INFLUENCE OF THE ALTERATION LAYER MORPHOLOGY ON THE SILICATE GLASS CORROSION MECHANISMS: ROLE OF CA AND ZR

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This study investigates the long term behavior of glasses used for confinement of nuclear wastes. The results have been obtained from a fruitful collaboration between different CEA laboratories (LLB, LIONS, CEA Marcoule) and the Ecole Polytechnique. The corrosion process of the glasses by water creates at the glass surfaces, an alteration porous layer, hydrated and amorphous, called "gel". This gel, which is the result of the release of soluble elements, of hydrolyses and of silica network recondensation can in specific conditions strongly limit the exchange process between the glass and the solution. Our hypothesis to describe this phenomenon is the closure of the gel porosity.

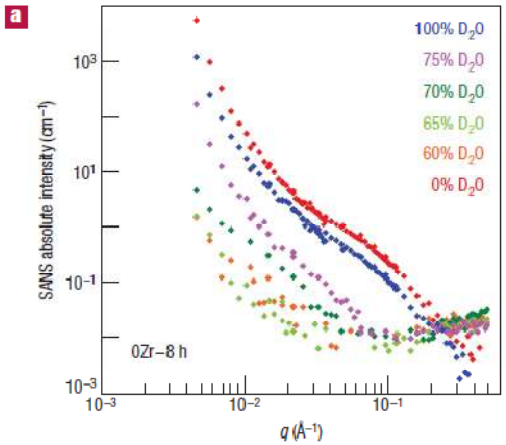

Fig. 1: Scattered intensity (SANS) for different isotopic mixtures for the sample without Zircon (0Zr) after 8 hours of alteration (a), after two months;

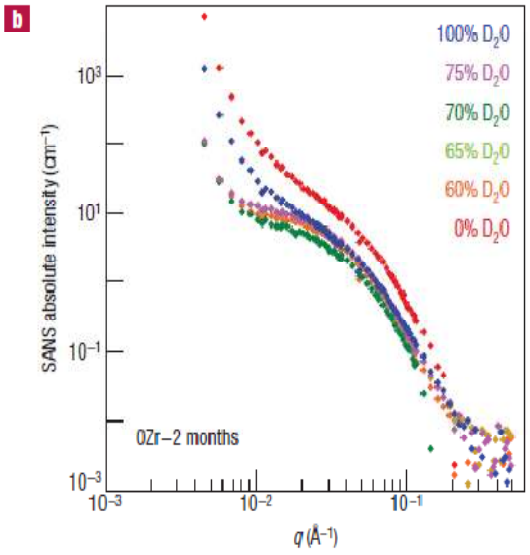

Fig. 1: Scattered intensity (SANS) for different isotopic mixtures for the sample without Zircon (0Zr) after 8 hours of alteration for the sample containing 4% of Zircon (4Zr) after leaching 2 months;

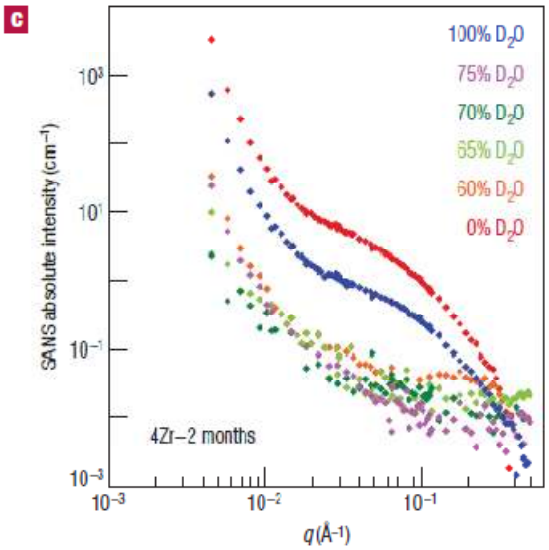

Fig. 1: Scattered intensity (SANS) for different isotopic mixtures for the sample without Zircon (0Zr) after 8 hours of alteration (a), after two months (b), for the sample containing 4% of Zircon (4Zr) after leaching 2 months (c). The residual signal observed on figure (b) for the « matching » composition (70%D2O) illustrates the existence of the closed porosity.

We present an original approach of the corrosion of silicate glasses, usually describe in term of chemical thermodynamic, and based on the influence of the morphological modifications of the gel on the slowing down of the kinetic of dissolution. The studied glasses are of composition of SiO_2-B_2O_3-Na_2O-CaO-ZrO_2. These elements constitute the different species present in nuclear glasses which can be classed according to their reactivity with water: soluble (B, Na), partially soluble (Si, Ca) and less soluble (Zr). We have been interested in the specific effects of Calcium and of Zirconium on the kinetic of alteration. We have observed that substituted the Calcium by the sodium improves the reticulation of the glass network to finally gives a decrease of the alteration rate. Regarding Zirconium, the increase of Zr-content decreases strongly the initial dissolution rate, which was expected, but increases paradoxically the degree of glass corrosion. Conversely, the increase of pH increases the initial dissolution rate but decrease the corrosion. To explain this surprising effect, the morphology of gels has been probed by Small Angles X-ray Scattering (SAXS).

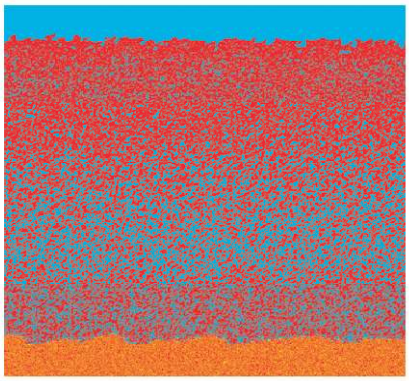

Fig. 2: Monte Carlo simulation of the altered gel without Zirconium (0Zr). The silicon atoms are shown in red, other element in yellow, water in blue.

These experiments have highlighted the reorganization of the porous network of the gel during the alteration and show that this reorganization is limited by the increase of the Zr-content. This suggests that this is the restructuration of the gel which is at the origin of the blockage of the alteration observed with the glass containing low Zr-content. This hypothesis has been successfully confirmed by Small Angle Neutron Scattering (SANS) according to an original application of the contrast matching method. Measurements for various solvent compositions (H_2O-D_2O) have showed the porosity is closed for the glasses without Zircon (0Zr) and stay open for the glasses containing Zircon (figure 1).
These experiments of Neutrons Scattering, coupled with Monte Carlo1 (figure 2) simulations, permit to clearly establish a link between the gel morphology and the kinetic of alteration for a series of simplified glasses mimicking composition of nuclear glasses.

References:

[1] C. Cailleteau, F. Angéli, F. Devreux, S. Gin, J. Jestin, P. Jollivet, O. Spalla, Insight into silicate glass corrosion mechanisms, *Nature Materials*, 7, 978-983, 2008.

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