Nuclear glass/iron/claystone interactions: a study relying on multi-scale characterizations and geochemical modeling

A Delanoë, C Carrière, P Dillmann, D Neff, O Bildstein, J-E Lartigue, C Martin, S Gin

Nuclear glass/iron/claystone interactions: a study relying on multi-scale characterizations and geochemical modeling

A. Delanoë[1*], C. Carrière[1], P. Dillmann[1], D. Neff[1], O. Bildstein[2], J-E. Lartigue[2], C. Martin[3], S. Gin[4]

[1] LAPA NIMBE-IRAMAT, CEA, CNRS, Université Paris-Saclay, 91191, Gif-sur-Yvette, France,
[2] CEA-DES-IRESNE-DTN, Saint-Paul-les-Durance, F-13108, France,
[3] Andra, Recherche et Développement, 92298 Châtenay-Malabry, France,
[4] CEA, DES-ISAS, DE2D, SEVT, Bagnols-sur-Ceze F-30207, France
*alexis.delanoe@cea.fr

In France, deep geological repository is considered as the reference case to dispose of high-level wastes. The stainless steel canisters filled up with vitrified High-level wastes would be stored inside disposals cells dug into the Callovo-Oxfordian claystone host rock. The study of waste packages alteration by groundwaters on multiseculars durations is essential to predict the release of radionuclides into the geosphere. After the claystone saturation, the canisters could be corroded and fractured releasing iron, and the glass would be altered by a Fe-containing solution.

An experimental set-up was developed to investigate the interactions between the mains materials involved in a geological repository (glass, iron and claystone): two SON68 borosilicate glasses coupons were put in the vicinity of an iron piece, inserted inside Callovo-Oxfordian claystone cylinder (as shown on the Figure 1). The materials were saturated with synthetic carbonated groundwater, in equilibrium with the claystone. One of the glass coupon was doped with ^{29}Si and ^{57}Fe to monitor the behaviour of these two elements into the materials. Two identical mockups were prepared and run in parallel, in anoxic conditions, 50°C, and for two durations: 2.5 years [1] and 6.1 years. Post-mortem solids analysis were performed to investigate the glasses alterations layers and the iron corrosions products (SEM, Raman spectroscopy, ToF-SIMS, HRTEM and STXM with synchrotron).

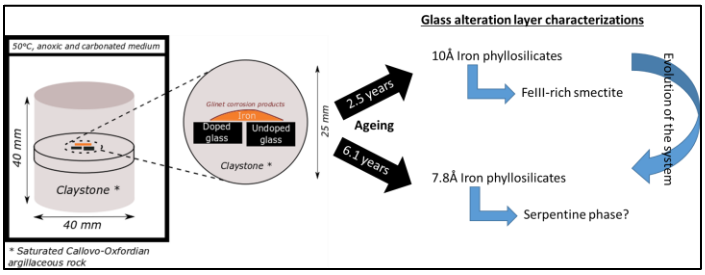

Figure 1. Experimental mockup with the main characterizations

Neoformed iron phyllosilicates are identified in both experiments with HRTEM and STXM. They prevent the formation of a $SiO_{2(am)}$ passivating layer on the glass surface. Regarding to the glass alterations rates, the alteration remains high after 6.1 years ($r_0/4$), far from the residual rate ($r_0/1550$) expected for the passivating layer (r_0 represents the initial alteration rate at 50°C). Nevertheless, it is noticed that the phyllosilicates structure is different between the two experiments: 10Å-phases and 7.8Å-phases are observed after 2.5 and 6.1 years of alteration, respectively. Furthermore, their Iron oxidation state differs too: 90% Fe^{III} and 70% Fe^{III} afters 2.5 and 6.1 years, respectively, according to STXM characterizations. These results stress the importance of understanding the effects aqueous keys parameters such as pH, [Si], [Fe] on the evolution of the materials. For that, a modeling approach is under development. Reactive transport simulations are performed using Hytec and Crunch codes in order to reproduce the observed paragenesis and the geochemical evolution of the experimental systems. Preliminary 1D geometry results of the glass/iron interface indicated that claystone could not be excluded. 2D geometry modelling is required.

References

[1] C. Carrière and al. *NPJ Materials Degradation*, *5,* 2021. (The fate of Si and Fe while nuclear glass alters with steel and clay)