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 at Bure, 500m deep. The radionuclides will be confined in a vitreous matrix surrounded by several steel elements. The packages will evolve in a clay formation, in an anoxic environment saturated with carbonated water. This study focused on the interaction between steel elements and environment outside the package.

Previous theoretical (Bataillon et al, 2010) and experimental studies on archaeological analogue (Leon et al, 2014) and laboratory sample (Leon et al, 2017) allowed to identify a $Fe^{II/III}$ submicrometric layer at the interface Metal/Corrosion Product layer (CPL) that seems to induce steel passivation. At the same time, conductive magnetite islets connected to the metal inside the CPL were identified by CAFM which allow electrons from the metal anodic reaction to 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, oxidation state, porosity, conductivity and areas of electrons consumption need to be clarified. Therefore, short-term corrosion experiments (640 hours) were performed to see how CPL properties are set up. 3 types of substrate; a pure ferrite, a carbon steel corresponding to the metallic overpack of the nuclear waste package, which contain cementite inclusions, and, coupons cut from an iron rebar from the Metz's cathedral (15th century) presenting an heterogeneous matrix characteristic of historical artefacts with cementite and Si/P slag inclusions, were corroded to identify the impact of the substrate microstructure on corrosion process. Futhermore, experiments were performed on carbonated and silicated environment to study the impact of the environment on the corrosion layers.

First results (SEM-EDS and µ-Raman) acquired on samples from the carbonated system showed CPL whose chemical properties are similar to tests carried out over longer periods. Nevertheless, submicrometric STXM/XANES analysis showed that the oxide is present discontinuously at the M/CPL interface. Conversely, in silicated system, the oxide layer at the M/CPL interface seems to be well in place with thickness around 1 µm. Depending on the substrate microstructure, the inner layer doesn't have the same morphology on carbonated system: e.g., steel has more localized corrosion than pure ferrite and old iron which can be attributed to the presence of cementite. Electrical properties investigated by CAFM showed that CPL from pure ferrite contain magnetite islet arranged in discontinuous edgings in the insulating matrix of siderite which are electrically connected to the metal. In contrast, Metz's cathedral CPL has conductive zones throughout the inner layer of corrosion products. The conductivity differences observed for these zones in the CPL will have an impact on the location of the cathodic reaction and, consequently, on the corrosion rate.