

Incorporation of chlorine in nuclear waste glasses using high-pressure vitrification: Solubility, speciation, and local environment of chlorine

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ABSTRACT

The solubility, speciation, and local atomic environment of chlorine have been determined for aluminoborosilicate glasses equilibrated with various sources of chlorine (NaCl and PdCl₂) at high pressure (0.5–1.5 GPa) and high temperature (1350–1400 °C). The Cl solubility reaches up to 11 mol% in borosilicate glass and appears to be strongly influenced by the concentration of network-modifying cations (Ca and Na) and increases with increasing CaO + Na₂O content. The Cl solubility is enhanced in Ca-bearing rather than Na-bearing borosilicate glass, suggesting a higher affinity of chlorine for alkaline-earth cations. Cl *K*-edge XANES and Cl 2p XPS spectra reveal that chlorine dissolves in glasses only as chloride species (Cl⁻) and no evidence of oxidized species is observed. Using PdCl₂ as a chlorine source leads to a pre-edge signal for PdCl₂ in the XANES spectra. The EXAFS simulations show that the Cl⁻ local environment is charge compensated by Na⁺ or Ca²⁺ at a distance to first neighbor on the order of 2.7 Å, which is comparable to the observed distances in crystalline chloride compounds. The coordination to charge compensating cation is lower in the case of Ca²⁺ (~1.1) than Na⁺ (~4.3).

Keywords: High-pressure, chlorine, nuclear waste glasses, spectroscopy; Experimental Halogens in Honor of Jim Webster