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A.M. Fernández, S. Kaufhold, D.M. Sánchez-Ledesma, J.J. Rey, A. Melón, L.M. Robredo, S. Fernández, M.A. Labajo, M.A. Clavero

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Evolution of the THC conditions in the FEBEX *in situ* test after 18 years of experiment: Smectite crystallochemical modifications after interactions of the bentonite with a C-steel heater at 100 °C

Fernández, A.M.⁽¹⁾, Kaufhold⁽²⁾, S., Sánchez-Ledesma, D.M.⁽¹⁾, Rey, J.J.⁽¹⁾, Melón, A.⁽¹⁾, Robredo, L.M.⁽¹⁾, Fernández, S.⁽¹⁾, Labajo, M.A.⁽¹⁾, Clavero, M.A.⁽¹⁾

⁽¹⁾ CIEMAT – Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas.
Dpto. Medio Ambiente. Avda. Complutense 40, 28040 Madrid, Spain.

⁽²⁾ BRG – Bundesanstalt für Geowissenschaften und Rohstoffe, Stilleweg 2, D-30655 Hannover, Germany

Abstract

Chemical and mineralogical investigations of the FEBEX repository demonstration experiment after 18 years confirmed those reactions which were identified in previous large scale tests: Fe-corrosion, Mg-accumulation, cation exchange, and mineral dissolution/precipitation. These reactions were mostly restricted to the bentonite-heater contact. However, other processes were detected. Fe oxidation of carbon-containing steels was dominated by oxidic corrosion and hydrolysis possibly through a similar Fischer-Tropsch synthesis reaction, leading to the monitored gas generation of H₂, CO₂ and both reduced (alkanes, alkenes) and oxidized hydrocarbons (carboxylic acids), which are in partial equilibrium with CO₂/carbonate under oxidation states highly reduced. Therefore, temperature, water, oxygen (due to no gas-tight conditions) and other oxidizing agents regulated the redox state and activities of all species involved in the bentonite barrier, being sulfates reduced to H₂S and pyrite, Fe-oxides (hematite/goethite) to magnetite and siderite, and Fe(III)-bearing smectite to saponite and chlorite. These mineral phases were detected as main corrosion products. The dissolved Fe²⁺ ions generated by reduction of Fe-oxides diffused away forming surrounding greenish halos in the bentonite. Because air was not excluded, most of the corrosion was oxidic but locally reducing conditions were established.

Significant Mg accumulation was observed at the heater contact, which is related with the highest salinity values of the porewater (Na-Mg-Ca-Cl water-type, 0.41 M ionic strength), the presence of saponite (trioctahedral Mg-smectite), brucite, a Fe-rich chlorite, and a modification in the dehydroxylation temperature of clay mineral particles, together with the precipitation of carbonates and an increase of Ca/Mg at interlayer sites, Na being depleted.

The mechanism for the structural clay mineral alteration seems to be Fe(III) structural reduction, rather than the C-steel heater/liner corrosion. Because Fe²⁺ cations are more stable in trans octahedral sites, rearrangements in crystal lattice seem to have formed cis-trans interstratifications favouring the migration of Mg to octahedral sites and the segregation of Mg²⁺ trioctahedral domains. Thus, both a solid-state transformation, producing high-charge/low charge layers similar to vermiculite ones; as well as dissolution-precipitation transformation, with the crystallization of a trioctahedral Mg-smectite (saponite), brucite and chlorite in localized zones of the bentonite barrier, seem to be inferred, depending probably on $f(\text{O}_2)$, temperature, the amount of structural Fe(II) and Mg concentration in the pore water.

The observed clay mineral transformations induced changes in some of the physico-chemical properties of the bentonite, decreasing the total cation exchange capacity and BET surface area. However, these modifications were restricted to the bentonite at close contact with the heater. The rest of bentonite from the FEBEX *in situ* test maintained its performance as an engineered barrier.

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