Precipitation of slow kinetics (Barite) and fast kinetics (Gypsum) minerals in natural-compacted porous media

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Several countries have proposed to confine their radioactive waste in deep geological facilities based upon a multi-barrier system. In France, Switzerland and Belgium, argillaceous formations are considered as a potential host-rock for such facilities as they display very good containment properties, *i.e.* high retention capacity and very low permeability. However, the anthropogenic materials (*e.g.* waste, steel, concrete, *etc…*) are out of equilibrium regarding the *in situ* physicochemical conditions and thus they can react with the natural medium. For instance, large amount of soluble salts contained in some radioactive wastes are expected to be leached, generating a saline plume towards the natural medium. The presence of saline plume may enhance some physicochemical reactions such as dissolution/precipitation. In this situation, these reactions may alter the host-rock containment properties and therefore alter transport properties of some radionuclides. Thus, the evolution of rock containment properties due to mineral dissolution/precipitation needs to be envisaged for geologic time and space scale. Such impacts can be estimated at lab scale, which can be further extrapolated for larger time and space scales using chemistry transport codes.

But, prior to such long term simulations, it is essential to test the robustness of the physical and empirical laws used in these codes to reproduce mineral precipitation impact on total porosity of studied porous sample and on subsequent tracer diffusivity. However, these claystones are composed of diversified minerals and very low accessible porosity (of size few nanometers). The clayey minerals present in these claystones possess strong negative charge due to which there is sorption of cations, and anion exclusion through pore network. Thus for claystones it is complex to derive interpretable mineral precipitation impacts on total porosity and tracer diffusivity. For this reason in first step, mineral precipitation was studied on simple material chalk which is composed of calcite with presence of cocolithos adding heterogeneities into the system. Moreover, as chalk pores have neutral surface, there is no alteration in cationic and anionic diffusion making it a system with limited degrees of freedom. In our study, mineral precipitation was carried out by two extremities of sulfate alkali family: sparingly soluble barite of slow kinetics and fairly soluble gypsum of fast kinetics. The precipitation of these minerals in chalk and their subsequent impact on tracer diffusivity was carried out using a classical through diffusion setup. At the end of experiment, barite and gypsum precipitated samples were subjected to post-mortem imaging using: X-ray micro-tomography (µCT) and Scanning Electron Microscopy (SEM). These imaging techniques allowed us to determine the distribution and morphology of mineral precipitates in chalk matrix.

The lab-scale chalk results were finally reproduced by means of 1D and CrunchTope simulations. At the end of simulations, the experimental and numerical results would be compared to assess two important parameters: (i) can codes reproduce precipitation impact on porosity for simple chalk system and (ii) can codes reproduce the precipitation impact on diffusivity? The assessment of both of these parameters would hence determine the robustness of these codes for simple systems. In addition to this, quasi 2D simulations were also carried out under a heterogeneous porosity field to determine the impact of such porosity field on numerical evolution of barite and gypsum. In addition to chalk, we are also studying barite and gypsum precipitation in compacted kaolinite and cesium-illite clayey materials. Kaolinite has low negative surface charge with pore size close to claystones. Cesium-illite, in our study is a modeled material with higher anionic exclusion and cationic sorption compared kaolinite and pore size smaller than kaolinite case. This second part of our study will thus demonstrate whether if barite and gypsum will precipitate in similar fashion as me move from simple material as chalk until complex material as illite.