Magnesium silicates precipitation from nuclear containment glass and ground water interactions

P. FRUGIER* AND M. GUIOTON

Commissariat à l'Énergie Atomique (CEA), DEN, DTCD, Marcoule, 30207 Bagnols-sur-Cèze, France
(*correspondence : pierre.frugier@cea.fr)

Nuclear containment glass alteration kinetic in ground water solutions has been proved to depend on magnesium silicates precipitation [1] [2]: silicon provided by the glass is consumed by groundwater magnesium. High orthosilic acid activities required for glass alteration rate to decrease cannot be achieved as long as Mg is available in the fluid and pH is sufficiently high for Mg precipitation. As a consequence, glass alteration rate predictions are directly dependent on data concerning magnesium silicate stoechiometry and solubility. However, crystallized minerals available in databases (sepiolite, talc) are stongly oversaturated in glass alteration conditions. Therefore, simple precipitation experiments were conducted in order to assess the nanocrystalline magnesium silicate that control glass alteration at 90 °C. Based on geochemical calculations assuming sepiolite precipitation with a solubility product modified to prevent oversaturation [1] [2], a methodology was proposed to design experiments. Fourteen experiments were prepared by mixing three solutions containing respectively: 2Na+Si, Mg+2Cl, HCl and changing their respective volumes. They were designed i). to precipitate around half of the elements in order to keep final concentrations in the same order of magnitude than initial concentrations; ii). to ensure no amorphous silica nor brucite precipitation. Due to those conditions, final pH ranged from 7 to 8.2 at 90°C: precipitation is difficult below pH 7; Mg concentrations are low above pH 8.2, Experiments lasted several days to ensure concentrations reach a steady state. The magnesium silicate precipitated with a Si/Mg ratio of 1 +/- 0.18. The ratio variations were independent from pH and Si/Mg ratio in the initial or the final solution, but consistent with experimental uncertainties. The log $K90°_C$ of the dissolution reaction written with Mg^{2+} and orthocilic acid was measured at -33.5 +/-2. Such solubility was very consistent with the one that had to be implemented to fit magnesium concentrations in glass alteration experiments performed in ground water [1] [2] even if the Si/Mg in the modeling [1] [2] was chosen based on sepiolite (1.5).

[1] P. Jollivet, et al. (2012) *JNM* **420**, 1–3, p. 508-518 [2] M. Debure et al. (2012) *JNM* **420**, 1–3, P. 347-361