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

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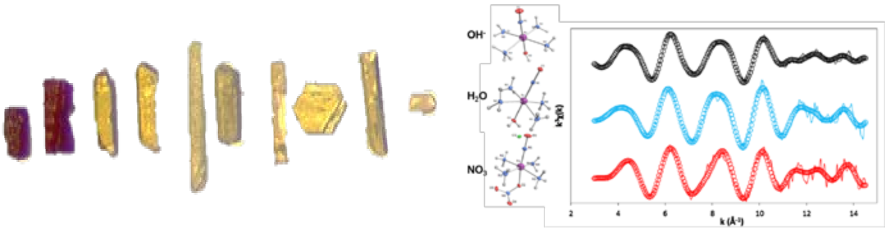

ABSTRACT

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 $[RuNO(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5-x-y-z}]^{3-(x+y+z)}$ 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

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