High temperature alkali metal chloride based melts are prospective media for non-aqueous pyrochemical reprocessing of spent nuclear fuels. Understanding uranium, TRU and fission product elements speciation and behaviour in molten salts is key to the development of a successful industrial process. X-ray absorption spectroscopy is sensitive and element-specific technique that allows to gain information on coordination and oxidation state of a chosen element in liquid and quenched melts.

In the present study we investigated the species formed by uranium, yttrium, zirconium, technetium, rhenium and technetium (to simulate technetium) in a variety of chloride melts, LiCl, LiCl-KCl, NaCl-KCl, NaCl-CsCl and LiCl-BeCl₂. U L₃-edge, Y K-edge, Zr K-edge, Ru K-edge, Tc K-edge and Re L₃-MM-edge spectra were recorded in transmission or fluorescence (for quenched samples) modes at stations 9.3 and 16.5 of CLRC Daresbury Radiation Source. Depending on the composition of melts the measurements of liquid samples were performed between 380 and 750 °C. Samples were prepared by dissolving anhydrous metal chlorides or by reacting correspondingly metals or oxides with gaseous Cl₂ or HCl directly in the melts. Electronic absorption spectra of molten and quenched samples were also recorded.

All oxidation states of uranium (III, IV, V and VI) are stable in molten LiCl. U(V) and U(VI) form complex ions containing two oxygen and four chlorine atoms around central uranium. At 750 °C U-O distance is 1.80 and 1.75 Å for U(V) and U(VI), respectively. U-Cl distance increases with decreasing uranium oxidation state from 2.65 Å for U(VI) to 2.71 Å for U(V). U(III) and (IV) form six-coordinated chloro-complexes with U-Cl distances of 2.72 and 2.63 Å, respectively. Similar values were obtained in LiCl-KCl melts. The EXAFS spectra of LiCl-based melts containing U(III), (IV) and (V) also showed quite a complex structure at high k values (see Fig.) which can be associated with the presence of uranium atoms at 3.5-5.5 Å. There is no apparent symmetrical order in their position and a reliable fit with a statistically justified number of parameters could not here be obtained.

U(III) and U(IV) are the most stable oxidation states in LiCl-BeCl₂ eutectic melt; even under a Cl₂ atmosphere (but in the absence of oxygen) U(VI) species are converted into U(IV), U(III) and U(IV) ions are present in the melt as hexachloro complexes.

Fig. EXAFS spectra of U(IV) in LiCl at 750 °C (melt) and room temperature (quenched sample).

Yttrium in LiCl melt at 750 °C forms six-coordinated YCl₆³⁻ ions with Y-Cl distance around 2.62 Å. Presence of two neighboring Y atoms at 4.0 Å indicates that the YCl₆ octahedra are joined into chains by sharing two chlorine ligands between every two Y atoms with Y-Y angle around 80 degrees.

Zirconium in LiCl melt can form Zr(II) and Zr(III) ions with the energy of Zr(II) edge around 6 eV less than the energy of Zr(IV) absorption edge. Zr(IV) forms six-coordinated ions with Zr-Cl distance of 2.27 Å. For Zr(II) species this distance increases to 2.45 Å.

Technetium is capable of forming species of at least two oxidation states in chloride melts, Tc(IV) and Tc(VII). Technetium(IV) can be prepared by reacting TcO₂ with HCl and Tc(VII) by reacting TcO₂ with Cl₂ in LiCl-KCl, NaCl-CsCl and NaCl-KCl melts. Under the same conditions rhenium always yields Re(IV) species. The EXAFS spectra were currently measured of only quenched samples. Tc(IV) and Re(IV) form TcCl₆³⁻ and ReCl₆²⁻ species, respectively, with the metal-chlorine distances around 2.36 Å. Technetium(VII) forms TcO₂ ions with Tc-O distance of 1.72 Å.

Ruthenium-containing melts were obtained by reacting Ru or RuO₂ with Cl₂ or HCl in LiCl-KCl and NaCl-KCl melts. In molten state (in LiCl-KCl and NaCl-KCl between 450 and 750 °C) ruthenium forms six-coordinated complexes with Ru-Cl distance around 2.37-2.39 Å (essentially independent from temperature and melt composition).