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A macroscopic and molecular study for a complete description of technetium (VII) and uranium (VI) co-extraction mechanism with monoamides

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DE LA RECHERCHE À L'INDUSTRIE

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A MACROSCOPIC AND MOLECULAR STUDY FOR A COMPLETE DESCRIPTION OF TECHNETIUM (VII) AND URANIUM (VI) CO-EXTRACTION MECHANISM WITH MONOAMIDES

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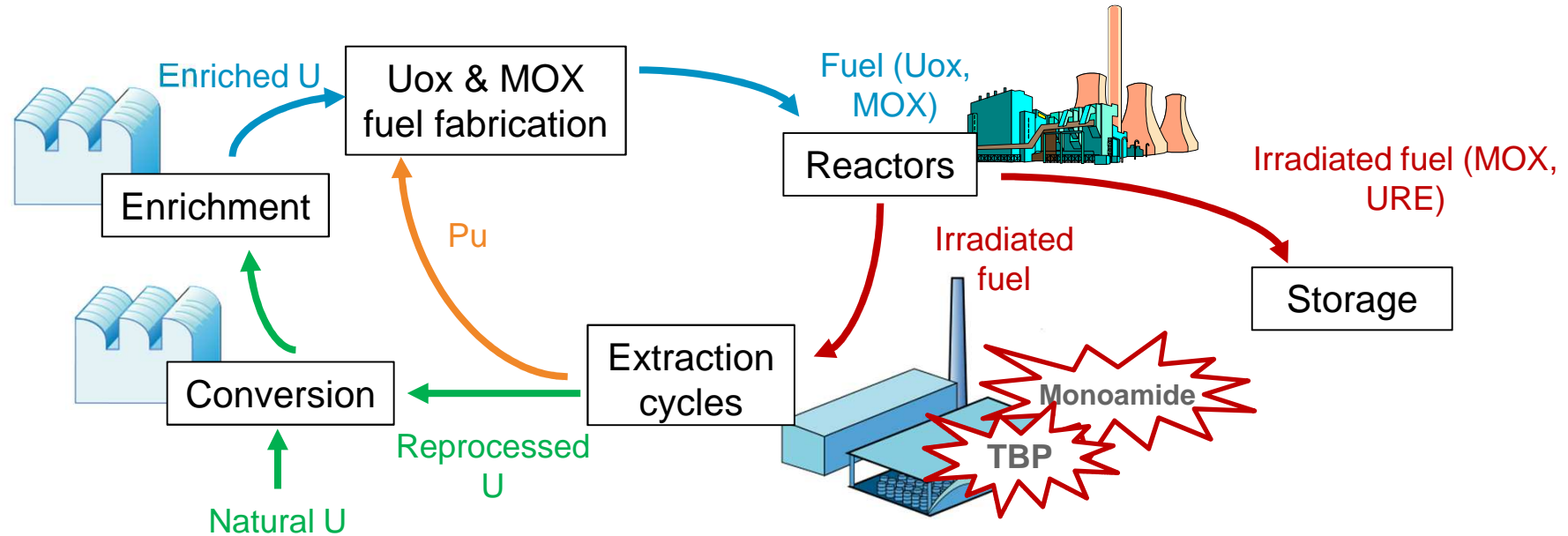
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RANC 2016

