLW disposal have motivated a dedicated research effort on the corrosion of C-steel under repository conditions.

Important insight into the long-term behaviour of C-steels in rock environments has been obtained from the research work led by the oil and gas industry [11,12]. This knowledge has been complemented by several specific studies devoted to understand the synergy between steel corrosion and matrix alteration in clay or clay materials [13–33]. The results of these studies have been fed into models based on a geochemical approach to improve the long-term understanding of these corrosion systems [34–39]. As a complementary approach, characterization of archaeological artifacts have been implemented to identify corrosion mechanisms and products of likely preponderance over timescales inaccessible to laboratory experiments or modern industry (e.g. [40–50]). To consolidate this body of knowledge, the French Agency for the Management of Nuclear Waste (Andra) has designed an *in situ* experiment in the COx claystone. In this experiment, C-steel coupons were in contact at 85 °C with water seeping from clay in a test chamber under monitored and nominally reducing physico-chemical

Table 1
List of rods investigated in this study.

Rod	Introduction time (days)	Removal time (days)	Reaction time[a] (days)
Series 2-Rod 1	$t_0 + 643$	$t_0 + 748$	104 days
Series 2-Rod 2	$t_0 + 643$	$t_0 + 643$	104 days
Series 2-Rod 3	$t_0 + 643$	$t_0 + 643$	104 days
Series 3-Rod 1	$t_0 + 1035$	$t_0 + 1169$	134 days
Series 3-Rod 2	$t_0 + 1035$	$t_0 + 13143$	279 days
Series 3-Rod 3	$t_0 + 1035$	$t_0 + 1783$	748 days
Series 3-Rod 4	$t_0 + 1035$	$t_0 + 1783$	748 days

conditions (pH, Eh, water and gas composition). Periodically, sets of coupons were retrieved for gravimetric assessment of corrosion rates, and, for some of them, replaced by new sets. Analysis of the borehole water revealed the occurrence of a pH transient attributed to oxidation of the COx claystone after borehole drilling and before installation of the test chamber [51]. These acidic conditions were invoked to explain high rates of corrosion (up to 200 μm/a) observed for coupons initially present in the test chamber [51,52]. The present study focuses on coupons introduced in the test chamber after the acidic transient, when the pH was back to basic values. Macroscopic measurements and microscopic characterizations were performed to unravel the relationship between corrosion rates and the nature of Corrosion Products (CPs).

2. Material and methods

2.1. Nature of C-steel samples

Corrosion experiments were performed on coupons ($23 \times 16 \times 2$ mm^3) of A37, SA516 and P235 grade C-steel, and from a P235 welded zone (P235s; the weld zone being in the middle of the coupon) [51]. Metallurgical analysis showed that coupons of plain C-steel exhibit a ferrite-pearlite microstructure with pearlite bands either parallel or perpendicular to the smallest surface, and ferrite grains of about 20–30 μm. The welded zone of the P235s sample displayed a martensitic microstructure with grain diameters up to 300 μm. These coupons were positioned on a rod-shaped, PEEK-made sample holder.

2.2. Experimental setup and physico-chemical monitoring

The "MCO" (for "Materials Corrosion") experimental setup has been described elsewhere [51]. Briefly, *in situ* corrosion was performed in a test chamber at the bottom of a vertical descending borehole in the COx claystone of the French Underground Laboratory (Bure). The test chamber was initially half-filled with a synthetic clay porewater which was gradually replaced by water seeping from the clay formation during the experiment. The test chamber was connected to cabinets located in the gallery of the laboratory by a series of stainless steel (SS) lines for heating of the test chamber, on-line monitoring, and periodic sampling of the fluids. Temperature, pH, oxidoreduction potential (Eh), conductivity (Ec) and gas/liquid flowrates were continuously monitored by appropriate sensors. The total pressure was also monitored *in situ* by a sensor located at the bottom of the test chamber.

