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**Experimental study of iron-clay interactions.**

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Bentonites are envisaged for engineering barriers in geological disposal facilities of high-level nuclear wastes. Different concepts foresee emplacing steel containers in tunnels backfilled with compacted bentonite [1]. Bentonites are recommended because of their swelling capacity, their low hydraulic conductivity when compacted to high density and their high sorption capacity. If natural occurrence of old bentonites is an indication of their long-term stability, the very specific conditions of high-level nuclear wastes repository sites has to be taken into account, particularly the temperature increase, fluids percolation and the eventual presence of available iron. Thus, interactions between the bentonite and the container corrosion products in the presence of fluids are of particular interest. The key problem is the stability of swelling minerals and the permanence of their mechanical, hydraulic and geochemical properties. Experiments have been conducted with the MX80 bentonite (Wyoming). We experienced different parameters to test their influence on the stability of the smectite; various temperatures (80 to 300 °C) fluid compositions (low-salinity sodi-calcic to alkaline solutions with pH ranging from 5 to 13) and liquid-clay ratios (ranging from 5 to 50) in the presence of metallic iron and/or iron oxides to provide a source of available Fe and simulate various redox conditions. Clay minerals of the experimental samples were characterised by their structural (X-Ray diffraction, scanning electron microscopy and high-resolution transmission electron microscopy) and chemical properties (cation exchange capacity, transmission mössbauer spectroscopy, electron energy-loss spectroscopy and energy dispersive spectroscopy). These experiments show different transformations of the montmorillonite as a function of the experimental parameters. In the presence of metallic iron, montmorillonite transforms to Fe-chlorite at 300°C [2] and to berthierine at 80°C. In the presence of iron oxides, montmorillonite partly transforms to tri-octahedral smectite (saponite) and this transformation is enhanced at higher temperature [3]. In the presence of alkaline solution, montmorillonite partly transforms to tri-octahedral clay (saponite and/or vermiculite) enriched in Fe and Mg. All these transformations are accompanied by the formation of zeolites. Results have been compared to thermodynamical modelling.

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**Synthetic routes and crystallographic and thermal study of the microporous titanosilicate ETS10.**

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Within the silicon-based microporous materials, titanosilicates are comparatively less studied systems characterized by a zeolite-like  $[\text{SiO}_2]_\infty$  framework interwoven with  $[\text{TiO}_3]_\infty$  chains, where Ti is octahedrally coordinated. We present here some results on ETS10, which has chemical formula  $(\text{Na}_{1.5}\text{K}_{0.5})\text{TiSi}_5\text{O}_{13}\cdot x\text{H}_2\text{O}$ , and is characterized by a disordered mixture of two polymorphs with tetragonal and monoclinic symmetry [1], giving rise to a system of channels defined by 12-atoms rings. ETS10 is structurally related to another titanosilicate, ETS4, synthetic analogue of the mineral zorite. Samples of ETS10 were prepared according to the traditional method based on the  $\text{TiCl}_3$  precursor, and also following a synthetic route employing  $\text{TiO}_2$  as initial titanium source. In both cases, the synthesis was carried out in hydrothermal vessels at 230 °C, with carefully controlled pH and gel formation from the sodium silicate solution. The samples obtained were studied by SEM, TGA-DTA and X-ray powder diffraction techniques. The X-ray powder pattern is consistent with the simulation obtained by the DIFFAX programme [2], on the basis of a completely disordered stacking sequence of the monoclinic and tetragonal polymorphs. However, the sample prepared by the  $\text{TiO}_2$  route is much better crystallized than the other one, according to diffraction intensities and peak widths. This is confirmed also by SEM images, which show crystallites with larger size in the former case. The thermal study revealed a weight loss of about 12% below 500 °C, corresponding to the dehydration process. A fraction of water was regained reversibly on cooling, so that a part of  $\text{H}_2\text{O}$  only appears to be strongly bonded inside the channels. On further heating, ETS10 decomposes at 750 °C into a mixture of phases, which were identified by X-ray diffraction to be quartz and narsarsukite ( $\text{NaTiSi}_4\text{O}_{11}$ ).

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