Chlorine solubility and speciation in Low Activity Waste nuclear glass synthesised under high pressure and different redox conditions

Guillaume Lefebvre*[1,2,3], Yann Morizet[1,2], Nicolas Trcera[3], and Michael Paris[2]

[1]Laboratoire de Planétologie et Géosciences [UMR$_C$6112] –
–LeMansUniversité, Universitéd′Angers, InstitutNationaldesSciencesdel′Univers, CentreNationaldelaRechercheS
UFRdesSciencesetdesTechniques – –France

[2]Institut des Matériaux de Nantes Jean Rouxel – Institut de Chimie - CNRS Chimie, Centre National de la Recherche Scientifique, Nantes université - UFR des Sciences et des Techniques, Nantes Université - Ecole Polytechnique de l'Université de Nantes – France

[3]Synchrotron SOLEIL – Centre National de la Recherche Scientifique, Centre National de la Recherche Scientifique : UR1 – France

Abstract

Among the radioactive waste produced in nuclear power plants, the radioisotope chlorine 36 poses a serious threat for the public health and the environment due to its high mobility in the environment and its long half-life (301ky). The volatile character of Cl strongly limits the use of classical melt-quenching to form nuclear-waste glass. To propose a more efficient and durable solution for the immobilisation of halogens radioisotopes, a method using high-pressure has been proposed and shows strong increase in the Cl incorporation. Whereas the effect of glass composition and intensive conditions on Cl incorporation are fairly well-constrained, the effect of various oxidation conditions are partially known. Recent work suggested a decrease in Cl solubility with increasing oxidation conditions in discrepancy with recent results for iodine showing the opposite behaviour. In contrast with previous results, we found that the increase in oxidation conditions does not decrease the Cl solubility but instead slightly increases Cl solubility with perchlorate initial source.

The mechanism behind this behaviour is not yet clear as Cl speciation does not appear to change to an oxidized species. Therefore, a better understanding of the dissolution mechanism is required under various oxidizing conditions to formulate a semi-empirical model for Cl behaviour in nuclear waste glasses.

Glasses have been synthetized under high-temperature (1250◦C) and high-pressure conditions (1.0 GPa) with the following compositions: 65 mol.% SiO2, 5 Al2O3, 10 to 15 B2O3, 7 to 13 CaO and 5 to 22 Na2O. Two glass series were prepared with varying Cl sources that mimic different oxidation conditions: NaClO4, NaClO3 and NaCl between 9 to 16.8 mol.%. The Cl content after experiment reaches up to 6.5 mol.%. To characterize the redox and the structural environment of the Cl in the glasses synthetized, Cl K-edge X-ray Absorption Spectroscopy (XAS) and Cl 2p X-ray Photoelectron Spectroscopy (XPS) have been used.

The investigation by XAS of Cl k-edge showed X-ray Absorption Near Edge Structure (XANES) spectra dominated by Na-Cl and/or Ca-Cl signals with a threshold at 2823.8

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*Speaker

eV and Emax at 2826.1 eV respectively, in agreement with previous work. The Extended X-ray Absorption Fine Structure (EXAFS) spectra confirm the structural environment of the Cl- in glasses charge compensated by Na+ and/or Ca2+ cations at around 2.8 Å. Moreover, the EXAFS revealed the presence of a short local bonding around 1.7 Å that can be explained by the presence of Si-Cl bonds around 1.6 Å or Cl-Cl bonds at 1.85 Å. Cl 2p XPS results show a peak at _˜198.5 eV which can be attributed to Cl- species; no peak for the Cl oxidized species (i.e. ClO3- and ClO4-) are present. Although the spectra can be simulated with a single Cl- in agreement with previous work, we reconsidered the simulation of the Cl 2p XPS spectra in regards of our XAS results. Those simulations showed position of the bonding in agreement with previous studies for alkali/alkaline-earth cations bonded to Cl- and Si-Cl.

Keywords: Chlorine, X, ray Absorption Spectroscopy, X, ray Photoelectron Spectroscopy, Nuclear waste, Glass, high, pressure