Multiscale analyses of carbon steel corrosion in cement grout for radioactive waste disposal

Charlotte CARRÉ[1], Philippe DILLMAN[1], Delphine NEFF[1], Valérie DEYDIER[2], Yannick LIENARD[3], Sophia NECIB[3], Michel SCHLEGEL[4]

[1] CEA Saclay - LAPA, NIMBE, France

[2] Andra, France

[3] Andra - Meuse/Haute Marne Center, France

[4] CEA Saclay - Den - SEARS, France

The French national radioactive waste management agency (Andra) is investigating disposal of High-Level radioactive Waste (HLW) in a deep geological disposal. The reference concept for HLW disposal cells consists of a multi-barrier system: horizontal tunnels of about 0.7 m in diameter drilled in the Callovo Oxfordian (COx) claystone, cased with carbon steel (C-steel) and containing C-steel overpacks with the HLW packages. To neutralize any acidity due to the oxidation of sulphur-containing minerals present in the claystone, a cement-bentonite mixture is injected between the C-steel casing and the geological medium [1]. As the grout should impose alkaline conditions (pH ~10), passivation of C-steel, or, at least, formation of a magnetite protective layer, is expected.

In order to assess the efficiency of the cement-bentonite grout regarding its physical properties, several in-situ experiments were performed at Andra's Underground Research Laboratory (URL). One of them corresponds to a full-scale disposal tunnel, made by A C-steel tube surrounded by a grout in-filling within the clay host rock. To understand the behaviour of carbon steel in this specific grout, samples of the steel-grout interface were taken thanks to a robot capable of coring small samples - about 10 cm length and 2 cm in diameter - from inside a HLW micro-tunnel. Characterizations of the samples with different exposure times (6 months and 1 year) were carried out in order to identify the evolution of the interface. The corrosion products were investigated by µ-Raman spectroscopy and by scanning electron microscopy coupled with energy dispersive X-ray analysis.

For a reaction time of 6 months, the C-steel surface exhibits a calamine layer due to elaboration and tube fabrication. In addition, heterogeneous corrosion is observed, with about 10 % of the surface showing large and deep depressions (up to 170 µm) filled with a mixture of goethite, lepidocrocite, magnetite, and Fe sulfide. In moderately corroded areas, the relatively rough C-steel surface and the calamine layer were overlaid by a crumpled outer layer of Fe(III) hydroxides (goethite, lepidocrocite), siderite, and magnetite. Finally, investigation of the Fe content in the grout in contact with C-steel failed to reveal any significant enrichment or diffusion profile above the intrinsic variability of Fe content of the grout. Results obtained for the sample reacted for one year may help unravel the influence of the residual oxygen on the formation mechanism of the corrosion layer will be discussed.

[1] Michau N, Bourbon X. BOPI. Patent FR3031103(A1), 2014 December 24.