Budapest, April 12th 2016





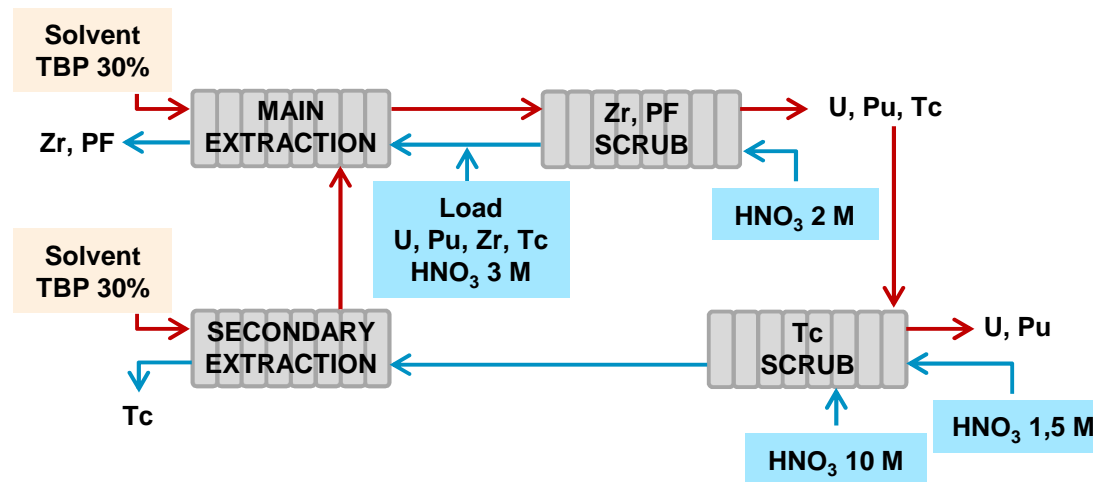
Monoamides for U & Pu extraction ...

- Innovative liquid-liquid extraction processes for the reprocessing of spent nuclear fuels
- Good stability towards radiolysis and hydrolysis

... But what about fission products extraction?

Techneium in the PUREX process

- ^{99}Tc = Long-lived β emitting radionuclide (with a radioactive half-life of 2.1×10^5 y)
- Radionuclide potentially mobile in the environment
- Present as HTcO_4 in nitric acid dissolution solutions
- Can cause some issues in the PUREX process if not correctly scrubbed (hydrazine destruction, U & Pu contamination)
- Measurements implemented in La Hague plant

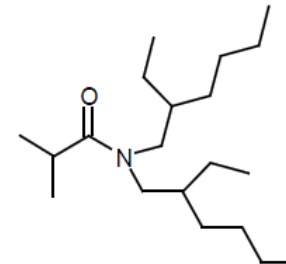


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Towards a new process ...

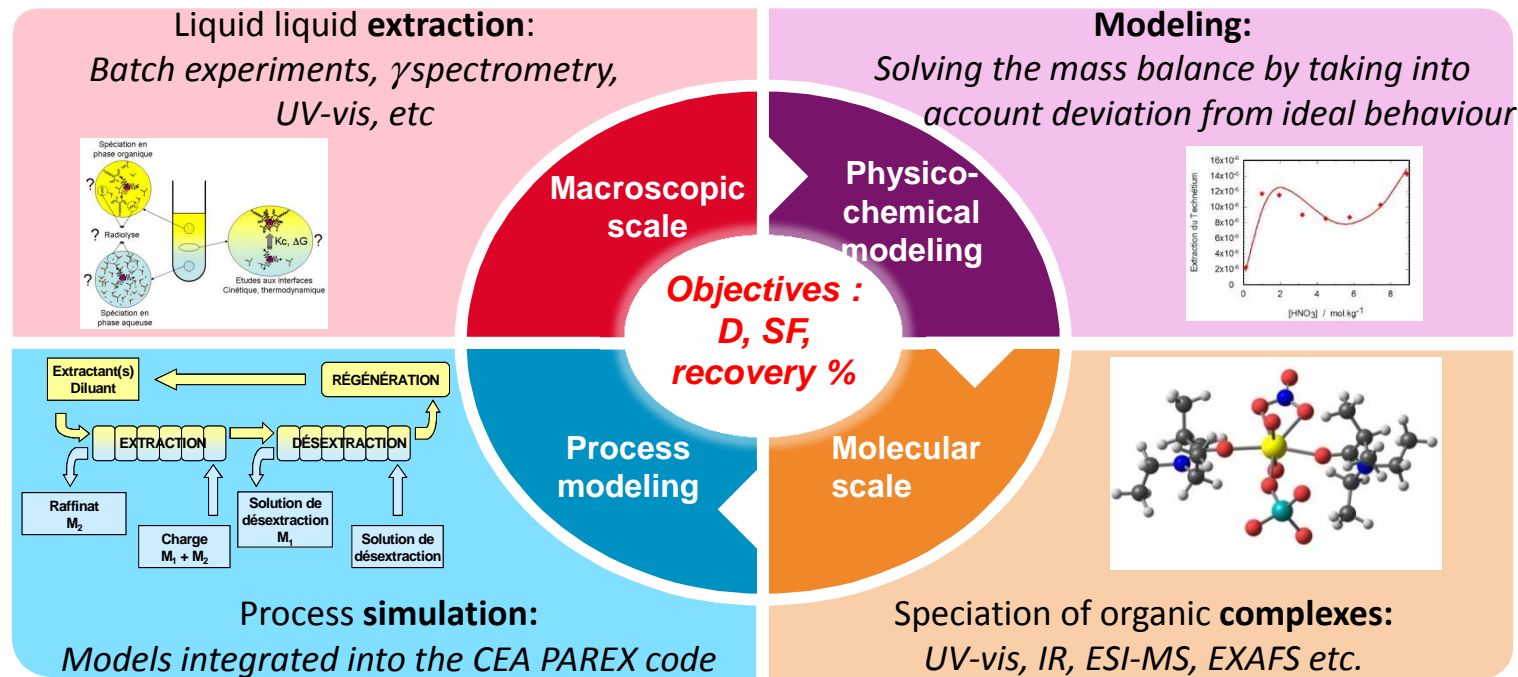
- DEHiBA (N,N-di-2-ethylhexyl-isobutyramide) = promising extractant for future processes



