EFFECTS OF CLAY ON THE DISSOLUTION BEHAVIOUR OF NUCLEAR WASTE GLASS

Background

In the concept for the geological disposal of vitrified nuclear HLW (high-level waste), the biosphere is protected from the waste by multiple barriers, each with their specific safety functions. A first barrier is the waste matrix itself, which should be resistant against leaching, resulting in a slow radionuclide release into the surrounding host rock. As a second barrier, the previous reference disposal design for HLW glass in Belgium foresaw a bentonite buffer. The third barrier would be the Boom Clay host rock. Therefore, our laboratory has performed many experiments with glass in contact with bentonite or Boom Clay, making from the interaction of waste glass and clay an important field of expertise.

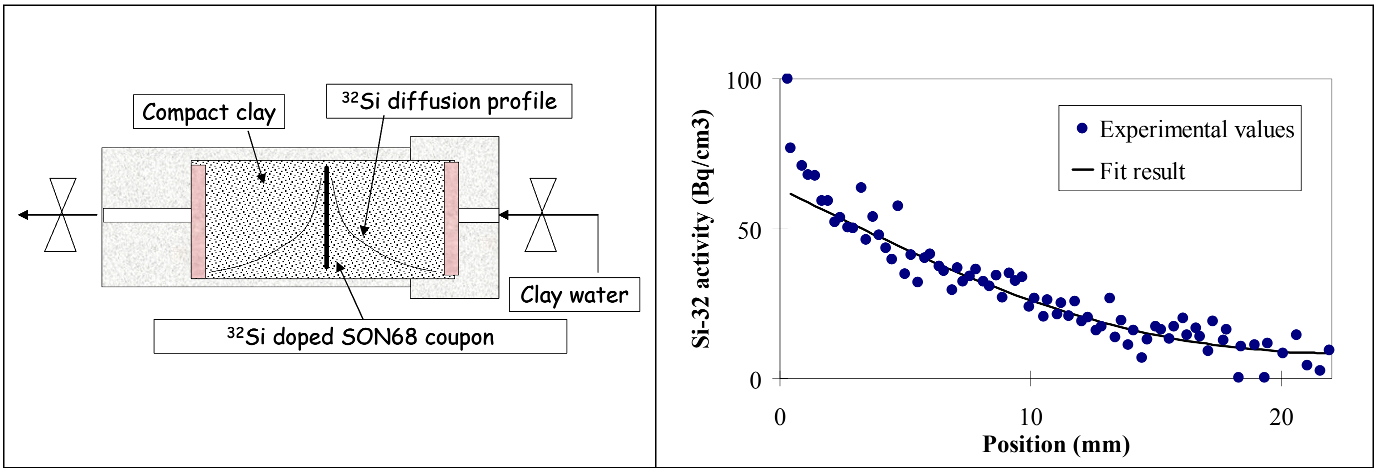
Objectives

The objectives of the studies on the stability of waste glass in conditions representative of the relevant disposal concept, are to create a database for the evaluation of the radiological long-term safety, and to validate certain simplified hypotheses in these evaluations, which allow the modelling of the glass dissolution behaviour.

Principal results

For a long time the sorption of silica by clay has been considered as a key driving force for glass dissolution, but the process was not sufficiently quantified. Thanks to the combined efforts of the laboratories of the sections R&D Waste Packages and Geological Disposal of SCK•CEN, we now have a more precise picture of the dominant processes, based on three types of experiments: (1) dynamic experiments with silica rich solutions passing over Boom Clay suspensions, (2) batch sorption experiments with ^{32}Si, and (3) migration/percolation experiments with ^{32}Si labelled clay water. It appears that Si-sorption on Boom Clay can be described relatively well by a single K_d (distribution coefficient) value for the Si concentrations expected *in situ*. K_d is about 0.011 – 0.025 m³ kg^{-1} in diluted suspensions, and about 0.025 – 0.075 m³ kg^{-1} in compacted clay. A comparison of the main Si diffusion and sorption parameters for compact FoCa-clay (a candidate backfill bentonite) and Boom Clay at 25°C suggests a slightly higher sorption for the FoCa-clay.

