

### Background

As part of the studies on the long-term performance of the French R7T7 HLW (high-level radioactive waste) glass in a deep underground repository that is backfilled with clay, we have performed during the last 10 years the CORALUS project (CORrosion of alpha-Active gLass in Underground Storage conditions). The CORALUS project combines underground (or: '*in situ*') and surface laboratory integrated tests on the alteration of SON 68 reference glass that simulates the R7T7 HLW glass. Knowledge of the behaviour of this type of waste in disposal conditions contributes to formulate radionuclide source terms, which are mathematical descriptions of the release of radionuclides from the waste as a function of time.

### Objectives

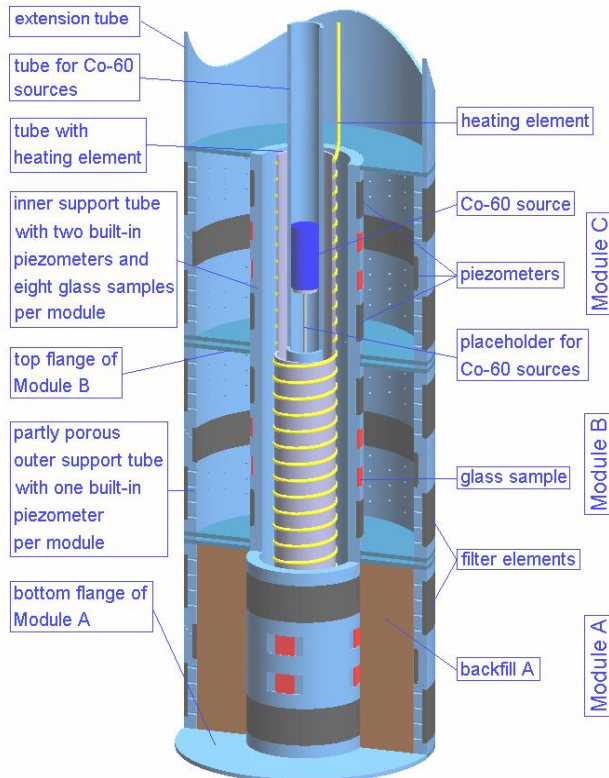
The objectives of the CORALUS project are:

- to compare the results from integrated *in situ* glass corrosion tests, performed under realistic disposal conditions, with results from surface laboratory experiments and modelling predictions, and this for two temperatures (30 °C and 90 °C) and three backfill materials;
- to study, under realistic disposal conditions, (a) the combined effect of high temperature and gamma irradiation and (b) the effect of the specific alpha activity of the glass, on the glass corrosion.

The results will help to assess the validity of the insights in the SON 68 glass corrosion, as these were mostly obtained from less integrated surface laboratory experiments performed under less representative conditions.

### Principal results

In the CORALUS *in situ* tests, four test tubes were placed in the Boom Clay surrounding the HADES underground research facility, for durations between 1.3 and 10 years. As seen from the picture below, each test tube consists of three modules, containing 'inactive' (doped with natural U and Th) and highly alpha-active (doped with  $^{237}\text{Np}$ ,  $^{238-241}\text{Pu}$ , or  $^{241}\text{Am}$ ) SON 68 glass samples in direct contact with a backfill material with swelling pressure of 2 MPa. The specific alpha activity was 0.22 MBq/g glass for the Np-doped samples,



Three-dimensional cut-away modelling view of a test tube with  $^{60}\text{Co}$  sources.

48 MBq/g for the Pu-doped samples, and 1 GBq/g for the Am-doped samples. Together with the alpha activity, also the beta-gamma activity of the glass samples increased. Three backfill materials were studied: dried Boom Clay, and two bentonite-based materials, one of them containing 5 weight% of powdered glass frit. The addition of the glass frit aims at establishing high solution concentrations of the main glass constituents, thus slowing down the glass dissolution rate. Two test tubes contain  $^{60}\text{Co}$  sources, and are heated at 90 °C. These test conditions represent a hypothetical accidental situation occurring shortly after disposal of the HLW glass, exposing the HLW glass directly to the backfill. The two test tubes at 30 °C do not contain  $^{60}\text{Co}$  sources. They simulate the normal evolution scenario conditions some 500 years after disposal of the waste, after corrosion of the overpack and glass canister. In addition to the *in situ* tests, supporting surface laboratory experiments with U/Th-doped samples were performed to allow optimal interpretation of the results of the *in situ* tests.

