CHEMICAL DURABILITY OF ALUMINOSILICATE GLASSES CONTAINING LOW SOLUBILITY CHEMICAL ELEMENTS

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ABSTRACT

The chemical durability of aluminosilicate glasses was investigated experimentally between 90 and 200°C. In order to evaluate their potential for containment of minor actinides, these glasses were doped with Nd (to simulate the presence of trivalent actinides) or U. The proportions of the glass network formers, Si and Al, were near those found in basaltic glasses (tholeitic end members). The differences between the chemical compositions allow the clarification of the influence of glass network modifier elements on the chemical durability of silica glasses. More precisely, we tested the ability of Ti, Zr, Nd and N to potentially improve the chemical durability.

Two types of leach tests were conducted:
- Dynamic leach tests to determine the initial dissolution rates at 90, 150 and 200°C and the activation energy (Ea) of the glass dissolution reaction;
- Static leach tests at high SA/V (200 cm⁻¹) and 90°C to determine the long-term alteration rates and the apparent silica solubility.

For all the glass compositions tested, the initial dissolution rates at nearly neutral or weakly basic pH are similar at the same temperature. Consequently all alumino-silicate glasses have the same activation energy, 60 kJ/mol. This suggests that the initial hydrolysis mechanism is controlled by the breakdown of Si-O and/or Al-O bonds, whatever the nature of glass network modifier elements.

On the other hand, modifier elements have major effects on the formation of protective films at the glass surface. The nature of this protective film depends on the chemical composition of the glass. A phenomenon similar to metal passivation, has been observed on a glass highly enriched with Nd (53.8 oxide wt%) which may lead to alteration rates in undersaturated media up to two orders of magnitude lower than those observed for basaltic glasses. This “passivation” effect disappears when a sodium sulfate solution (a Nd complexing agent) is used as a leachant. Nitrogen does not improve the chemical durability of aluminosilicate glasses. Finally, all these glasses have the same low dissolution rate (10⁻⁴ g/m²/day) under saturated conditions.