Influence of environmental parameters and metal microstucture on the corrosion mechanisms of iron anoxic media.

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In France, radioactive waste storage will take place 500 m deep in clay. The radionuclides will be confined in a vitreous matrix surrounded by several steel envelopes. The packages will evolve in an anoxic environment saturated with carbonated water for several thousand years. Understanding the corrosion mechanisms is crucial to define the size of these metallic elements.

Previous theoretical (Bataillon et al, 2010) and experimental studies on archaeological analogues (Leon et al, 2014) and laboratory samples (Leon et al, 2017) allowed to identify a $Fe^{II/III}$ submicrometric layer at the interface Metal/Corrosion Product layer (CPL) that seems to passivate steel. At the same time, conductive magnetite islets connected to the metal inside the CPL were identified by CAFM, suggesting that electrons from the metal anodic reaction could circulate through the CPL (Mercier et al, 2018).

The aim of this study is to clarify CPL properties at an earlier corrosion stage. Chemical, physical and electrochemical properties of the CPL such as phase distribution, porosity, conductivity and cathodic reaction location need to be clarified. Therefore, short-term corrosion experiments (640 h) were performed to see how CPL properties are set up. Three substrates (a pure ferrite; a carbon steel with cementite inclusions, corresponding to the overpack of the nuclear waste package; and coupons cut from a 15^{th} century iron rebar from the Metzs cathedral, presenting an heterogeneous matrix typical of historical artefacts, i.e. cementite and Si/P slag inclusions), were corroded to identify the impact of the substrate microstructure on corrosion process. Futhermore, experiments were performed in carbonate and silicate media to study the impact of the environment on the corrosion layers.

Results (SEM-EDS and µ-Raman) acquired on samples from the carbonate system showed CPL whose chemical properties are similar to CPL developped on experiments carried out over longer periods and on archaeological analogues. Nevertheless, submicrometric STXM/XANES analysis showed that the oxide is present discontinuously at the M/CPL interface. Conversely, in silicate system, the oxide layer at the M/CPL interface seems to be present with thickness around 1 µm. Depending on the substrate microstructure on carbonate system, the M/CPL front presents a quite uniform morphology (pure ferrite) or more locally advanced front (steel and old iron) which can be attributed to the presence of inclusion in the substrate. Electrical properties investigated by CAFM showed that CPL from pure ferrite contain magnetite islets arranged in discontinuous edgings in the insulating matrix of siderite which are electrically connected to the metal. In contrast, Metzs cathedral CPL has conductive zones throughout the inner corrosion layer. These conductivity differences will have an impact on the location of the cathodic reaction and, consequently, on the corrosion rate.