Diffuse transport in clay media: μm to nm scale characterization of pore space and mineral spatial organization

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In the framework of radioactive waste repository, clayrock formations are foreseen as barrier materials due to their diffusion properties. In clay materials, the dominant transport mode is diffusive and depends mainly on various parameters such as the mobility of the species in water, the accessible porosity, the pore space geometry and the retardation as a result of reactions such as sorption or ion exchange (Tournassat and Appelo, 2011). In this way, the European CATCLAY project (EURATOM FP7), in the context with research on transport in porous materials, was proposed to describe the cation migration processes in natural clayrocks. The project is structured along 3 RTD workpackages, combining modeling and experimental studies from a simpler, analogous system (monophasic compacted clay system) to clayrocks (Callovo-Oxfordian argillites, Opalinus Clay and Boom Clay). Part of this experimental studies focuses on small scale structure (µm – nm) property of rocks in order to determine how the spatial distribution of mineral and pores at small scales can influence diffusion driven transport of sorbing cations. The present study focuses on compacted illite properties (simpler analogous system) in hopes to extent this study to the natural clayrock formation. Illite was chosen by the way that is the main constituent of clayrock. Compacted illite material represents thus an analogy with the clay matrix constituting clay-rocks. Our approach is mainly based on imaging the small scale structural organization of compacted illite material and analyzing the obtained images in order to extract information on pore space and mineral spatial distribution.

Techniques for imaging the texture of illite material like water saturated, in compacted state, were first developed. The first step was to improve classic resin impregnation method in order to preserve the texture without losing the clay confinement and modifying the pore space geometry. This has been done by taking into account the molecule size of the monomer, the low viscosity, the dipole moment (adapted for the clayrock with swelling clay content) and the controlled time polymerization. MMA monomer proved to be the most suitable resin in our study. The small scale structure of impregnated sample was then imaged in 2D using Transmission Electron Microscopy (TEM) and in 3D using Focused Ion Beam coupled to Scanning Electron Microscopy (FIB/SEM). For TEM observations, a set of ultra-thin serial sections (50 - 100 nm) were cut using a microtome. A set of 2D images were then acquired using a resolution ranged between 100 nm and 10 Å. TEM images clearly show us the multi-scale organization of clay materials (Figure 1 and 2); we observe the 10 Å spacing sheets constituting the illite particles, nanometer size illite clay particles more or less aggregated and the surrounding pores having a size ranging from few hundred nanometers to nanometer.

FIB/SEM analysis is currently in progress. From FIB/SEM, a set of serial images can be acquired using the “slice and view” method (Keller et al., 2011). Then, 2D FIB/SEM images need to be aligned to reconstruct a 3D volume. Image resolution is limited to 10-20 nm. Both methodologies (FIB-tomography and TEM techniques) are thus complementary method for the up-scaling characterization of the structural organization of compacted clayey materials. TEM images analysis allow to scale down the resolution size since only a part of the pore space could thus be imaged with FIB/SEM method (Keller et al., 2011).

Viewing and performing a qualitative description of images constitute a major result and can help us to better understand how the transfer pathways and retention sites are organized in the porous media. Thanks to image analysis method, pores and minerals can be thresholded from grey level TEM and

FIB/SEM images. Quantitative parameters can be then computed based from segmented images. In this objective, we currently focus our analysis in order to determine the size and the morphology of pores, the main geometrical features of clay particles (number of layers, size, shape…), the spatial distribution of clay particles (individual/aggregates, type of contact between the clay particles, orientation…) and the pores connectivity. Quantitative parameters are expected to be used in various transfer modeling approaches. This will be done in the framework of SIMISOL project which is focused on the modeling cation diffusion from atomic to nanometer scales.

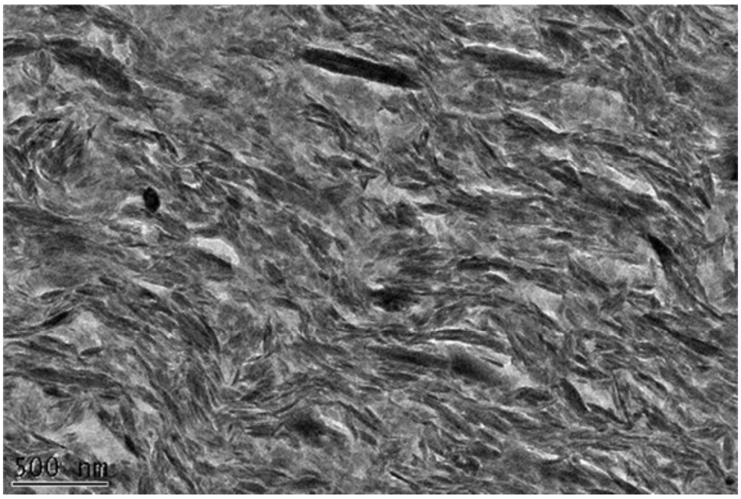

Figure 1. TEM image of compacted illite (ρ_d = 1.7 g/cm^3). Spatial distribution of clay particles at nm scale.

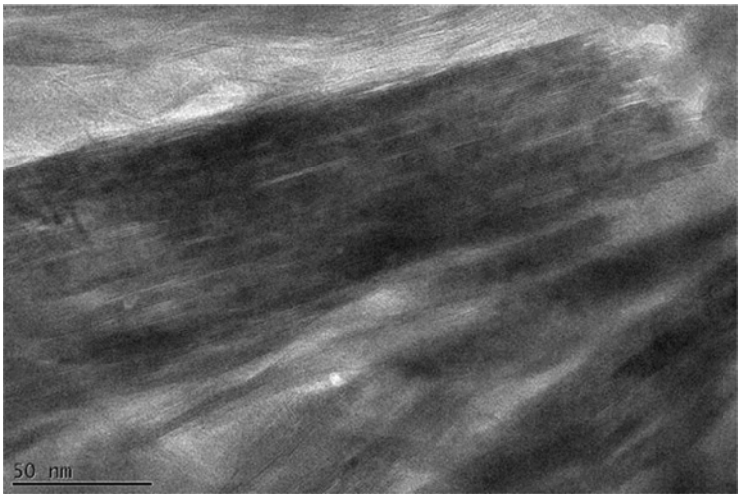

Figure 2. TEM image of compacted illite (ρ_d = 1.7 g/cm^3). Aggregate of illite particles showing planar contact

References

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