DEHiBA

Objectives:

- Understanding the mechanisms involved in the extraction of technetium with DEHiBA
 - Modeling technetium extraction
- Integrating the model into the CEA PAREX code to improve the modeling of extraction processes and help flowsheets design

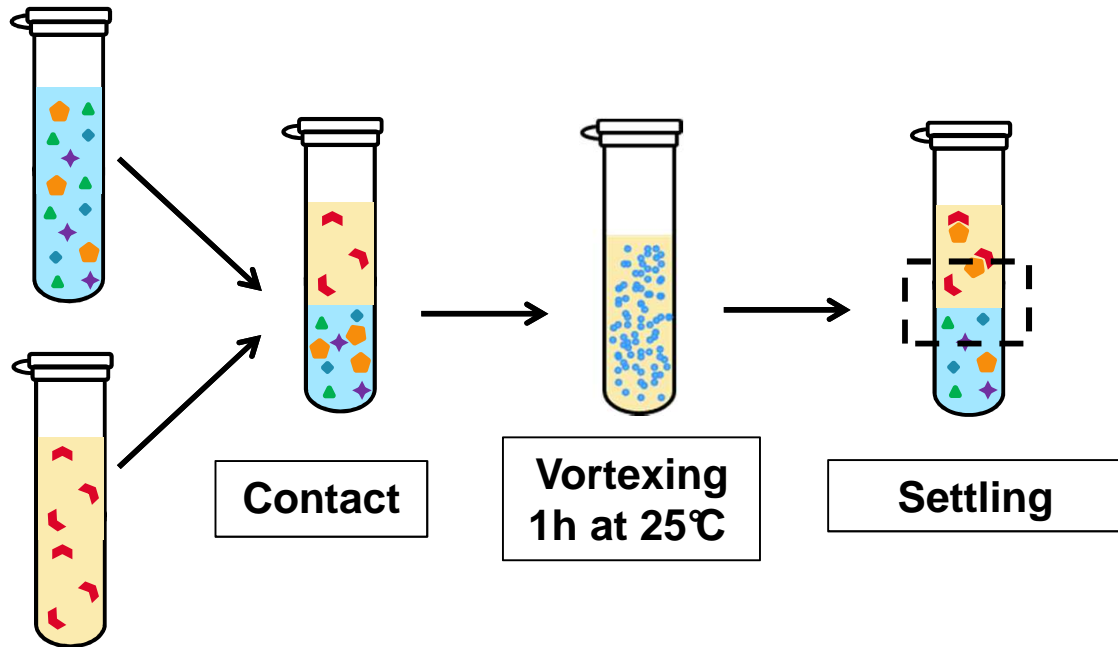


Aqueous phase:

