AN X-RAY ABSORPTION SPECTROSCOPY STUDY OF YTTRIUM AND ZIRCONIUM COMPLEXES IN MOLTEN LITHIUM CHLORIDE

V.A. Volkovicha, I. Mayb, T.R. Griffithsc, J.M. Charnockd, B. Lewine

a Department of Rare Metals, Ural State Technical University – UPI
Ekaterinburg, 620002, Russian Federation

b Centre for Radiochemistry Research, University of Manchester,
Manchester, M13 9PL, UK

c Redston Trevor Consulting Ltd.
University of Leeds, Leeds, LS2 9JT, UK

d CLRC Daresbury Laboratory
Warrington, WA4 4AD, UK

e British Nuclear Fuels plc
Sellafield, Cumbria, CA20 1PG, UK

ABSTRACT

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 β-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 Y2O3 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 YCl63-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 ZrCl4 in LiCl, contained ZrCl62- 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 Cl2 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.
INTRODUCTION

Developing an understanding of metal complex speciation in molten salts is key to the development of novel high temperature solvent systems for the chemical or electrochemical processing of spent nuclear fuel. Previous studies have relied heavily on electronic absorption spectroscopy to determine oxidation state and give some indication of solution speciation. Synchrotron radiation has been available for some time for X-ray studies but detailed investigations of dilute molten salt systems have not previously been made.

Alkali metal chloride based melts have considerable potential for use in modern industry, including nuclear technology. In particular, inorganic melts have high radiation stability and so are excellent for this purpose. The electrorefining of plutonium is performed in chloride melts and such media represent prospective solvents for pyrochemical reprocessing of spent nuclear fuel. There are two processes currently developed to the pilot plant scale, in the USA (ANL) and in Russia (RIAR). Understanding the speciation of metals, particularly of fission fuel elements in molten chlorides, is therefore of prime importance for designing and operating a successful industrial process.

Electronic absorption spectroscopy generally offers a convenient tool for characterising the complex species formed as well as for investigating and monitoring processes and reactions involving transition metals in molten salts. In addition to the charge transfer bands of transition metal complexes, solutions of metals with partially filled d- or f-orbitals exhibit characteristic absorption peaks in the uv-vis-nir region, due to d-d or f-f transitions, respectively. Unfortunately, not all fission product elements that are formed in high yield have suitable spectra, particularly in high oxidation states at the beginning of transition metal groups, for example, the complexes of yttrium and zirconium. Thus the nature of the complexes formed in molten chlorides has been interpreted on the basis of their chemical similarities with their neighbours in the Periodic Table.

X-ray absorption spectroscopy, an element specific technique, can provide considerable information concerning coordination, bond lengths and structure of metal complexes in a range of different solvent media and solid materials. However, few conventional XAS (X-ray Absorption Spectroscopy) studies have been performed on molten salts systems, and both XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) techniques were first employed on such systems less than ten years ago, and have so far been mostly limited to studies of pure molten salts or simple binary mixtures (1-10), rather than solutions. Three studies have recently been published, investigating the solutions of transition metal species in molten salts (11-13), and we have contributed one on uranium in all its major oxidation states, (III), (IV), (V) and (VI), in LiCl at 750°C and on the corresponding quenched melts (14).

Okamoto et al. (11) have investigated molten yttrium trihalides and their molten mixtures in LiCl-KCl melt containing 15 to 50 wt% YCl3. Molten pure rare earth halides consist mainly of octahedral complexes bonded to one another by chloride bridges and hence the complexes at low concentrations in molten LiCl are expected to be octahedral.
For YCl$_3$-LiCl-KCl mixtures Okamoto et al. (11), with data analysis limited to only the first coordination sphere, found YCl$_6^3$+. In a similar manner, Okamoto and Motohashi (12) reported an XAFS study of ZrCu$_4$ (12 wt%) in molten LiCl-KCl eutectic and identified ZrCl$_6^{2-}$ species.

