
Effect of boron and aluminum on the formation mechanisms of borosilicate glasses alteration gel

Mélanie Taron^{*1}, Stéphane Gin^{†1}, and Jean-Marc Delaye¹

¹CEA, DES, ISEC, DPME, Université de Montpellier, Marcoule, France – Commissariat à l'Energie Atomique CEA – France

Abstract

When nuclear glass is altered in a confined environment, a silicated and nanoporous alteration layer called "gel" forms at the glass/solution interface, limiting the transport of reactive species and leading to a decrease in the glass alteration rate. The mechanisms behind the formation of this gel have long been debated. In order to obtain a global understanding of the different mechanisms at the origin of the formation of the gels with respect to the composition of the glass, six five-oxides glasses were designed, displaying various B, Al and Si content, deviating from nuclear glass compositions. The glasses were synthesized and numerous experiments were conducted, in diluted (initial rate) and silica-saturated (residual rate) conditions. By means of several surface analysis techniques (ToF-SIMS, MET) as well as in situ and post-mortem isotopic tracing experiments, the gels were characterized extensively. Results indicate the existence of a continuum between two gel formation mechanisms: either by dissolution/precipitation or by in situ hydrolysis/condensation. The predominance between these two mechanisms depends on the Al content in the glass, reinforcing the vitreous network: it is beneficial in the initial alteration rate regime but detrimental in the residual rate regime, slowing down the reorganization of the silicate network into a passivating gel. At low B content, B and Na behave differently: B is not that mobile compared to Na which is exchanged through interdiffusion with H^+/H_3O^+ . At high content, B percolation opens paths allowing for Na release, and passivation may be due to closing of these canals during gel reorganization.

Keywords: borosilicate, glasses, gel, alteration, boron, aluminum

^{*}Speaker

[†]Corresponding author: stephane.gin@cea.fr