

## **Combined modeling and experimental studies of SON68 glass dissolution in hyperalkaline solution at 30 °C and 70 °C**

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The Belgian Nuclear Research Centre is investigating the dissolution mechanisms of the Belgian HLW glasses in hyperalkaline conditions in a research program financed by ONDRAF/NIRAS. Static leach tests with SON68 glass were performed under Ar atmosphere at 30°C and 70°C in a synthetic cement water of pH 13.7 simulating the cement pore water in the first stage of concrete degradation. The data are interpreted by means of geochemical modeling using the PHREEQC code coupled to the LLNL database.

In the beginning of both experiments the concentrations of easily soluble elements, such as boron, molybdenum and alkalis show square root of time dependence indicative of a diffusion-dominated process. The fitted diffusion coefficients based on boron concentrations at 30 and 70 °C are  $7.0 \times 10^{-20}$  and  $3.4 \times 10^{-19}$  m<sup>2</sup>/s, respectively. This diffusion process corresponds to diffusion of boron through the alkali-silica gel evidenced by a much lower apparent diffusional activation energy (33 kJ/mol) than that of inter-diffusion (around 80 kJ/mol) reported in literatures. However, a simple diffusion-type relationship can't produce a good fit for silicon, aluminum, calcium and other hardly soluble elements such as iron, since these elements are involved into the formation of alkali-silica gel (ASR) and secondary phases. Geochemical modeling study shows that soon after the leaching of the glass elements, the ambient solution becomes over-saturated with respect to several aluminosilicates and C-S-H phases, especially at 70 °C when the glass dissolution is much faster. If the precipitated elements are assumed to form a diffusion barrier and dissolution is coupled with mineral precipitation in the model, the fitting for silicon, aluminum and calcium can be improved significantly. This study shows that in an alkaline medium, diffusion through alkali –silica gel limits glass dissolution in the beginning. With more and more high-valences cations such as calcium, iron and zinc accumulated into the gel layer, the gel layer condenses. The gel layer will also incorporate aluminum from the solution, but a point is probably soon reached at which zeolites or C-A-S-H begin to form as separate constituents, i.e., resumption starts.