EXPERIMENTAL

Synchrotron X-ray measurements

$Y$ $K$-edge and Zr $K$-edge spectra were recorded in transmission or fluorescence modes (for selected quenched samples) on station 9.3 of the CLRC Daresbury Radiation Source, operating at a typical beam current of 150 mA and an energy of 2 GeV. The radiation was monochromated with a Si 220 double crystal, detuned to 50% of maximum intensity to minimise harmonic contamination. Up to 12 scans per sample were collected. X-ray absorption spectra were recorded up to $k_{\text{max}} = 15$ Å$^{-1}$ but the analysis of the spectra of molten samples was normally limited to $k_{\text{max}} = 9-13$ Å$^{-1}$ due to the increasing noise-to-useful signal ratio at higher energies. The quenched melt samples were re-melted in the horizontal portion of inverted T-shaped silica cells, 20 mm wide with 2 or 3 mm path lengths. The cells were held in a custom modified optical furnace equipped with beryllium windows. The spectra were summed, calibrated and their background subtracted using the Daresbury Laboratory programs EXCALIB and EXBACK. The spectra were simulated using the EXCURV98 program. Where necessary, the effects of multiple scattering were included in the final analysis. With the present design of the furnace and experimental cells the measurements could be carried out only in transmission mode, which necessitated the use of a weakly X-ray absorbing salt, LiCl.

Sample preparation

Yttrium-containing melts were prepared by reacting Y$_2$O$_3$ in molten LiCl at 750°C with HCl gas. The resulting melts were colorless and contained only trivalent yttrium (as shown by chemical analysis). Zirconium has two stable oxidation states in chloride melts, Zr(II) and Zr(IV). Zr(IV)-containing melts were prepared from dissolving anhydrous ZrCl$_4$ in LiCl. 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 in the form Zr(II). Details of the systems investigated are given in Table 1.

Table 1. Y- and Zr-solutions in LiCl melts used for XAS studies

| Sample preparation | Metal concentration, wt.% | Metal oxidation state* |
|--------------------|---------------------------|------------------------|
| Reaction Y$_2$O$_3$ + HCl | 6.75 | 3.0 |
| Dissolution of ZrCl$_4$ | 1.00 | 4.0 |
| Reaction of Zr + Cl$_2$ | 1.56 | 3.5 |

* As determined by oxidimetric analysis of rapidly quenched melt samples.
RESULTS AND DISCUSSION

Yttrium

The EXAFS spectrum of the LiCl-YCl\(_3\) melt at 750 °C is shown in Figure 1 and the corresponding Fourier transform in Figure 2. At high energies the experimental EXAFS spectrum exhibits quite a complex structure and the results of curve fitting with only two nearest shells is given. The structural parameters obtained are listed in Table 2.

![Figure 1. Y full range EXAFS spectrum (solid line) and fit of first shells (dashed line), LiCl melt, 750 °C.](image1)

![Figure 2. Fourier transform of Y EXAFS spectrum over fitted range, LiCl melt, 750 °C. Solid line – experimental data, dashed line – calculated.](image2)

Table 2. Structural parameters from EXAFS curve fitting for Y in molten LiCl

| Sample                  | k\(_{\text{max}}\) of fit, Å\(^{-1}\) | Shell | CN | Distance, Å | Debye-Waller factor (2σ\(^2\)), Å\(^2\) | R   |
|-------------------------|--------------------------------------|------|----|-------------|----------------------------------------|-----|
| Y\(_2\)O\(_3\) + HCl in LiCl at 750 °C | 12                                   | Y-Cl | 6  | 2.62        | 0.033                                  | 29.7|
|                         |                                       | Y-Y  | 2  | 4.00        | 0.021                                  |     |

The data obtained show that yttrium forms six-coordinated YCl\(_6\)\(^{3-}\) complex ions with a Y-Cl distance around 2.62 Å. The presence of two neighboring Y atoms at 4.0 Å indicates that the YCl\(_6\)\(^{3-}\) octahedra are joined into chains by sharing two chlorine ligands between every two Y atoms, with a Y-Cl-Y angle around 80 degrees. A representation of the possible structure modeled on the basis of EXAFS spectroscopy data is given (Figure 3).

![Figure 3.](image3)

The Y-Cl bond length of 2.62 Å obtained here agrees well with that of 2.68 Å found by Okamoto et al. (11) in a LiCl-KCl-YCl\(_3\) melt (15 mol. % YCl\(_3\)) at 700 °C. However, the presence of neighboring yttrium atoms at ca. 4 Å was only observed by Okamoto et al. (11) in molten YCl\(_3\). The Fourier transform of the EXAFS spectrum of their melt containing 50 mol. % YCl\(_3\) in LiCl-KCl did not have a corresponding peak. They concluded that the presence of potassium ions in the melts stabilizes individual octahedral YCl\(_6\)\(^{3-}\) ions. This conclusion seems to agree with our findings for a LiCl melt,
if we assume that the small lithium ions, having a large surface charge per unit area, stabilize polymeric rather than monomeric yttrium complexes.

