The Corrosion of Carbon Steel in Simulated Concrete Pore Water under Anoxic Conditions

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This work is focused on the corrosion of carbon steel in simulated concrete pore water to understand and predict the accumulation of corrosion damage to the carbon steel over-pack of the supercontainer for the storage of High Level Nuclear Waste (HLNW) for over 100000 years in Belgium. Multiple carbon steel specimens were prepared and each one was polarized at a different voltage in a deareated solution of saturated $Ca(OH)_2$ + 0.3M NaOH + 0.1M NaCl [pH(25°C) = 13.5] at 80°C for one year. The change of the open circuit potential (OCP) was also monitored by assigning one extra specimen to the open circuit condition. It was observed that the OCP kept drifting in the positive direction within the first 100days before reaching a plateau at around -50mv *vs.* SHE, a very positive value implying significant ennoblement as the passive state on the specimen develops. The current density for each specimen under potentiostatic polarization control was recorded as a function of time, and the results show that the current became stable after 200 days polarization at all voltages. However, the values of the steady state current were found to be negative, indicating that the cathodic reaction (assumed to be water reduction, $2H_2O + 2e^- = H_2(g) + 2OH^-$) was dominant in the system, and thus further analysis of the current data is required to extract the anodic passive current density, in order to obtain the corrosion rate. Mott-Schottky testing showed that the passive film behaves as an n-type semiconductor. Electrochemical impedance spectroscopy (EIS) was employed to investigate the passive states by step-scanning the frequency at each potential from 5000Hz to 0.01Hz and immediately from 0.01Hz back to 5000Hz. Almost a perfect match of the impedance measured at the same frequency in the two scan directions was obtained, which demonstrates good stability of the system, which was also confirmed by Kramers-Kronig transformation. The impedance data was then interpreted in terms of the Point Defect Model (PDM) assuming a bi-layer structure of passive film. The PDM adopted here has been modified by incorporating the cathodic reduction of water, so as to delineate the partial anodic and cathodic processes, which is vital for determining the corrosion rate. The new model successfully yields the passive current density versus voltages for different times as depicted in Figure 1. Thus, it is observed that, as the polarization time is extended, the passive current density drops significantly, due to the gradual development of a more passive state. The passive current density also decreases as the applied voltage rises, which is inconsistent with the prediction for an n-type film of the PDM that the steady state current should be potential-independent, but it is recognized that the potential is so negative that the system is in the active-to-passive transition. As the potential becomes more positive the passive current tends to a voltage-independent value as

required by the PDM for the fully passive state. The corrosion rate was then calculated to be about 2μm/year using the current density data at -370mv *vs.* SHE.
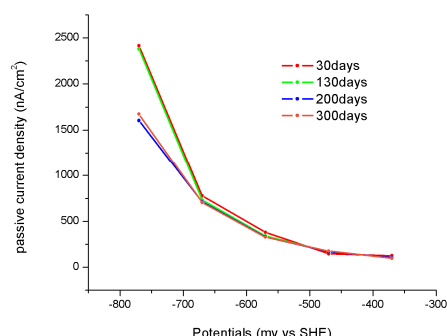
Figure 1. The passive current density versus applied potential during different polarization time for the carbon steel in deareated saturated $Ca(OH)_2$ + 0.3M NaOH + 0.1M NaCl solution at 80°C.