

## Chemistry of ruthenium in the PUREX process: new insight on the speciation in the organic phase TBP-TPH

Charbonnel Marie-Christine<sup>1\*</sup>, Lefebvre Claire<sup>1</sup>, Dumas Thomas<sup>1</sup>, Pier Lorenzo Solari<sup>2</sup>

<sup>1</sup>CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes, SPDS- BP 17171, F-30207 Bagnols sur Cèze, France

<sup>2</sup>Synchrotron SOLEIL, L'Orme des Merisiers, BP 48, St Aubin, F-91192 Gif-sur-Yvette, France

### 1. Introduction

The PUREX process enables the recovery of uranium and plutonium from spent nuclear fuels. The fission product ruthenium remains one troublesome element due to its complexed chemistry, its high contribution to the  $\beta$ - $\gamma$  radioactivity in the process and difficulty to remove ruthenium when quantities are extracted in the organic phase. Different teams have performed studies to better describe the complexes [1] but this issue remains important to simulate the behavior in the PUREX process.

In nitric acid solutions Ru is present as a mixture of  $[\text{RuNO}(\text{NO}_3)_x(\text{NO}_2)_y(\text{OH})_z(\text{H}_2\text{O})_t]^{(3-x-y-z)+}$  complexes. During further liquid-liquid extraction steps, ruthenium is partly extracted by the TBP/TPH solvent. According to previous studies the Ru partition coefficient ( $D_{\text{Ru}}$ ) is strongly related to its speciation in aqueous phase. More particularly, the complexes with three and four nitrate ligands are extracted with a quantitative yield whereas less nitrated complexes are poorly extracted [2]. These conclusions are mainly deduced from old chromatographic studies. Recent studies have been carried out to modelize the behavior of ruthenium thanks to distribution data [3]. Even if a good agreement was obtained with the model in the extraction part, the scrubbing part remains difficult to modelize. Preliminary studies performed at two acidities ( $\text{C}_{\text{HNO}_3}$  1 and 4 mol/L) probed the interest of a combined analysis with FTIR and X-ray absorption spectroscopy (EXAFS)[4].

### 2. Experimental

FTIR spectra were carried out with a Bruker Equinox 55 FT-IR spectrometer equipped with an attenuated total reflectance cell.

EXAFS data at ruthenium K-edge (22 keV) were recorded at Synchrotron SOLEIL (St Aubin, France) at the MARS beamline. The data were collected in transmission mode.

### 3. Results and Discussion

Thanks to a preliminary study with crystallized forms of selected ruthenium nitrosyl compounds, the authors could improve the methodology and reduce the parameters necessary to analyze EXAFS spectra and then propose an average formula for organic complexes  $\text{Ru}(\text{NO})(\text{OH})_x(\text{NO}_3)_y(\text{H}_2\text{O})_z$  with a high accuracy.

The modification of the speciation of Ru with acidity was studied. Studies lead to the conclusion that the TBP molecule was always in the outer sphere of Ru, linked by hydrogen bonds. Additional studies were performed to follow the evolution with time in the organic phase. The modifications in the coordination sphere of Ru will be presented and links with the high retention of Ru in the organic phases will be discussed.

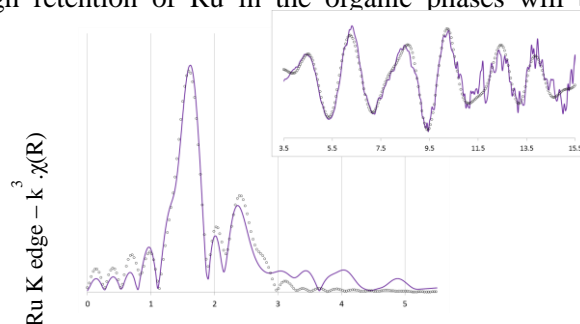


Figure 1: EXAFS spectra of Ru in TBP30%-TPH (equilibrated with  $\text{HNO}_3$  4M) (● experimental and — calculated)

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