

## XAFS measurement on molten chlorides containing uranyl chloride

Haruaki MATSUURA\*<sup>1</sup>, Yoshihiro OKAMOTO<sup>2</sup>

<sup>1</sup>Res. Lab. for Nucl. Reactors, Tokyo Tech., Ookayama, Meguro-ku, Tokyo, 152-8550, Japan

<sup>2</sup>Synchr. Rad. Res. Center, JAEA, Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan

### Introduction

During the course of development of pyrochemical reprocessing of oxide nuclear fuels, one of the several critical issues is remained, that is, how to make realization of the uranium-plutonium oxides (MOX) co-electrodeposition process. To electrodeposit MOX fuel effectively, one has to clarify the relationship between local structure around actinide species and electrochemical behaviour depending upon chlorine – oxygen gas ratio, melt bath composition, temperature, co-existing fission and cladding elements etc. In a real process, these materials are usually diluted in molten chloride baths. In such condition, the local structure around actinides depending upon various melt baths should be much importantly evaluated. We had finished ‘cold tests’ using yttrium chlorides and have started ‘hot tests’ using uranyl chlorides in molten alkali chlorides.

### Experimental

The  $\text{UO}_2\text{Cl}_2$  with various melt baths were prepared in a dried argon circulated glove box in Kyoto University Research Reactor Institute. A certain amount of the samples was sealed in a specially designed quartz cell. The electric furnace used was the similar to that originally designed for the laboratory XAFS, but slightly modified to improve thermal homogeneity as well as vacuum tightness. We have carried out the XAFS measurement of hexavalent uranyl chlorides with various alkali chlorides at molten and solid phases, using Si (111) double crystal monochromator at U-L<sub>III</sub> X-ray absorption edge.

### Results and discussion

These quartz cells could successfully confine the samples during performing the experiments at high temperatures in whole experiments. XAFS spectra and radial structure factors of both molten and solidified NaCl-KCl (1:1 molar ratio) –  $\text{UO}_2\text{Cl}_2$  ( $x_{\text{UO}_2\text{Cl}_2}$ =10wt%) using transmission mode are shown in Fig. 1 and 2, respectively. On the contrary to the results on molten LiCl-KCl (eutectic)- $\text{UCl}_3$  [1], similar phase and different phases are somewhat mixed in XAFS spectra between solid and molten samples, as identified in Fig. 1. These facts clearly influence to the structural factors in Fig. 2. The peaks at ca 1.3 Å are attributed to the closest U-O contributions, and decreasing intensity upon melting is only due to temperature effect, since  $\text{O}=\text{U}=\text{O}^{2-}$  ion is known to be rigid. However, the peaks at between 2 and 2.5 Å are corresponding to U – Cl coordination, that is, chlorides are expected to be in horizontal plane if

$\text{O}=\text{U}=\text{O}^{2-}$  is placed in axial. This second coordination sphere becomes much looser upon melting. Although unharmonicity effect increases at high temperature, the distance between U-Cl decreases drastically upon melting definitely. Thus, we conclude that the variation of 2<sup>nd</sup> coordination spheres in various conditions is good indication of ‘stabilization’ of the local environment around uranyl ions, which would be highly related to electrochemical behaviour. We are planning to follow the similar strategy in other systems, and try to develop new processes in pyrochemical treatment for not only applicable to oxide fuels but also variety types of nuclear fuels.

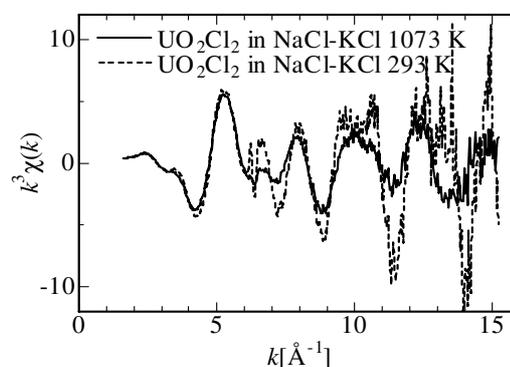


Fig. 1 Extracted oscillation of XAFS of NaCl-KCl (1:1 molar ratio) –  $\text{UO}_2\text{Cl}_2$  (10wt%) mixture.

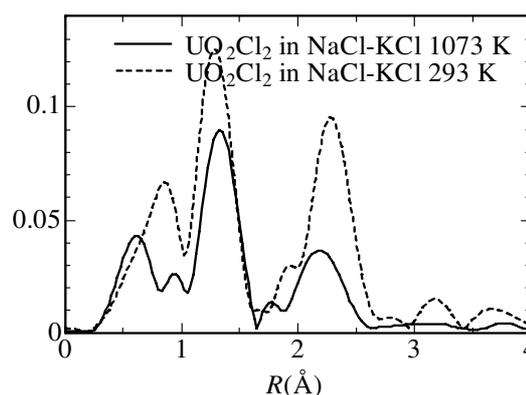


Fig. 2 Fourier transformed radial structure factors of NaCl-KCl (1:1 molar ratio) –  $\text{UO}_2\text{Cl}_2$  (10wt%) mixture.

### References

[1] Y. Okamoto et al., J. Nucl. Sci. Technol. Suppl 3, 638 (2002).

\* hmatsuur@nr.titech.ac.jp