

Micro-beam analyses of glass and iron corrosion layers in clayey rock.

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Many designs of deep geological disposal concepts propose low alloy steel overpacks and a clayey host-rock. Corrosion of overpacks is therefore a key phenomenon in the performance assessment of radioactive waste disposal as well as the dissolution kinetic of vitrified waste in this near-field. Obviously, the vitrified waste will be affected by the crystal-chemistry of the corrosion products.

A representative model of deep geological disposal has been tested in laboratory scale experiments to elucidate the nature of corrosion products of iron and their impact on glass dissolution kinetics. The experiments of ternary system with glass/iron/clay have been performed in strictly anoxic conditions at 90°C for up to 2 years. Inactive glass coupons were placed in contact with pure iron foil and then raw Callovo-Oxfordian clayey mudstone. Reactive transport (diffusion only) of species and mineralogical changes have been characterised using micrometer spatial resolution probes of chemistry and crystal-chemistry: SEM-EDS, μ -XRF, μ -XRD, μ -Raman spectroscopy, NRA and μ XAS.

The products of iron corrosion are dominated by iron(II) silicates and carbonates. Magnetite is formed in minor amount and located in the zone of the initial iron surface. Solid solution between siderite and calcite precipitated at the interface between clay and iron whereas iron exhibits a diffuse plume in clay correlated to the incorporation of iron into the newly formed iron-rich clay minerals. These product phases are iron-rich smectites or serpentine-like minerals either formed from the reorganisation of initial smectite and illite-smectite swelling layers or from the dissolution of initial quartz and metallic iron. The diffraction patterns also reveal the presence of an amorphous gel phase, an intermediary of the clay transformations.

After the first stage of iron corrosion, the glass has been altered in the corrosion products associated to transformed clay. The altered glass is divided into two layers. An Si-Al-Fe amorphous gel with high porosity is formed in the internal zone. Its thickness is relevant with high dissolution rate and seems not to be passivating. The second layer is composed of crystalline phases including rare-earth elements and calcium, molybdenum and phosphor.

The spatial distribution of mineralogy and elements in this complex system give insights of key transformations that will occur in a disposal and may govern long term behaviour.