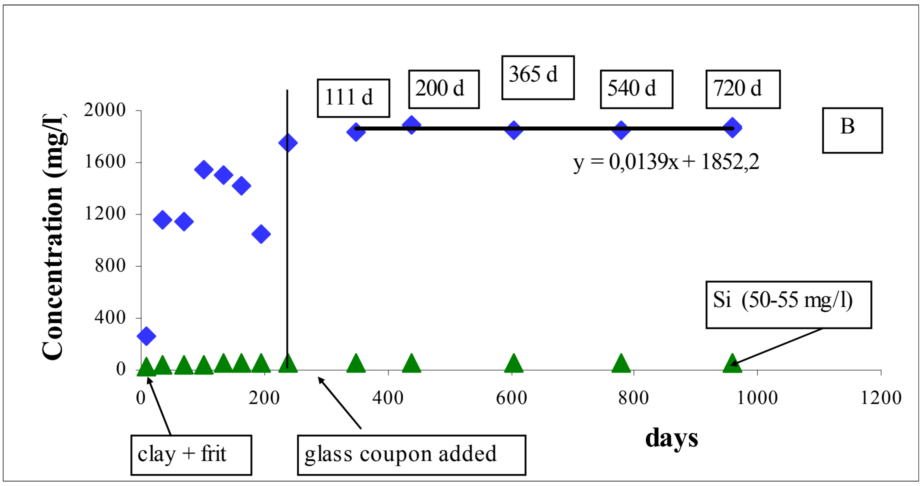
The parameter values obtained in this way can be used directly in a model calculating the glass dissolution as a function of time. To validate this model and the previously measured parameter values, we have performed combined glass dissolution – diffusion experiments in Boom Clay with ^{32}Si doped glass. In these experiments, glass samples slowly dissolve due to contact with the water-saturated clay, and the diffusion profile into the clay of ^{32}Si released by the glass is measured. The resulting data (glass mass loss, clay water concentrations, and ^{32}Si diffusion profiles) are then modelled. Below, we show the experimental set-up, the ^{32}Si diffusion profile in the clay of an experiment of 887 days at 30°C, and the corresponding fitted profile by the model, combining the effects of glass dissolution and silica sorption/diffusion in the clay.



(left) view of the experimental set-up, with the ^{32}Si doped glass sample sandwiched between the compact clay, and the resulting ^{32}Si diffusion profile in the clay , (right) the experimental and calculated ^{32}Si diffusion profile after 887 days at 30°C

A good fit was obtained with parameter values within – or close to – the anticipated range. This corroborates the confidence in the model, and the applied parameter values.

Based on these experiments, we conclude that silica precipitation in the clay is not important at low temperature on the short term. On the long term, however, this may change. To study the long-term effects, we have performed experiments where the glass is put in contact with clay presaturated with silica by the addition of silica-rich components (glass frit). This system simulates the long term situation, where enough glass has dissolved to saturate the sorption sites of the contacting clay. The experiments have been performed with diluted Boom Clay and FoCa clay suspensions, and with compact clay. A typical result for the suspensions is given in the figure below (glass SON68 in contact with Boom Clay at 40°C). It shows the boron (B) and silica (Si) concentrations in the water of the clay suspension contacting the glass. Boron (B) is an important glass corrosion indicator, whereas silica is the most important glass matrix component. The glass coupon was added to the clay suspension after 238 days, when the clay was presaturated with silica, due to the partial dissolution of the glass frit. After the addition of the glass, the boron and silica concentrations do not change any more. In agreement with this, very low glass mass losses were registered.



Evolution of the concentration of boron (B) and silica (Si) in the clay water of a suspension of Boom Clay, which was presaturated with silica by addition of glass frit (first 238 days), after which a SON68 glass coupon was added. The boron and silica evolution in the first 238 days is due to the dissolution of the glass frit. The concentrations do not change any more after the addition of the glass coupon. The glass mass losses were much lower than in similar tests with fresh (unsaturated) clay. The test temperature was 40°C.

Similarly, very low glass mass losses were measured in contact with compact, Si-saturated FoCa clay.
These experiments prove that an initially aggressive clay will eventually become almost inert towards the glass, irrespective of the clay concentration.

We conclude that the experiments performed in the last years have allowed us to better understand and model the impact of clay on glass dissolution. Extrapolations to the long term become increasingly reliable, but experimental confirmation of the long-term behaviour remains important.

Future work

To obtain long-term data, we have started glass dissolution experiments with Boom Clay and presaturated FoCa-Clay with durations of more than 10 years. To further refine the model concept, we need to better understand the impact of distance between interactive materials like overpack corrosion products or backfill clay, and the glass. This will allow us to determine whether materials that are separated from the waste by the engineered barriers (*e.g.* the Boom Clay layer, or even the outer part of the backfill clay) can still have an effect on the glass dissolution. In this respect, we will study the effect of a layer of metallic corrosion products, in the frame of the EC-co-funded NF-PRO (Near Field PROcesses) project.

Main contact person

Karel Lemmens, karel.lemmens@sckcen.be

Main references

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