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Corrosion of steel in clay porewater interface under repository conditions: microstructural characterization of the corrosion interface

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ABSTRACT

Introduction

Most of the research effort devoted to the design of nuclear waste repositories aims at guaranteeing the confinement of high-level nuclear waste (HLW) over geological periods. For example in France, HLW nuclear glass kept in stainless steel containers would be inserted in carbon steel (C-steel) overpacks introduced in C-steel liners within the Callovo-Oxfordian (COx) clay of the Paris Basin [1]. Until 2014, the French concept planned technical voids between the overpack and the liner, and between the liner and the clay formation, which would be gradually refilled by porewater seeping out of borehole walls. In addition radioactive decay would result in a steady increase in temperature (up to 90°C). As a consequence, long term corrosion of liners and overpacks was expected to occur under high temperature, anoxic conditions and either in seeping clay water or in the vapor phase. In order to predict the fate of C-steel under such conditions, the French Agency for the management of nuclear waste (Andra) designed an *in situ* experiment in a test chamber drilled in the COx clay [2]. C-steel coupons were contacted under reducing conditions at 90°C with seeping porewater or with the overlying gas phase. A low pH transient was observed at the beginning of the experiment (down to pH 4.5), resulting from oxidation of the host rock-forming sulfide as well as trapped CO₂. This transient probably caused the important corrosion observed for the first series of sample inserted in the test chamber. At the end of the pH transient, a second set of samples was inserted in the test chamber, when slightly alkaline conditions prevailed. The nature of the corrosion interfaces in seeping porewater are described in the present contribution.

Materials and methods

The corrosion setup is extensively described elsewhere [2]. Briefly, a vertical test chamber was drilled in the COx host rock of the Bure underground laboratory, shielded from the borehole by an inflatable rubber packer, and half-filled with synthetic clay porewater. This initial water was gradually replaced by seeping water from the clay formation. The evolution of the pH and composition of the borehole water and atmosphere in the test chamber was monitored. Rods with steel coupons at both ends were inserted in the test chamber, so that half of the coupons were in the seeping porewater and half in the overlying atmosphere. At given times some of the rods were recovered and sometimes replaced by new rods. The present contribution deals with rods inserted after 643 days of reaction, at a time when pH remained higher than 7 to the end of the experiment. Some of these coupons were corroded only at 85°C. Others experienced episodes at room temperature due to breakdown of the heating system.

After rod recovery, some of the coupons were immediately used for gravimetric assessment of corrosion. Other coupons of P235 grade were rinsed with ethanol, dried, embedded in epoxy resin. Cross-section of corrosion interfaces were polished and investigated using microscopic, microspectroscopic and microdiffractometric techniques [3].

Results and interpretation

For coupons reacted at high temperature only, the surface was covered by an extremely thin ($< 5 \mu\text{m}$) and continuous layer of Fe-silicate. This layer of corrosion products (CPs) was locally enriched in sulfide solids. The coupons extremities inserted in the slits of the sample holder during reaction time, were also covered with an outer layer of Ca-rich siderite (ankerite), suggesting favorable conditions of supersaturation of this carbonate phase.

For the sample experiencing low-temperature episodes, most of the surface was covered by a thin ($< 20 \mu\text{m}$) and cracked duplex layer of CP. For short reaction times, the chemical composition and structure of CP corresponded to partially oxidized Fe (hydr)oxide, locally identified as magnetite. With increasing reaction time, this solid was gradually replaced by a duplex layer of Fe silicate, covering a S-rich sulfide layer in contact with metal (Fig. 1). In addition, in a few areas of the corrosion interface, large depressions developed and filled with siderite and chukanovite located under the interfacial Fe silicate phases. The bottom of these depressions could locally contain $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$, indicating spatially decoupled anodic and cathodic reactions. These depressions were covered by large deposits of corrosion products (siderite, chukanovite, and Fe silicate). As for the other samples, the coupons extremities were covered by thick massive deposits of ankerite. Overall, this interface suggests spatial decoupling between the cathodic reaction occurring over the surface covered by the thin Fe silicate layer (and possibly protective conducting Fe sulfide), and the anodic reaction occurring in the depressions.

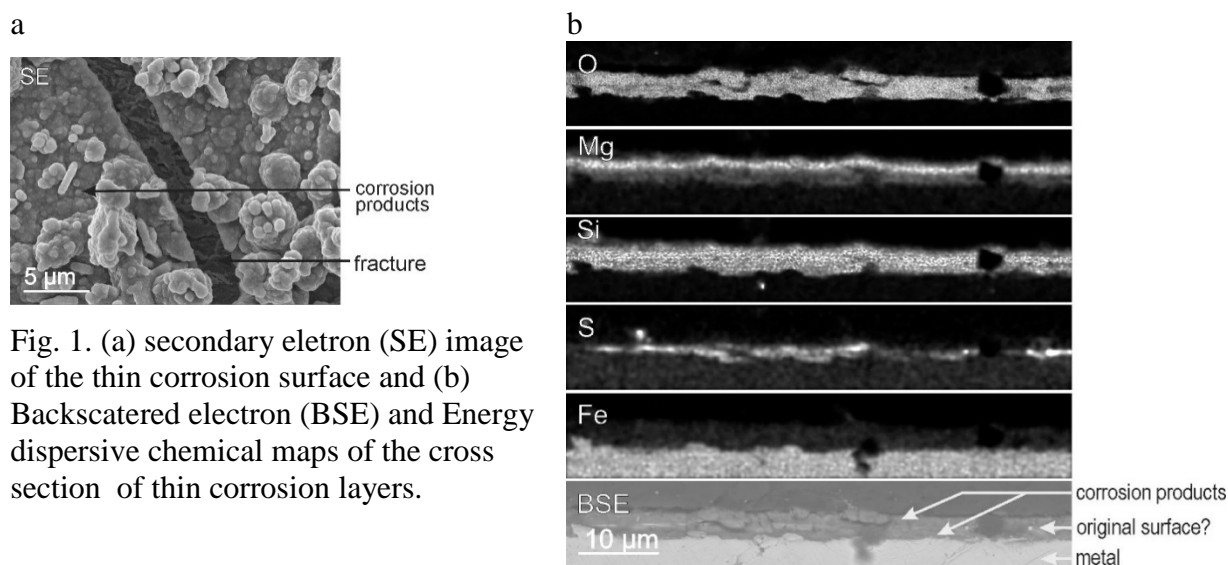


Fig. 1. (a) secondary eletron (SE) image of the thin corrosion surface and (b) Backscatered electron (BSE) and Energy dispersive chemical maps of the cross section of thin corrosion layers.

References

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