Report on the experiment CRG n° 32-2-137 done at the BM32 line from 13/11/2002 to 18/11/2002

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"Grazing Incendence X-rays Scattering of altered surfaces of glass monoliths"

Objectives of the experiment and scientific context

Glass can be altered by water. Indeed, a long contact between water and a glass surface produces the formation of a superficial layer from which some elements are extracted. The thickness of the layer increases with time and its composition depends both, on the type of glass and the alteration conditions (pH, surface/volume ratio). In the case of the French nuclear glass (R7T7) tailored in CEA Valrhô for nuclear waste storage, the alteration layer has been shown to present a secondary retention capacity for the radioelements. This very useful property is not fully understood and may be linked to the morphology of the altered layer. On the other hand, in glass fibers application, the composition has to be optimized in order to obtain a rapid degradation in the physiological conditions of accidentally inhaled fibers. Since a few years, our main objective is to understand the elementary mechanisms of formation of an alteration layer in relation with the initial composition of the glass and the conditions of alteration.

There were two main objectives in this study. A first one was to demonstrate that the mechanism that the average porous structures observed (last year on D2AM) at the surface of sub-millimetric grains are identical to the ones developed on macroscopic monoliths. Indeed, the future geological storage of nuclear waste will be involved macroscopic glass containers. The second and main question is to explore the occurrence of gradients in the porous volume and surface perpendicular to the interface. Indeed, the outer part of the altered layer has been altered for a much longer time that the inner part and redistribution of the atoms position can occur.

Samples and environment

Monoliths of glass have been studied both in reflectivity and in GISAXS configuration. Around 10 glass compositions were used ($SiO_2/B_2O_3/Na_2O/ZrO_2$)=(70/15/15/0-10). With such a variety of compositions, the thickness of the altered layer can increase up to a few microns depending on the conditions of alteration. The samples were made as disks of 3cm in diameter and a few mm thick. The initial surfaces were polished to the optical grade. Prior to the venue at the ESRF, the glass monoliths were altered in hot water (90°C) at different pH for varying time up to two months. The glass disks had to be examined under water at ambiant temperature (20°C) in a special cell developed in the Saclay lab.

Geometry of the GISAXS experiment

In order to cross the 3 cm of water the incident energy was 20keV. The size of the beam was 100*300microns at the sample position. In the GISAXS configuration, the absolute scaling using normalisation through secondary standard (Lupolen) and a direct normalisation after measuring the whole geometry of the set-up. Both method yield the same results. As a test, the absolute signal of pure water (3cm cell) was obtained at the correct value ($0.016cm^{-1}$) and corresponds to a rate of counting equal to 0.03 counts/s per pixel. The reading background for a counting time of 100sec was equal to 61.1 counts per pixel. Each sample was aligned using the CCD camera (cooled at 60°C) following the procedure inspired from the one used in reflectivity. The camera was located at 163cm from the center of the sample yielding a q range of $0.01\text{-}0.37Å^{-1}$.

The monoliths were all different and altered in different conditions. Therefore, we had to change of sample every hour. Since the sample has to be always under water, the challenge (prior to the venue at the beamline) was to design a sample holder able to reposition the surface to examine at a few microns from the beam center and allowing to change a sample without drying it at any stage. This was done using a cell fixed on a magnetic positionner developed in the Saclay lab. The system works correctly and was left on long term loan to the beam-line team. The windows of the cell are made of Nalophan which scatters very very weakly (far less than kapton or millar).

Nevertheless, we had a slight experimental problem with the scattering by the last window of the vaccum tube which is located before the beam-stop and therefore scatters part of the direct beam not intercepted by the sample at very low angle (below 0.16° for a the chosen geometry). We did not succeed to stick on this window at the right position a piece of lead to stop the scattering. Therefore we recommend an improvement to be done on the line : fixing a beam-stop inside the vacuum tube would make experiment much easier. Therefore, we had a background signal higher than what could have been reached.

