Impact of increasing MoO_3 loading on the composition of multicomponent borosilicate glass

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One option to dispose solid Mo(VI)- and Cs(I)-rich residual material sedimenting in storage tanks for high level liquid waste (HLLW) is immobilisation in borosilicate glass. Due to its low solubility in glass melts, Mo(VI) tends to form separate molybdate-rich phases during the vitrification process [1]. These phases may crystallise during melt cooling and are able to incorporate radionuclides within their crystal structure. If water-soluble alkali molybdates form, the release of radionuclides will be facilitated in case of water intrusion into a deep geological repository. The chemical composition of the separate molybdate phases depends strongly on the vitrification temperature, the waste concentration and the borosilicate glass composition. Understanding factors favouring the formation of chemically stable crystalline Mo(VI) phases in borosilicate glasses allows development of glass compositions capable of incorporating high Mo loadings by simultaneously ensuring durability under repository conditions.

In this work, a multi-component borosilicate glass [2] with varying Mo-rich nuclear waste simulate loadings was prepared and characterised by several techniques. Powder X-ray diffraction (XRD) and Raman spectroscopy studies confirm formation of crystalline $CaMoO_4$ and $BaMoO_4$ phases at total MoO_3-concentrations above 5.3 wt% and at 1300 °C melting temperature. Linear combination least squares (LCLS) fit analyses of Ba L_3 edge X-ray absorption near edge structure (Ba-L-XANES) and Raman spectra permit a quantitative estimation of the degree of crystallinity as a function of the MoO_3-content. Mo K edge high energy resolution XANES (Mo-K-HR-XANES) reveals variations in the chemical environment of the MoO_4^- anion. LCLS fit analysis shows that Na^+ cations preferably compensate molybdate charge at low Mo loading (0.5 wt%). Ca/$BaMoO_4$ species are increasingly observed at higher loading reaching 65% at 12 wt% MoO_3 content. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) show formation of spherical structures enriched in Ba, Ca and Mo. In addition, µ-XRF, µ-Mo-K-XANES and µ-XRD studies give access to the elemental Mo speciation and distribution of crystalline phases in the glass products, which are confirmed by transmission electron microscopy (TEM). TEM distinguishes between spatially separate $CaMoO_4$ and $BaMoO_4$ crystalline clusters with very similar lattice parameters. We demonstrate that the combination of advanced spectroscopy and microscopy techniques allows characterising crystalline regions with high Mo, Ba and Ca content. No evidence for formation of water-soluble alkali crystalline molybdates is found, indicating that the chemical composition of the glass used is favourable for immobilisation of Mo-rich nuclear waste with this specific chemical composition [3].

References

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