Glass-Iron-Claystone interactions: a study relying on characterizations and geochemical modeling

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500 words

Carbon steel containers session

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In France, Andra considers to dispose High-level waste in deep geological repository. The concept rely on disposal cells dug into the Callovo-Oxfordian claystone, where stainless steel canisters filled up with vitrified borosilicate glass would be disposed. Understanding the waste forms degradation in contact with groundwater is crucial to assess the release of radionuclides in the geosphere. Canisters corrosion would release iron into the groundwater, and therefore the Fe-containing solution would alters the glass.

The purpose of this work is to investigate the glass-iron-claystone interactions in conditions close to that expected in a geological repository. A mockup experiment composed of two SON68 glass coupons (one of them doped with ^{57}Fe and ^{29}Si) in contact with an iron piece surrounded by a Callovo-Oxfordian claystone cylinder was setup. The claystone was saturated with synthetic groundwater, under anoxic atmosphere. Two identical mockups were prepared and run in parallel at 50°C for 2.5 [1] and 6.1 years, respectively.

Post-mortem multi-scale characterizations were performed on the samples. They rely on SEM, EDS, Raman spectroscopy, LA-ICP-MS, Tof-SIMS, HRTEM, and STXM to identify the phases, investigate the corrosion products and alteration layers, and discuss the underlying mechanisms.

The release of Fe and Si into the groundwater lead to the formation of iron phyllosilicates into the glass alteration layer and iron corrosion products. Their precipitation on the glass surface prevents the formation of an amorphous silica passivating layer, keeping high glass alteration rates (around $r_0/4$, where r_0 represents the initial dissolution rate of the glass) which is far from the residual rate ($r_0/1550$). Interestingly, two types of phyllosilicates were characterized in the iron corrosion products and the glass alteration layer: 10.4Å-phyllosilicates and 7.8Å-phyllosilicates, after 2.5 and 6.1 years respectively. These results suggest an evolution of the system between the two mockup. Aqueous parameters (pH, [Si], [Fe], …) might play a relevant role on phyllosilicates formation, glass alteration and iron corrosion. A modeling approach is under developement using Hytec and Crunch reactive transport codes to reproduce the phenomena observed and the geochemical evolution of the mockup.

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