

MINERALOGY OF THE A2 TEST PARCEL BENTONITE LOT PROJECT AT ÄSPÖ HRL

Siv Olsson, Ola Karnland*

Clay Technology, Lund, Sweden

The ongoing LOT test series at the Äspö Hard Rock Laboratory in Sweden is focused on quantifying the mineralogical alteration in the buffer in a repository-like environment. The LOT A2 test parcel was exposed to temperatures up to 130°C for almost 6 years. The parcel was retrieved in 2006 and the bentonite has thereafter been analyzed and tested. The chemical and mineralogical characteristics of bentonite from defined positions in the parcel were compared with reference materials. The aim of the study was to elucidate how the bentonite has altered. The present study concern two bentonite blocks from the hottest section and one block from the cool section of the test parcel.

The entire volume of the two warm blocks 09 and 11 was exposed to temperatures > 80°C, and the innermost 4 centimeters to temperatures exceeding 100°C. Block no. 33 was never exposed to temperatures exceeding 30°C, apart from the innermost centimeter. The blocks were sampled contiguously at five positions along the radius from the warm copper tube to the rock. Both the bulk material and the clay fraction of the bentonite samples have been analyzed. The chemical composition of the reference and the parcel bentonite was determined by ICP emission spectrometry (AES) and ICP mass spectrometry (MS). Total carbon and sulfur were determined by evolved gas analysis (EGA). Carbonate carbon was determined as CO₂ evolved on treatment with hot 15% HCl. Prior to the chemical analysis of the clay fractions, carbonates were removed by treatment with an acetic acid-sodium acetate buffer with pH 5. The purified clay was thereafter converted to homo-ionic Na-clay by repeated washings with 1 M NaCl solution and excess salts were removed by repeated centrifuge-washing with water followed by dialysis. The cation exchange capacity (CEC) of bulk materials and of clay fractions was determined by exchange with copper-(II)-triethylene-tetramine following the procedure of Meier & Kahr (1999), modified according to Ammann *et al.* (2005) to ensure complete exchange. The exchangeable cations of the bulk bentonite were also extracted into alcoholic ammonium chloride solution (Belyayeva, 1967, Jackson, 1975). An alcoholic solution was used to minimize dissolution of gypsum and calcite. The mineralogical composition was determined by X-ray diffraction analysis of two different types of preparations, one type consisting of unsorted and randomly oriented powders of the bulk materials, the other type consisting of aggregates with maximized preferred orientation of the clay minerals.

The chemical and mineralogical investigation of the bentonite of the warm blocks 09, 11 and the cold block 33 from the LOT A2 parcel indicates that:

- *Cu has been incorporated in the bentonite matrix proximal (0-2 cm) to the Cu-tube in all blocks. The heated blocks have higher concentrations with a maximum of ~ 0.5% Cu in the mm-thick contact zone. A comparison of the results of the 5-year A2 test with those of the short term LOT A0 test suggests that the rate of copper mobilization/incorporation is not linearly related to the duration of the test conditions but seems to have proceeded at a higher rate during an early stage of the test. The Cu concentration of the clay fractions was 20-30% of that of the corresponding bulk samples, which suggests that the major fraction of Cu is not incorporated in the structure of the montmorillonite.*
- *Sulfates have been redistributed along the thermal gradient in the heated blocks. Anhydrite has accumulated approximately 3-5 cm from the heater, whereas the peripheral parts of the blocks are depleted in sulfates.*
- *The carbonate content decreased with increasing temperature in the heated blocks.*
- *Dissolution/precipitation reactions involving sulfates and carbonates of calcium have influenced the pore water composition and, consequently, the pool of exchangeable cations. Accordingly, some exchangeable sodium has been replaced by calcium in the inner parts of the heated blocks.*

- *Exchangeable Mg increases* with increasing temperature in the heated blocks. The trend is paralleled by an increase in the content of non-exchangeable Mg of the clay (Na-saturated fraction < 2 μm).
- *The proportion between exchangeable and non-exchangeable interlayer cations (the equivalent ratio $(\text{Ca}+\text{Na})/\text{K}$) has increased* in samples adjacent to the Cu-tube in the heated blocks, i.e. no relative K fixation has taken place.
- *CEC of the bulk samples and of the clay fractions tends to increase* towards the Cu-tube in the heated blocks. The changes in CEC were, however, close to the analytical resolution (Figure).
- The available XRD-data provide *no evidence of a structural change of the montmorillonite*. Both the expansion behavior, a complete, periodic diffraction pattern of the basal reflections and the *b* cell dimension of the clay mineral from the parcel are typical of montmorillonite and similar to that of the reference material. Thus, the changes found in the chemical composition and in the cation exchange properties of the clay mineral do not manifest themselves in the X-ray diffraction characteristics of the clay mineral.

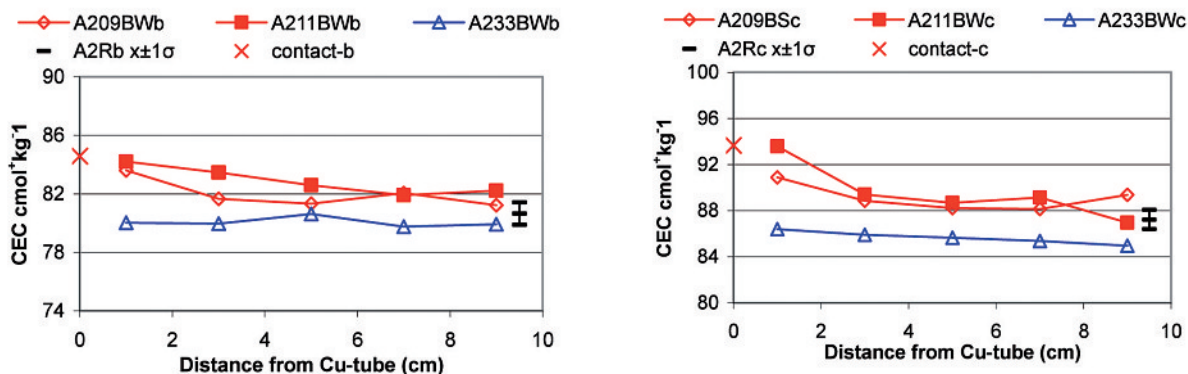


Figure 1: Plot of the CEC of bulk samples (left) and of clay fractions (right) versus radial distance for blocks 09, 11 and 33 of the LOT A2 parcel. Values from five reference samples are shown at position 9.5 cm as the mean \pm 1 standard deviation.

References:

- Ammann, L., Bergaya, F., Lagaly, G., 2005. Determination of the cation exchange capacity of clays with copper complexes revisited. *Clay Minerals* 40, 441-453.
- Belyayeva, N.I., 1967. Rapid method for the simultaneous determination of the exchange capacity and content of exchangeable cations in solonetzic soils. *Soviet Soil Science*, 1409-1413.
- Meier, L.P., Kahr, G., 1999. Determination of the cation exchange capacity (CEC) of clay minerals using the complexes of copper(II) ion with triethylenetetraamine and tetraethylenepentamine. *Clays and Clay Minerals* 47, 386-388.