Periodically, borehole water and gas were sampled in 316 SS gas-tight vials for analysis of pH, alkalinity, and composition. The concentration of dissolved Li$^+$ ([Li]$_{aq}$), Na$^+$ ([Na]$_{aq}$), K$^+$ ([Mg]$_{aq}$), Mg^{2+} ([Mg]$_{aq}$) and Ca^{2+} ([Ca]$_{aq}$) were analysed by a Dionex ion chromatograph using an IonPac CG 12 A, 4×50 mm guard column and a CS 12 A, 4×250 mm analytical column. The concentrations of dissolved Cl$^-$ ([Cl]$_{aq}$), SO$_4^{2-}$ ([SO$_4$]$_{aq}$), S$_2$O$_3^{2-}$ and acetate were analysed by a Dionex ion chromatograph ICS 1500 using an IonPac AG 22, 4×50 mm guard column and a AS 22, 4×250 mm analytical column. NH$_4^+$ and total sulfide (H$_2$S, S^{2-}, HS$^-$) were analysed photometrically. Dissolved Si ([Si]$_{aq}$), Cr, and Fe ([Fe]$_{aq}$) were analysed by inductively coupled plasma mass spectrometry. The composition of the gas samples

was determined using a Shimadzu GC17A gas chromatograph equipped with two capillary columns. A Swagelock system allowed a rapid and direct connection of the sample cells with the evacuated inlet system of the gas chromatograph (8 Port Dual External Sample Injector, Valco Europe) without contact with atmosphere.

2.3. Corrosion experiment

For the corrosion experiments, coupons-carrying rods were inserted in the test chamber. The samples from the rod lower level were bathed by the seeping porewater. An initial set of seven rods ('Series 1') was introduced at t_0, and kept at ambient temperature for 77 days. The borehole temperature was then ramped up to a plateau of 85 °C (attained at $t_0 + 193$ days). Rods were recovered after various reaction times. Some of the empty slots were then filled with new rods, first at $t_2 = t_0 + 643$ days ("Series 2") and then at $t_3 = t_0 + 1035$ days ("Series 3"). The coupons investigated in this article are from "Series 2" and "Series 3" rods (Table 1). Two heating failures occurred from $t_0 + 709$ to $t_0 + 792$ days, and again from $t_0 + 1432$ to $t_0 + 1539$ days. Rods "Series 3-Rod 1" and "Series 3-Rod 2" were reacted at 85 °C only, whereas the other rods were also partially corroded at 25 °C.

Recovered rods were disassembled in a glove box. Some C-steel coupons were swabbed for microbial analysis, and then all coupons were rinsed with ethanol and dried to prevent post-oxidation. Some coupons were heat-sealed in aluminium bags and shipped for microstructural characterization [51]. Gravimetric measurements were performed on the remaining coupons as previously detailed [51]. From these measurements, the damaged thickness e$_{cor}$ (in μm), was calculated according to

$$e_{cor} = \frac{\Delta m}{S \cdot \rho_{Fe}},$$ (1)

where S is the surface area, Δm is the weight loss, and ρ_{Fe} is the iron density (7.87 g cm^{-3}). The time-averaged corrosion rate r is then calculated as

$$r = \frac{e_{cor}}{t},$$ (2)

where t is the full reaction time. Thus temporal fluctuations in corrosion rates are smoothed out.

2.4. Microbial analysis

For microbiological characterisation, coupons (essentially SA516 grade) taken from the sample holder were immediately swabbed and the swabs inserted into tubes containing a sterile, anaerobic solution under non-growth conditions (neutral pH, saline conditions with a reducing agent). Prior to characterization, the swabs were ultrasonically treated to re-suspend and disperse microorganisms. Microbial analyses were also performed on borehole water samples.

Total cell counting was performed by epifluorescence microscopy using the SYBR green marker and an Olympus BH-2 microscope with computer-controlled Lhesa 4036 camera. About 40 frames per sample were taken, and processed using the Labview-based Micromar software.