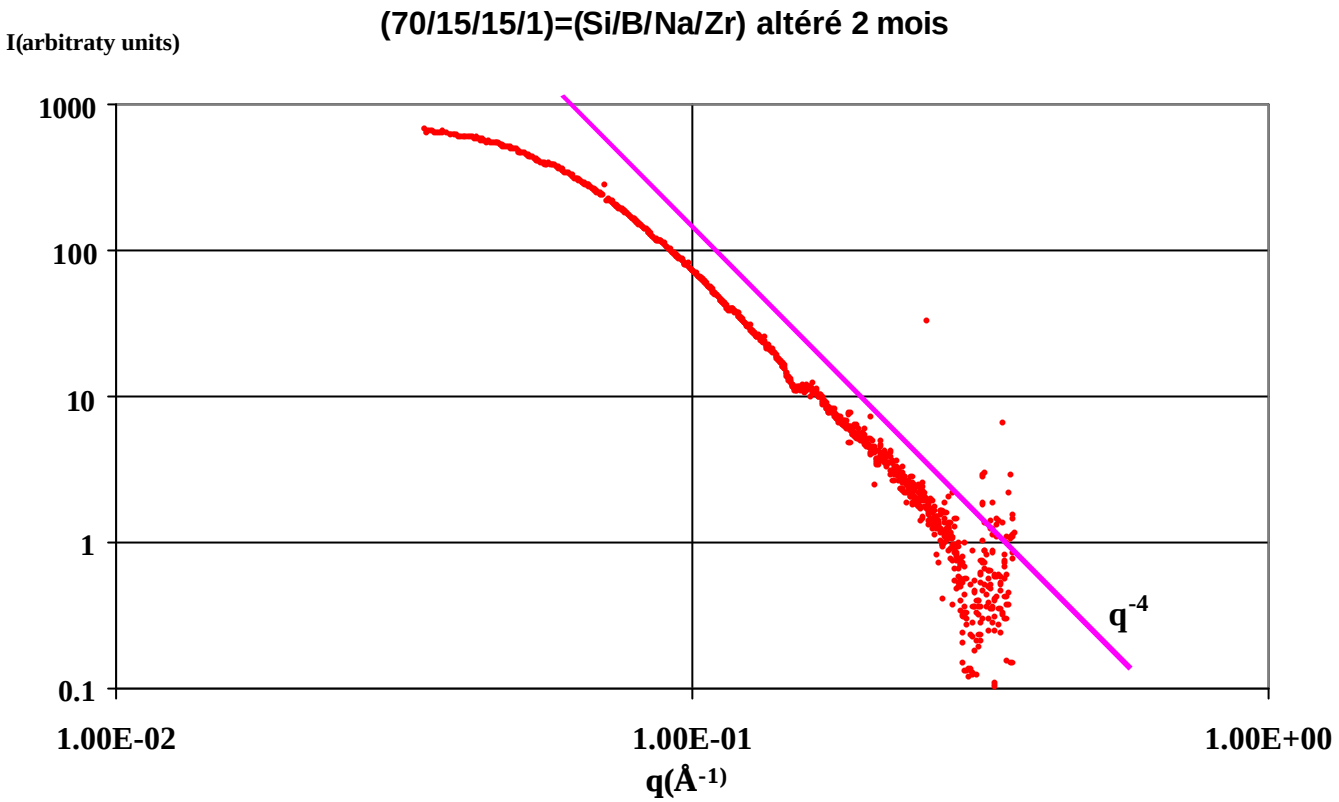
Geometry of the GISAXS experiment

The geometry of the experiment done to the sample was exactly the same as for the GISAXS configuation. Instead of a CCD camera, a classical scintillator NaI with a 710mm vacuum tube and low aperture slits (1*1mm) were used to obtain reflectivity curves. Everything worked correctly.

Results

After one day of setting and alignement, we spent the first day working in a reflectivity configuration and the last three days with the GISAXS configuration. Thirty samples were examined in reflectivity and forty samples were examined in GISAXS. The data are still under treatment. Nevertheless, we can already give the primarly conclusions. For the unaltered samples, the critical angle were around 0.03° which is quite low and in agreement with theoretical calculations. For the weakly altered grains there still exist a critical angle and the characterisitics of the altered layer can be determined (thickness-composition and roughness). For the deeply altered samples, a critical angle does not exist anymore and above an incident angle of 0.04° the signal was totally due to the diffuse scattering. These samples were examined in details in the GISAXS geometry. The diffuse scattering could be extracted from the background with a counting time of 100 sec. An example is given in the figure below. Using the Born approximation and taking into account the geometrical corrections due to the finite size of the sample, we are extracting the data at the absolute scale with a degree of approximation (Born) which is equivalent to the classical one done in transmission SAXS experiments. Several angles 0°-0.04°-0.06°-0.08°-0.12°- were registered in a row on the same sample. Therefore, the comparison of the diagrammes accumulated at different incident angles will allow to seek for a potential porous gradient since a different depth is probed when the angle is higher. This work is under

progress.



Done in Paris december the 16th

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