![Figure 3. Model of yttrium chloride complex structure in LiCl melt at 750 °C on the basis of XAS measurements.](image)

Zirconium

Zirconium differs from yttrium in that it can form ions in two oxidation states, +2 and +4. The energy of the XAS absorption edge depends on the oxidation state of studied element and increases with increasing oxidation state. It is normally taken that increasing the oxidation state by unity shifts the absorption edge by 2-5 eV (15), provided that the coordination does not change. In the presence of a mixture of several oxidation states the position of the absorption edge is determined by the species of the lowest oxidation state.

The XANES spectra of Zr-containing melts are shown in Figure 4 and the energies (calculated from the first derivative of the spectra) are given in Figure 5. These results show that Zr(II) ions were indeed formed according to:

\[
\text{Zr(IV) + Zr(0) \rightarrow 2 Zr(II)} \tag{1}
\]

Taking into account the results of the oxidimetric analysis, Table 1, we can conclude that this mixed melt contained Zr(IV) and Zr(II) species in a 3 : 1 ratio. The EXAFS spectra of Zr-containing melts are shown in Figures 6-13 and the results of their analysis in Table 3.

The first coordination sphere of zirconium in the melt containing only Zr(IV) consists of six chloride ligands in an octahedral configuration. The length of the Zr–Cl bond is 2.27 Å. This coordination remains in the quenched melt but the Zr–Cl distance increases, due to distortion of the symmetry from regular octahedral (16).
Figure 4. Zr XANES spectra in LiCl melt, 750 °C, 1 – Zr(II,IV), 2 – Zr(IV).

Figure 5. Zr absorption edge energy: 1, Zr(0), as metal; 2, Zr(II) in LiCl melt, 750 °C; 3, Zr(IV) in LiCl melt, 750 °C.

Table 3. Structural parameters from EXAFS curve fitting of Zr in LiCl

| Sample                              | k_max of fit, Å⁻¹ | Shell | CN | Distance, Å | Debye-Waller factor (2σ²), Å² | R  |
|-------------------------------------|-------------------|-------|----|-------------|-----------------------------|----|
| ZrCl₄ in LiCl at 750 °C (Zr(IV))    | 12                | Zr-Cl | 6  | 2.27        | 0.036                       | 32.9|
|                                     |                   | Zr-Zr | 12 | 3.39        | 0.046                       |    |
|                                     |                   | Zr-Cl | 8  | 4.10        | 0.033                       |    |
|                                     |                   | Zr-Zr | 6  | 4.83        | 0.034                       |    |
| As above, quenched melt             | 12                | Zr-Cl | 6  | 2.31        | 0.030                       | 35.6|
|                                     |                   | Zr-Zr | 12 | 3.41        | 0.025                       |    |
|                                     |                   | Zr-Cl | 8  | 4.13        | 0.032                       |    |
|                                     |                   | Zr-Zr | 6  | 4.82        | 0.021                       |    |
| Zr + Cl₂ in LiCl at 750 °C (Zr(II+IV)) | 10              | Zr-Cl | 6  | 2.45        | 0.029                       | 30.6|
| As above, quenched melt             | 11                | Zr-Cl | 6  | 2.46        | 0.013                       | 31.5|

A previous study of a LiCl-KCl melt containing ZrCl₄ (12 %) showed that the Zr(IV) had formed ZrCl₆²⁻ ions with a Zr-Cl distance of around 2.51 Å (12). The Fourier transform of the experimental EXAFS spectrum, Figure 11, indicates some structural ordering occurring in the melt, also observed by Okamoto and Motohashi (12) in a LiCl-KCl based melt. The results of the analysis of our EXAFS spectrum are given in Table 3.

Another zirconium melt investigated here contained a mixture of Zr(IV) and Zr(II) chloro-species. For mixtures of several complexes of the same element XAS presents an averaged picture concerning bond lengths and coordination numbers. Since only 25 % of the zirconium in our melt was present in the divalent state, and the error in determining the coordination number by this technique is around 20 %, it was not possible to draw a definite conclusion concerning whether the structure of the ions of Zr(II) were octahedral ZrCl₆²⁻ or tetrahedral ZrCl₄²⁻. If the four-coordinated ions are present then the "average" coordination number for zirconium in the mixture was 5.5 and
Figure 6. Zr(II,IV) EXAFS spectrum over fitted range, LiCl melt, 750 °C. Solid line – experimental data, dashed line – calculated.

