## Structural role of zirconium in nuclear glass and in corresponding alteration gel

## Laurence Galoisy<sup>1</sup>, Georges Calas<sup>1</sup>, Patrick Jollivet<sup>2</sup>, Frédéric Angeli<sup>2</sup> and Stéphane Gin<sup>2</sup>

<sup>1</sup> IMPMC (Université Paris Pierre et Marie Curie, UMR CNRS 7590) 4, place Jussieu 75005 Paris, France

<sup>2</sup> CEA-Marcoule, Valrho, Laboratoire d'étude du Comportement à Long Terme des matrices de conditionnement, 30200 Bagnols-sur-Cèze, France

Vitrification of liquid high-level radioactive waste in borosilicate glasses has received a great attention in several countries since many years. Glass leaching by water is an important mechanism to predict the evolution of glasses used to store these wastes. Indeed, in geological repository, as glass leaching by water severely affects the long-term evolution of borosilicate glasses.

We will present some structural features of the evolution of the SON 68 glass under forcing conditions. During the alteration of the glass, an amorphous gel is formed at the surface of the glass. The durability of the gel and its properties depend on the structural role played by elements such as  $Zr^{4+}$ . New generations of spent fuels require higher content of  $Zr^{4+}$  in glasses. The modifications of the  $Zr^{4+}$  environment in the gel has been investigated as a function of increasing  $ZrO_2$  content from 1 to 8 mol% in simplified 5-oxide glass compositions. Short- and medium-range local environment of zirconium in these glasses was determined by Zr L-2,L-3-edge and K-edge XANES and by Zr K-edge EXAFS.

These structural modifications illustrate the molecular-scale origin of the processes at the origin of the glass-to-gel transformation.