Pyrochemical reprocessing of spent nuclear fuels in molten salts is a promising and potential alternative to the modern day extraction technology. A key factor for developing a safe and effective process is the understanding of the behaviour and basic chemistry of the components of irradiated fuels, including fission products. Inorganic melts have high radiation stability and this allows reprocessing of fuels after a relatively short cooling time. Yttrium and zirconium isotopes are formed with high yields as fission products and as products of the $\beta$-decay of isotopes of Sr and Y, respectively.

We have investigated LiCl-based melts containing chlorides of yttrium or zirconium by X-ray absorption spectroscopy, XAS, (both EXAFS and XANES) at 750 °C. Yttrium-containing melts were prepared by reacting $Y_2O_3$ with HCl and analysis of EXAFS data showed that each Y atom was surrounded by six Cl atoms at ca. 2.62 Å and two Y atoms at ca. 4 Å. At the concentration employed, neighbouring $YC{l_6}^{3-}$ octahedra share two Cl ligands and the Cl-Y-Cl angle is around 80°.

Zirconium has two stable oxidation states in chloride melts, Zr(II) and Zr(IV). Zr(IV)-containing melts, from dissolving anhydrous $ZrCl_4$ in LiCl, contained $ZrCl_6^{2-}$ species with Zr-Cl distances of 2.27 Å. Melt samples containing only Zr(II) could not be prepared but by slowly reacting Zr metal with Cl$_2$ in molten LiCl, and then holding the melt in contact with excess Zr; 25% of the zirconium in the melt was reduced to Zr(II). The energy of Zr K-edge for such samples was shifted towards lower values by ca. 6 eV, compared to Zr(IV), but was still 6 eV higher than for Zr(0). The analysis of EXAFS data showed that the first coordination sphere of zirconium for the mixed Zr(II,IV) containing melts is filled by six Cl ligands with an average Zr-Cl distance of 2.45 Å.