COUPLED TRANSPORT AND CHEMISTRY IN CLAY STONE STUDIED BY ADVECTIVE DISPLACEMENT: EXPERIMENTS AND MODEL

C. Landesman[1]*, B. Grambow[1], C. Bailly[1], S. Ribet[1], K. Perrigaud[1], V. Baty[1] and E. Giffaut[2]

1. SUBATECH, Unité Mixte de Recherche 6457, École des Mines de Nantes, CNRS/IN2P3, Université de Nantes, BP 20722, 44307 Nantes cedex 3 France, 2) ANDRA, Parc de la Croix Blanche, 1/7 rue Jean Monnet, 92298 Châtenay-Malabry, France (catherine.landesman@subatech.in2p3.fr)

For assessing the mass transfer resistance of the Callovo-Oxfordien clay rock formation in case of implementing a nuclear waste repository, various strongly coupled processes need to be understood and quantified both in near and far field: multi-species diffusion/advection, mineral/pore water interaction, interaction with the waste matrix and engineered barrier material, radionuclide retention, colloid transport, pore water chemistry evolution etc. To study many of these processes in their interrelationship simultaneously, a series of high pressure stainless steel advection cell was designed and clay cores from different locations of different calcite and clay contents were machined to fit the inner diameter of the cells with a precision of 50µm. After assembling, simulated oxygen free clay pore water with bromine tracer was pushed by a High Pressure pump through the reactor by a pressure of up 100 bars at temperatures between 20 and 90°C and the out-flowing water was collected, protected from air and analyzed by ICP-MS, COT meter and ion chromatography in regular time intervals. The water flow rate was between 0.02 and 1.2 mL/d, corresponding to a clay rock permeabilities between 10^{-12} and 10^{-14} m/s at 25°C. Permeabilities increase with temperature as expected due to reduction of viscosity of water. The experiments last up to 2 years. The first drops of out flowing allow estimating the initial pore water composition. This is particular useful to assess mobile natural organic matter contents, Se concentrations and temperature effect on clay water composition. Results show that only very small organic molecules are mobile. Temperature had only little effect on water composition. After few months both tritiated (HTO) water and ^{36}Cl were added and from the evolution of the activities in the out flowing water dispersion coefficients and accessible porosity relations for anions and neutral species are determined. Strong effects of clay/calcite ratios on hydrodynamic properties were observed. Thereafter stable iodine and Se(VI) were injected to study radionuclide migration. No retention of iodine but strong retention of Se were observed. After test termination the clay core was sliced and elemental profiles were obtained. From anion analysis in the slices porosity distribution was obtained.

The experimental results were modeled using a 1D coupled geochemical/transport code Phreeqc considering activity coefficients, electrical double layers, mineral solubility, ion exchange properties, transport in micropores linked to interlayer space, limited mineral inventories (Celestite) and hydrodynamic properties. Good agreement of model and data from out flowing water and slices was obtained simultaneously for anions, HTO, major (Na, K, Ca, Mg, Cl, SO_4) and minor (Sr) element concentration and pH evolution.