

# SIMULATION OF THE LONG TERM ALTERATION OF CLAY MINERALS IN ENGINEERED BENTONITE BARRIERS: NUCLEATION AND GROWTH OF SECONDARY CLAY PARTICLES

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The long term stability of clay rich rocks used as barriers to the migration of radionuclides in the environment of nuclear wastes has been intensively studied, looking at the geochemical interactions between clay minerals and aqueous solutions. These studies combine experimental approaches for the short term and numerical modellings for the long term extrapolations, in the frame of the research supported by ANDRA in the French design for High Level Waste (HLW) repository.

## GEOCHEMICAL MODELLING COUPLING TRANSPORT, DIFFUSION AND REACTIONS

The main objective of the geochemical numerical tools devoted to clay-solutions interaction processes (Marty *et al.*, 2009) was to predict the feed-back effects of mineralogical and chemical transformations of clay mineral, in repository conditions as defined by Andra (2005), on their physical and transport properties (porosity, molecular diffusion, permeability). The 1D transport-reaction coupled simulation was done using the code KIRMAT (Gérard *et al.*, 1998), at 100°C for 100000 years. The fluid considered is that of the Callovo-Oxfordian geological formation (COX) and assumed to diffuse into the clay barrier from one side. On the other side, ferrous iron, is provided by the steel overpack corrosion. Under these conditions, montmorillonite of the clay barrier is only partially transformed into illite, chlorite, and saponite (Marty *et al.*, 2009). The simulation shows that only outer parts of the clay barrier is significantly modified, mainly at the interface with the geological environment. These modifications correspond to a closure of the porosity, followed by a decrease of mass transport by molecular diffusion. Near the COX, the swelling pressure of the clays from the barrier is predicted to decrease, but in its major part, the engineered barrier seems to keep its initial physical properties (porosity, molecular diffusion, permeability, swelling pressure).

## A FIRST IMPORTANT EXTENSION OF THE MODELLING TO THE PRECIPITATION KINETICS OF CLAY MINERALS

In this modelling approach, the very important role of secondary clay minerals has to be taken into account with relevant kinetic rate laws; particularly with elevated temperature. Thermodynamic effects are then combined with solubility products and kinetic effects on nucleation and growth of precipitated particles. It is a real challenge for geochemists to be able to account for precipitation kinetics in water-rock interaction models, particularly considering systems on short to mid terms ( $\times 1000$  y) compared to geological timescales. The recently developed code NANOKIN (Fritz *et al.*, 2009) models dissolution processes of primary minerals as well as the kinetics of precipitation of secondary minerals taking into account the first steps of nucleation and growth and the subsequent evolution of the classes of particles precipitated. With these modellings the predicted evolution of the clay phase gives information on the crystal size distribution of secondary particles precipitated as a function of time. The model also examines the state of the aqueous solution with various mineral phases and combines the classical theory of crystal nucleation with size and morphology dependent kinetic rate laws for growth and/or dissolution of particles i.e. Oswald ripening processes.

## A SECOND EXTENSION OF THESE MODELLINGS TO ACCOUNT FOR CATIONIC EXCHANGE IN THE NUCLEATION AND MINERAL GROWTH

Ion exchange in mineral phases, and particularly in clay minerals has to be considered as a possible geochemical process taking place in clay barriers under storage conditions. This process might control first the transfer or the fixation of the major cations present in aqueous solutions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  mainly but also  $\text{H}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ) but also radionuclide's cations if they might diffuse in the barriers after corrosion of the canisters on long term. When one considers this process from the simulation point of view, the challenge is not so easy. The same simulation has to combine kinetic processes with largely different time scales: near equilibrium cationic exchange reactions, which can be considered as quasi-instantaneous, and clay mineral precipitation which occurs on longer term in oversaturation state with respect to the solution. We have extended the code NANOKIN (Noguera *et al.*, 2009), in order to account for these ionic exchange processes. The approach is very similar to that used for the precipitation of solid solutions (Noguera *et al.*, 2010), except for time dependence of the cation fraction in the solid phase, which is assumed to be in equilibrium with the instantaneous state of the aqueous solution. With this extension, the code NANOKIN is able to simulate the formation of clay phases, by combining nucleation and growth in the oversaturation domain, together with cation exchange inside the newly formed particles.

## APPLICATION TO THE PREDICTION OF POSSIBLE CLAY MINERALS TRANSFORMATION

Illite-type clay is systematically predicted as a possible product of the partial transformation of montmorillonite-type minerals. The extension of this illitization remains however limited. We present new results of montmorillonite to illite transformations in storage like conditions using the code NANOKIN. The model provides a prediction of the nucleation and growth of illite among other secondary minerals and of the time dependent evolution of crystal size distribution of these clay minerals.

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