**A study of uranium(V) species in alkali chloride melts**

V.A. Volkovich,[1] D.E. Aleksandrov,[1] B.D. Vasin,[1]
T.K. Khabibullin,[1] I.B. Polovov,[1] T.R. Griffiths[2]
[1] Department of Rare Metals and Nanomaterials,
Ural State Technical University-UPI, Ekaterinburg,
620002, Russia
[2] Redston Trevor Consulting, Ltd., Leeds, LS17 8RF, UK

Molten alkali chlorides can be used for pyrochemical processing and reprocessing of ceramic uranium dioxide based nuclear fuels. Knowing and understanding the behaviour of uranium, the fuel's primary component, is important for optimising the above processes. Uranium in such melts can form U(VI) and (V) oxychlorospecies. In the present study we focused on reactions leading to the formation of U(V) ions in alkali chloride melts. The experiments were performed in LiCl, 3LiCl-2KCl, NaCl-KCl and NaCl-2CsCl melts at 450-850 $^{o}$C. The main experimental techniques employed were electronic absorption spectroscopy and electrochemistry.

Uranyl chloride is thermally relatively unstable and even being dissolved in chloride melts (forming $UO_2Cl_4^{2-}$ ions) can undergo a slow decomposition leading to the formation of U(V) species, $UO_2Cl_4^{3-}$, and liberation of chlorine. Such reaction, in principle, should be facilitated by lowering pressure of the atmosphere above the melt. In a series of experiments the melts containing $UO_2Cl_4^{2-}$ ions were placed under vacuum and the decomposition process was followed by measuring electronic absorption spectra. An example of the results obtained in NaCl-2CsCl melt and illustrating increasing U(V) concentration is shown in Fig. 1.

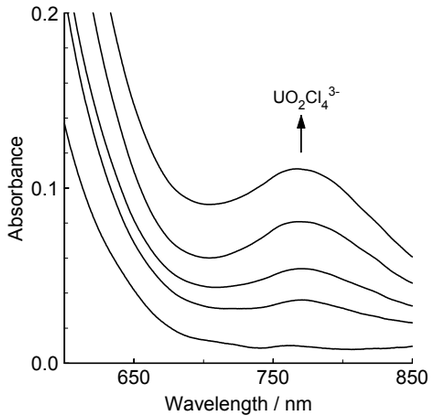


Fig. 1. Electronic absorption spectra recorded in NaCl-2CsCl-$UO_2Cl_2$ melt at 750 $^{o}$C under vacuum, time between registering the first and the last spectra was 173 min (arrow indicates the direction of spectra changing).

Cathodic reduction of $UO_2Cl_4^{2-}$ containing chloride melts is conventionally employed for obtaining uranium dioxide, $UO_2$. Electrochemical reduction of U(VI) was here studied using cyclic voltammetry and constant potential electrolysis. In the latter case the progress of the reaction was followed by *in situ* electronic absorption spectroscopy measurements.

Chemical reduction of U(VI) to U(V) can be achieved with a suitable reducing agent. Molybdenum metal, from its electrochemical properties, is one of them and a series of experiments on reduction of $UO_2Cl_4^{2-}$ with Mo was conducted in alkali chloride melts. In NaCl-2CsCl eutectic, for example, the reaction at 550-750 $^{o}$C leads to the formation of $UO_2Cl_4^{3-}$ and $MoCl_6^{3-}$ ions in the melt (Fig. 2), and some $UO_2$, forming a crystalline deposit on the molybdenum surface (Fig. 3). The amount of $UO_2$ formed increases with increasing temperature. The reactions taking place here are:

$$3\ UO_2Cl_4^{2-} + Mo + 6\ Cl^- \rightarrow 3\ UO_2Cl_4^{3-} + MoCl_6^{3-}$$
$$3\ UO_2Cl_4^{2-} + 2\ Mo \rightarrow 3\ UO_2 + 2\ MoCl_6^{3-}$$

The effect of certain other metals has also been investigated.

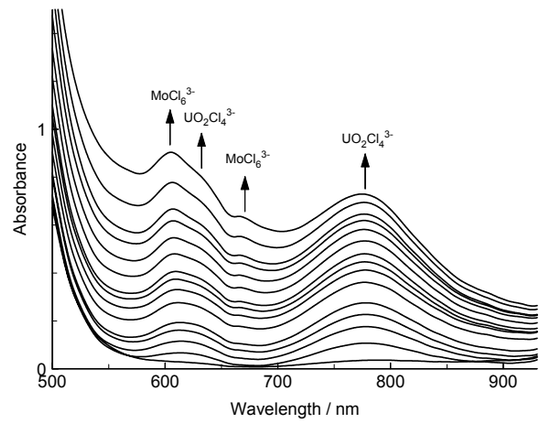


Fig. 2. Electronic absorption spectra recorded in the course of reaction of Mo metal with NaCl-2CsCl+$UO_2Cl_2$ melt at 650 $^{o}$C. Total time of reaction – 120 min. Arrows indicate increasing concentrations of the corresponding species in the melt.

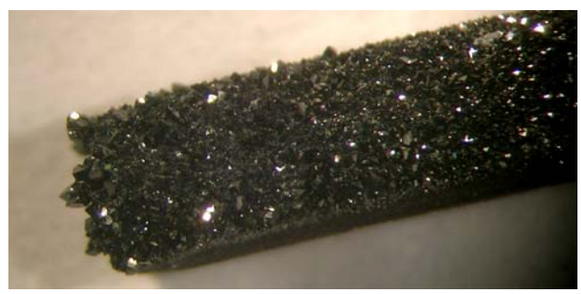

Fig. 3. Uranium dioxide deposited on the surface of molybdenum wire contacted with NaCl-2CsCl+$UO_2Cl_2$ melt at 650 $^{o}$C.

Uranium(V) containing melts can also be obtained by reacting $UO_2$ with HCl. The outcome of this reaction depends on the cationic composition of the melt and temperature. In molten LiCl at 750 $^{o}$C uranium dioxide is converted to $UO_2Cl_4^{3-}$, in 3LiCl-2KCl eutectic at the same temperature a mixture of $UO_2Cl_4^{3-}$ and $UCl_6^{2-}$ is formed with the U(V) species predominant. Under similar conditions in NaCl-KCl and NaCl-2CsCl melts and at 450-600 $^{o}$C in 3LiCl-2KCl melts the reaction yields essentially only U(IV) chloro-species, $UCl_6^{2-}$.