
Borosilicate glass alteration in vapor phase and aqueous medium : a NMR investigation

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Abstract

Prediction of the long-term chemical durability of borosilicate glasses is vital to ensure the safety of geological disposal solutions envisaged for nuclear waste glasses. The understanding of the glass alteration mechanisms over time helps to develop prediction models. While the evolution of the glass alteration mechanisms in aqueous medium over time is relatively well-understood,⁽¹⁾ the study of glass alteration in vapor phase is rather new, especially in the domain of nuclear waste glass long-term behavior. ⁽²⁻⁴⁾

In this study, a quaternary Na-alumino-borosilicate glass and its Ca-doped counterpart were altered in vapor phase (98% relative humidity, RH) and aqueous medium at 90°C at a very high SA/V ratio. Both the alteration media (i.e., the vapor phase and aqueous medium) were enriched in ¹⁷O, (the NMR active isotope of oxygen) while the glasses themselves only contained oxygen in natural isotopic abundance. ¹⁷O MAS and MQMAS spectra of the altered samples show that ¹⁷O recondenses with B, Si, Al and partially Na as B-¹⁷O-B/Si, Si-¹⁷O-Si/Al/Na only for the samples altered in vapor phase. In contrast, only Si and Al recondensed with ¹⁷O in the samples altered in aqueous medium. In addition, a noticeable difference in the relative proportions of Si-¹⁷O-Si/Si-¹⁷O-Al and Si-¹⁷O-B/B-¹⁷O-B in the gel layer formed in vapor phase compared to that of the pristine glass is observed. ¹¹B/²³Na/²⁷Al{¹H} REDOR NMR experiments allowed us to quantitatively distinguish the signals from the pristine glass and hydrated gel layer within a sample that was not altered to the core.

The altered glasses were also characterized by SEM, ToF-SIMS and ICP-OES to study the thickness of altered layers and behaviour of elements in the altered layer. For the Ca-doped glasses, ICP-OES and ToF-SIMS experiments showed that the gel layer is more passivating in aqueous medium than in vapor phase, as a consequence of the high retention of Ca in the alteration layer in the former case. ²⁹Si and ²⁷Al MAS NMR spectra indicated that precipitation of zeolites in the Ca-doped glass occurred in vapor phase. The NMR REDOR experiments corroborated the alteration kinetics results: i) a higher degree of hydration was observed for the altered Ca-doped glass in vapor phase and it is vice versa in aqueous medium; ii) for the two compositions, the alteration layer is more hydrated when formed in vapor phase than in aqueous medium as a result of the higher alteration of the samples in vapor phase.

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