Abstract

A series of simplified glasses were prepared to mimic the United Kingdom's Magnox radioactive waste glasses and determine the separate effect of the presence of Mg on the glass structure and the initial dissolution rate. These glasses had an alkaline earth (Ca/Mg) content of 6.5 mol% and relative ratios of Si, B and Na similar to 25 wt% waste loaded Magnox waste glass simulant. Each simplified glass had similar macroscopic properties, differing only in Ca/Mg ratio. ^{25}Mg magic angle spinning nuclear magnetic resonance (MASNMR) spectra of the simplified Mg endmember (MgEM) glass (with no Ca) and the full-component simulant glass were similar, consistent with the similar Mg local environments in both glasses. ^{11}B MASNMR spectra of the series of simplified glasses showed a systematic increase in the amount of three-coordinated boron ($^{[3]}$B) with increasing amounts of Mg. A clear change in the charge balancing of four-coordinated boron ($^{[4]}$B) by Mg compared with Ca is observed. However, ^{11}B NMR measurements of the leached material showed that the additional $^{[3]}$B was not preferentially leached from the Mg containing samples. Despite the structural changes in the glass induced by Ca/Mg substitution, initial dissolution rates (r_0) remained invariant, within error, with Ca/Mg ratio. This indicates that the poorer aqueous durability of Mg-containing Magnox waste glass measured experimentally in long-term leaching experiments, compared with SON68 glass containing Ca, is not caused by a primary structural effect in the glass.