H₂O
HNO₃ 0.1-6 M
UO₂(NO₃)₂ 0-120 g.L⁻¹
HTcO₄ 10⁻³ M + ^{99m}Tc as γ spiker

Organic phase:

DEHiBA / TPH

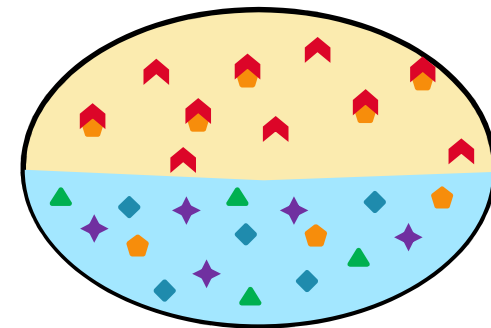


^{99m}Tc = short-lived γ emitter ($T_{1/2} \approx 6$ h)
Used as spiker for Tc measurements

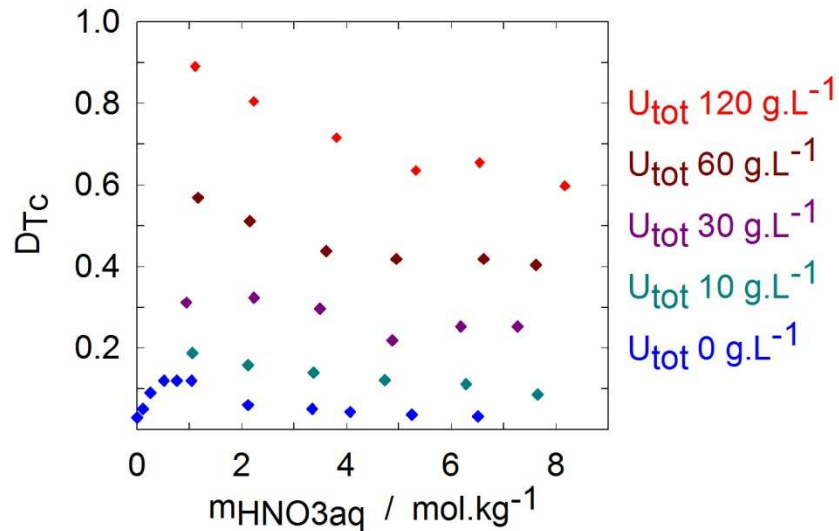


- Acid base titration
- γ spectrometry
- UV-vis spectrophotometry

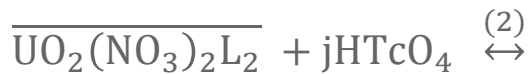
- Acid base titration
- γ spectrometry
- UV-vis spectrophotometry



Experimental results



- $D_{Tc} = [Tc]_{org}/[Tc]_{aq} \nearrow$ when $U_{tot} \nearrow$
- Assumption of the following extraction equilibria:



Mass balance equations

Equilibrium constants:

$$K_1 = \frac{\overline{(HTcO_4)L_i}}{[L]^i [HTcO_4]} \frac{\gamma_{\overline{(HTcO_4)L_i}}}{\gamma_{HTcO_4} \gamma_L^i}$$

$$K_2 = \frac{\overline{UO_2(NO_3)_{2-j}(TcO_4)_jL_2} [HNO_3]^j}{[L]^2 [UO_2(NO_3)_2] [HTcO_4]^j} \frac{\gamma_{\overline{UO_2(NO_3)_{2-j}(TcO_4)_jL_2}} \gamma_{HNO_3}^j}{\gamma_{UO_2(NO_3)_2} \gamma_{HTcO_4}^j \gamma_L^2}$$