Figure 7. Fourier transform of Zr(II,IV) EXAFS over fitted range, LiCl melt, 750 °C. Solid line – experimental data, dashed line – calculated.

Figure 8. Zr(II,IV) EXAFS over fitted range, quenched LiCl melt. Solid line – experimental data, dashed line – calculated.

Figure 9. Fourier transform of Zr(II,IV) EXAFS over fitted range, quenched LiCl melt. Solid line – experimental data, dashed line – calculated.

Figure 10. Zr(IV) EXAFS over fitted range, LiCl melt, 750 °C. Solid line – experimental data, dashed line – calculated.

Figure 11. Fourier transform of Zr(IV) EXAFS over fitted range, LiCl melt, 750 °C. Solid line – experimental data, dashed line – calculated.

168 Electrochemical Society Proceedings Volume 2004-24
in the limits of accuracy of the method this value is indistinguishable from the coordination number of 6, given in Table 3. Zr-Cl bond length increases with decreasing the oxidation state, as expected.

CONCLUSIONS

Internuclear distances can be determined by X-ray diffraction for yttrium and zirconium chloro complexes in molten LiCl and there is evidence of some polymerisation in the former at the concentration employed. The technique of EXAFS, using synchrotron radiation, for molten salt solutions is still in its infancy, and many more studies are required over a wide range of concentrations but already this approach is yielding interesting results concerning the nature and speciation of the complexes formed in molten salts.

ACKNOWLEDGMENTS

The authors are grateful to Prof. F. R. Livens (Centre for Radiochemistry Research, CRR, Manchester) for valuable comments and discussions; Dr I. Harvey and Mr R. Bilsborrow (Daresbury Laboratory) for help with EXAFS measurements; EPSRC for funding the beam time; and VAV thanks British Nuclear Fuels plc for a Post-Doctoral Research Fellowship.
REFERENCES

1. L. Hefeng, L. Kunquan, W. Zhonghua and D. Jun, *J. Phys.: Condensed Matter*, 6, 3629 (1994).
2. M. Inui, S. Takeda, K. Maruyama, Y. Shirakawa and S. Tamaki, *J. Non-Cryst. Solids*, 192-193, 351 (1995).
3. Y. Okamoto, K. Fukushima and Y. Iwadate, *J. Non-Cryst. Solids*, 312-314, 450 (2002).
4. K. Lu, H. Li, Z. Wu, J. Dong and Z. Cheng, *Physica B*, 208-209, 339 (1995).
5. Y. Okamoto, M. Akabori, H. Motohashi, A. Itoh and T. Ogawa, *Nucl. Instr. Methods Phys. Res. A*, 487, 605 (2002).
6. Y. Okamoto, H. Shiwaku, T. Yaita, H. Narita and H. Tanida, *J. Mol. Struct.*, 641, 71 (2002).
7. S. Takeda, Y. Kawakita, M. Inui and K. Maruyama, *J. Non-Cryst. Solids*, 250-252, 410 (1999).
8. M. Inui, K. Maruyama, Y. Shirakawa, S. Takeda and S. Tamaki, *J. Non-Cryst. Solids*, 205-207, 155 (1996).
9. Di Cicco and M. Minicucci, *Phys. Rev. Let.*, 78, 460 (1997).
10. Di Cicco, *J. Phys.: Condensed Matter*, 8, 9341 (1996).
11. Y. Okamoto, M. Akabori, H. Motohashi, H. Shiwaku and T. Ogawa, *J. Synchrotron Rad.*, 8, 1191 (2001).
12. Y. Okamoto and H. Motohashi, *Z. Naturforsch.*, 57a, 277 (2002).
13. Y. Okamoto, M. Akabori, A. Itoh and T. Ogawa, *J. Nucl. Sci. Technol.*, Suppl. 3, 638 (2002).
14. V. A. Volkovich, I May, A. I. Bhatt, T. R. Griffiths, J. M. Charnock and B. Lewin, *International Symposium on Ionic Liquids*, Eds. H. A. Øye and A. Jagtøyen, Cary le Rouet, France, June 26-28, 2003, Department of Materials Technology, NUST, Trondheim, Norway, 253 (2003).
15. I. Almahamid, J. C. Bryan, J. J. Bucher, *et al.*, *Inorg. Chem.*, 34, 193 (1995).
16. R. D. Shannon, *Acta Cryst.*, A32, 751 (1976).

170 Electrochemical Society Proceedings Volume 2004-24