Study of the corrosion of SF/HLW disposal canister materials during the oxic to anoxic transition

**B. Reddy**1, N.R. Smart1, A.P. Rance1, C. Padovani1, N. Diomidis2

1 Wood, HQ Building, Thomson Avenue, Harwell Campus OX11 0GD, United Kingdom.

2Nagra, Hardstrasse 73, Postfach 280, 5430 Wettingen, Switzerland

Corresponding author: nikitas.diomidis@nagra.ch

**ABSTRACT**

In a HLW repository in Opalinus Clay the resaturation of the nearfield with porewater will require approximately 100 years. During this time the disposal canisters will be exposed to an initially warm and oxic environment, which gradually evolves to anoxic at increasing relative humidity. An experimental programme is being conducted to investigate the corrosion of several candidate canister materials, namely carbon steel, and electrodeposited and cold sprayed copper coatings, under such early stage disposal conditions. To study the corrosion behaviour during this period, two types of measurement were carried out.

Long-term open circuit potentials were measured for samples embedded in compacted bentonite and immersed in groundwater during the transition from oxic to anoxic conditions. In addition to the working electrodes made from canister materials, the experiments contained platinum electrodes to provide information about the Eh values during the experiments. Three identical specimen assemblies were immersed in artificial groundwater in a sealed autoclave that was initially purged with 20% oxygen in nitrogen and the long-term rest potentials were recorded for more than two years. The aim of these measurements was to observe how the environmental conditions in the vicinity of the metal samples changed as oxygen was consumed and to monitor how the corrosion product film evolved over time.

The most rapid changes in corrosion potential of the carbon steel and copper electrodes occurred during the first 50-60 hours of exposure, during which consumption of oxygen appeared to be occurring, based on the platinum potentials. The long-term stable corrosion potentials are consistent with the formation of magnetite on the surface of the carbon steel. The corrosion potentials decreased in the order: cold spray copper > electrodeposited copper > wrought copper, although the spread was a maximum of 100 mV.

In a separate set of experiments, metallic coupons were embedded in bentonite and exposed to an oxygenated atmosphere (20% O2 / 80% N2) at various controlled humidities and temperatures, in small sealed glass cells. The corrosion behaviour and average corrosion rate were investigated by conducting weight loss measurements and post-test surface analyses. Thirty-seven tests were set up to enable three different humidity levels (25, 50 and 75%) to be assessed at two temperatures (60 °C, 80 °C) and three different durations. Blank cells containing only compacted bentonite, but no metal coupons, were also set up. The experiments were dismantled and analysed to assess the corrosion of the materials after different experimental durations as the environment progressed from an oxygenated to deoxygenated condition.

Post-test examination of the differential aeration cells showed that the oxygen concentration had reduced significantly after 300 days, even in the blank cell containing bentonite only, suggesting that the bentonite itself also consumed oxygen. Raman spectroscopy of the corrosion product on carbon steel specimens revealed that it was composed predominantly of magnetite, Fe3O4, with some residual FeOOH or Fe2O3 on the pre-corroded carbon steel specimen. For the copper samples, a mixture of Cu(II)O and Cu(I)2O was detected in different areas, with some indications of mixed carbonate-hydroxide (Cu3(CO3)2(OH)2) and oxy-hydroxide (CuO2(OH)4) species, in agreement with literature reports.

This paper will summarise the results obtained to date and discuss the implications of the work for defining the corrosion evolutionary path within a repository.