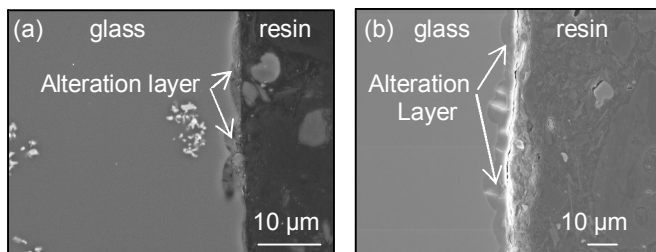
At present, we have stopped two of the four *in situ* tests (one after 1.3 years of alteration at 90 °C, and one after 3.3 years at 30 °C), and we have analysed the corroded glass samples and the clay they were in contact with.

The results confirm two well-known effects. First, the glass alteration at 90 °C is considerably higher than at 30 °C, with differences in mass loss of a factor 20. It is thus of high interest to avoid contact between the HLW glass and pore water during the thermal phase. Second, the addition of powdered glass frit to the backfill material diminishes the glass alteration with about two orders of magnitude. Optimisation of the repository performance is thus possible.

For dried Boom Clay, the mass losses of the 'inactive' U/Th-doped glass samples agree very well with the values from integrated surface laboratory experiments carried out in another research project. The good agreement between the results of the *in situ* test at 90 °C (with gamma radiation) and those of the surface laboratory test (without gamma radiation) might indicate that (i) the effect of gamma radiation is probably due to the concomitant decrease of the solution pH (the initial glass corrosion rate decreases when the pH drops from ~8 to ~6), and (ii) when other processes provoke a decrease of the pH (such as the observed thermal decomposition of organic matter in the dried Boom Clay backfill, with concomitant CO<sub>2</sub> generation), the effect of gamma radiation may become negligible.

Due to the loss of part of the alteration layer, the thickness of the alteration layer of the *in situ* corroded glass samples was almost systematically smaller than for the respective CORALUS surface laboratory tests. We attribute this to differences in swelling pressure and/or water pressure. If we take into account this loss of part of the alteration layer, the results compare fairly well with each other and with modelling predictions. This confirms the high degree of understanding of the glass alteration phenomena. Yet, for more valid modelling hypotheses, we need a better understanding of the processes governing the Si solution concentration at the glass-clay interface and Si transport in the clay.

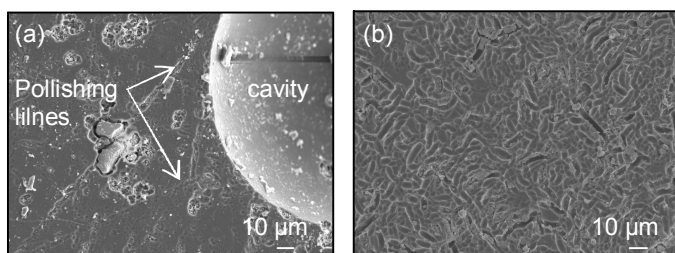
Despite the loss of part of the alteration layer, we observed slightly thicker layers for the radioactive samples, and the thickness seemed to increase with increasing alpha-beta-gamma activity of the samples, see picture below, left. Because of the lack of sufficient mass loss data, we cannot conclude that the thicker alteration layers go along with an increased mass loss. SEM (Scanning Electron Microscopy) analysis of the surface of the glass samples corroded at 30 °C showed a higher degree of alteration for the radioactive samples, see picture below, right. As this phenomenon of thicker alteration layers with increasing activity was also observed for the samples of test tube 3 (90° C, gamma radiation), for which the pH was already low and the gamma radiation dose rate high (> 100 Gy/h), we conclude that in our tests (high swelling pressure, high water pressure) this effect is probably due to the increasing specific alpha activity, and not to the increasing beta-gamma activity. We emphasise that the observed effects are small, and possibly of transient nature.



SEM observations of the polished cross section of *in situ* corroded SON 68 glass samples in contact with a bentonite-based backfill material after 3.3 years at 30 °C.

(a) U/Th-doped, 2500×,  
(b) Am-doped, 1000×.

SEM observations of the surface of *in situ* corroded U/Th-doped (a) and Am-doped (b) SON 68 glass sample in contact with dried Boom Clay, after 3.3 years at 30 °C; magnification 500×.



Based on the radionuclide concentration adsorbed on the clay, we calculated radionuclide retention factors in the alteration layers which vary between 1 and 3. These values are much smaller than the values normally reported for SON 68 glass alteration in water without clay or with a low clay concentration. This shows that in integrated experiments the radionuclide retention in the alteration layer decreases at the expense of a strong retention in the clay that was in contact with the waste glass.

### Future work

We plan to retrieve and dismantle the two other test tubes in 2009 (6 years at 90 °C) and in 2014 (10 years at 30 °C). The surface laboratory test systems will be stopped after the same durations. We will concentrate on studying the effect of the increasing alpha and beta-gamma activity on the glass alteration.

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### Main reference

Valcke, E., *et al.*, 2007. CORALUS-II – An integrated *in situ* corrosion test of alpha-active high-level waste glass – phase II. EUR report, European Commission, Luxembourg, to be published.

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