



HAL
open science

Speciation of ruthenium in TBP/TPH organic phases (structure and reactivity)

C. Lefebvre, T. Dumas, M.-C. Charbonnel, Pier Lorenzo Solari

► **To cite this version:**

C. Lefebvre, T. Dumas, M.-C. Charbonnel, Pier Lorenzo Solari. Speciation of ruthenium in TBP/TPH organic phases (structure and reactivity). 12th Soleil Users' Meeting, Jan 2017, Saint Aubin, France. cea-02435078

HAL Id: cea-02435078

<https://cea.hal.science/cea-02435078>

Submitted on 10 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

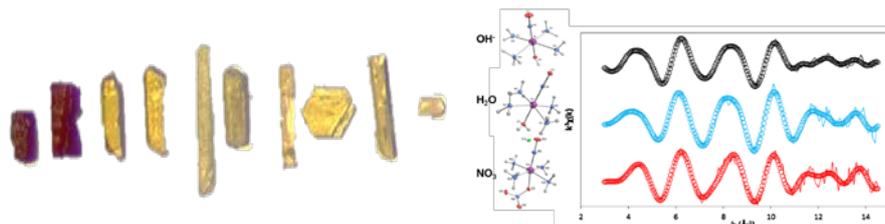
Speciation of ruthenium in TBP/TPH organic phases (structure and reactivity)

Claire Lefebvre^a, Thomas Dumas^a, Marie-Christine Charbonnel^b, Pier Lorenzo Solari^c

^a CEA Marcoule, DEN/DRCP/SMCS/LILA, Bât. 181, BP 17171, 30207 Bagnols-sur-Cèze, France

^b CEA Marcoule, DEN/DRCP/SMCS/DIR, Bât. 400, BP 17171, 30207 Bagnols-sur-Cèze, France

^c Synchrotron SOLEIL, L'Orme des Merisiers, BP 48, St Aubin, 91192 Gif-sur-Yvette, France



ABSTRACT

Ruthenium is one of the major fission products and draws attention to it because it is partly extracted with uranium and plutonium during the reprocessing of the used nuclear fuel. The decontamination factors of the recoverable materials are impacted by this unwanted transfer from the nitric acid phase to the tributylphosphate (TBP) phase[1].

During dissolution of used nuclear fuel, ruthenium forms trivalent nitrosyl complexes with nitrate, nitrite, hydroxo and aquo ligands. The admitted general formula is $[\text{RuNO}(\text{NO}_3)_x(\text{NO}_2)_y(\text{OH})_z(\text{H}_2\text{O})_{5-x-y-z}]^{3-(x+y+z)}$ where x , y , z depend on the chemical conditions. Only the most nitrated complexes must be extracted with a quantitative yield [2, 3].

The study of Ru complexes is made much more difficult by the co-existence of several species with low ligand exchange kinetics[4]. There must be several extracted species and polydispersity in both aqueous and organic phase.

In this study, different complementary spectroscopic techniques were used to have a better understanding of the ruthenium local environment in simulated reprocessing solutions. It includes vibrational spectroscopy and X-ray absorption spectroscopy (EXAFS).

The Ru nitrosyl form was firstly confirmed in both phases, and then the coordination sphere of this core was probed. The ruthenium extraction mode by TBP (direct complexation with Ru and/or second sphere coordination) was investigated as a function of initial conditions. Hydrolysis effect was highlighted as well as the ruthenium speciation in the organic phases, depending on acidity of the initial solution. At the end, the aging process of ruthenium in the TBP phase was qualitatively characterized.

This study was supported by synthesis of reference compounds under monocrystalline form and then structurally characterized by XRD. Their EXAFS spectra were recorded and used as a database to fit EXAFS spectra of experimental solutions. Some DFT calculations were also made to calculate Debye-Waller factors and compare them to the factors determined by fitting model compounds data. This will permit to restrict Debye-Waller factor for solvent extraction samples to obtain accurate stoichiometry.

REFERENCES

- [1] P. Swain, C. Mallika, C. J. Rao, U. K. Mudali, and R. Natarajan, *Journal of Applied Electrochemistry*, vol. 45, pp. 209-216, 2015.
- [2] J. M. Fletcher, C. E. Lyon, and A. G. Wain, *Journal of Inorganic & Nuclear Chemistry*, vol. 27, pp. 1841-1851, 1965.
- [3] G. Rudstam, *Acta Chemica Scandinavica*, vol. 13, pp. 1481-1501, 1959.

[4] G. G. J. Boswell and S. Soentono, *Journal of Inorganic & Nuclear Chemistry*, vol. 43, pp. 1625-1632, 1981.