



Corrosion of carbon steel in a specific cement grout in deaerated conditions at 80°C

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In France, it is envisaged to dispose of high and intermediate level long lived radioactive waste at a depth of ~500 m in a deep geological disposal, drilled in a very stiff clay (Callovo-Oxfordian claystone (COx) so called argillites) formation. To do so, a carbon steel casing will be inserted inside disposal cells which are horizontal tunnels drilled in the COx claystone. A specific cement grout (pH ~10) will be injected between the carbon steel casing and the claystone. A maximum temperature of 90°C is expected at the steel surface. The behaviour of carbon steel in contact with this specific cement grout in contact with two different electrolytes was studied during 6 months in deaerated conditions. The first electrolyte simulates the short-term behaviour of the environment and corresponds to the pore water from the cement grout. The second electrolyte simulates the long-term behaviour and corresponds to the pore water of the cement grout finally modified by the COx. These electrolytes have been prepared in deaerated conditions at 25°C according to a specific protocol.

12 carbon steel plates (6 per cell) positioned in a Teflon sample holder were covered with cement grout and remained for 8 weeks in a closed environment deaerated with Ar. After this period, electrolytes 1 and 2 were added to saturation in cells 1 and 2 respectively. The cells were then placed in an oven at 80°C and the test was conducted under anoxic conditions.

For cell 1, the solution used was composed of 10^{-5} M KCl + 0.025 M K_2SO_4 + 0.0002 M $Al_2(SO_4)_3$, $18H_2O$ + 0.008 M $CaSO_4$, $2H_2O$ + 0.0029 M Na_2SiO_3 , $5H_2O$ + 0.0125 M $NaHCO_3$ adjusted at pH = 10.5 ± 0.1 at 50°C with NaOH 1 M. For cell 2, the solution used was composed of 0.0085 M $CaSO_4$, $2H_2O$ + 0.035 M NaCl + 0.0005 M Na_2SO_4 + 0.0017 M Na_2SiO_3 , $5H_2O$ + 0.0008 M $Al_2(SO_4)_3$, $18H_2O$ + 0.0016 M Na_2S with pH = 10 ± 0.1 at 50°C.

At the end of the experiment, visual observations revealed some localized corrosion of the carbon steel plates. μ -Raman spectroscopy and X-ray diffraction analysis of the corrosion products revealed that the corrosion product layer was mainly composed of iron sulphides (greigite and mackinawite). The corrosion rates estimated by mass loss (ASTM G1) were relatively low (5 ± 1 $\mu\text{m}/\text{year}$). This indicates that the corrosion product layer mainly composed of iron sulphides protects efficiently the metal against corrosion. Scanning electron microscopy (SEM) observations showed that components of the cement grout were mainly present in the outer parts of the corrosion product layer and beyond this layer but also in the inner parts, close to the metal. The observed localized corrosion likely results from the heterogeneity of the corrosion product layer composed of iron sulphides and compounds originated from the cement grout.