Method:

- Free extractant concentration determined by an iterative method based on dichotomy resolution
- Calculation of U, Tc, H, H₂O concentrations in organic phase
- Optimization of the unknown parameter K by an iterative method based on least-squares analysis corresponding to the minimization of:

$$\min \sum \left(\frac{[\overline{X}]_{calc} - [\overline{X}]_{exp}}{[\overline{X}]_{exp}} \right)^2$$

In aqueous phase: the simple solutions theory

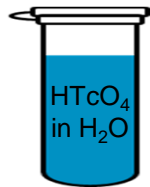
- Simple behaviour of isopiestic solutions (Zdanovskii-Stokes-Robinson)
- Mikulin equation to calculate activity coefficients

$$\gamma_{\text{HTcO}_4} = \frac{\nu_{\text{HTcO}_4} \gamma_{\text{HTcO}_4}^{\text{bi}} m_{\text{HTcO}_4}^{\text{bi}}}{\nu_{\text{HTcO}_4} m_{\text{HTcO}_4} + \nu_{\text{HNO}_3} m_{\text{HNO}_3} + \nu_{\text{UO}_2(\text{NO}_3)_2} m_{\text{UO}_2(\text{NO}_3)_2}}$$

Binary mixture data
= f(a_w)

Real mixture
composition

Procedure for binary data acquisition = triplet (Φ, γ, m)



Measurements of water
activity a_w



Osmotic coefficient
calculation

$$\phi = -\frac{\ln a_w}{\nu m M_{\text{H}_2\text{O}}}$$



Activity coefficient of the
electrolyte by integrating
Gibbs-Duhem equation

$$\ln \gamma = \phi - 1 + \int_0^m \frac{\phi - 1}{m} dm$$

Fitting according to a semi-empirical
equation (ex: NIST, Pitzer, ...)

$$\phi = f(m)$$

m = molality
(mole per kg of solvent)



In aqueous phase: the simple solutions theory

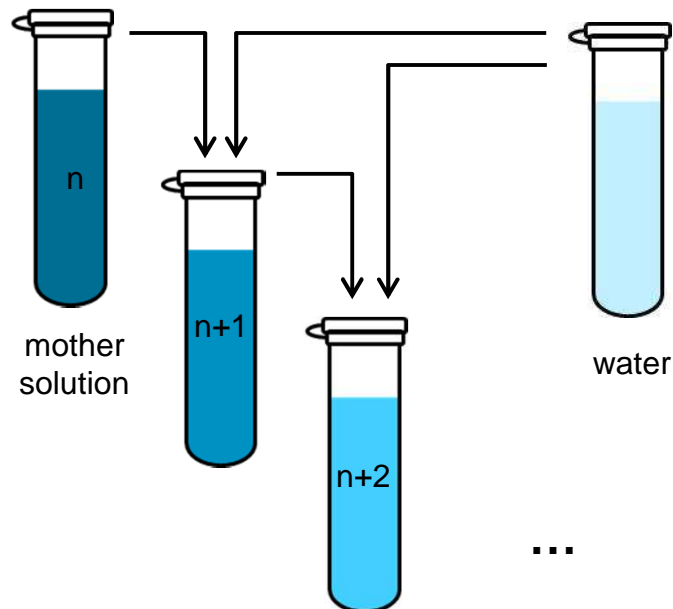
- Simple behaviour of isopiestic solutions (Zdanovskii-Stokes-Robinson)
- Mikulin equation to calculate activity coefficients

$$\gamma_{\text{HTcO}_4} = \frac{v_{\text{HTcO}_4} \gamma_{\text{HTcO}_4}^{\text{bi}} m_{\text{HTcO}_4}^{\text{bi}}}{v_{\text{HTcO}_4} m_{\text{HTcO}_4} + v_{\text{HNO}_3} m_{\text{HNO}_3} + v_{\text{UO}_2(\text{NO}_3)_2} m_{\text{UO}_2(\text{NO}_3)_2}}$$

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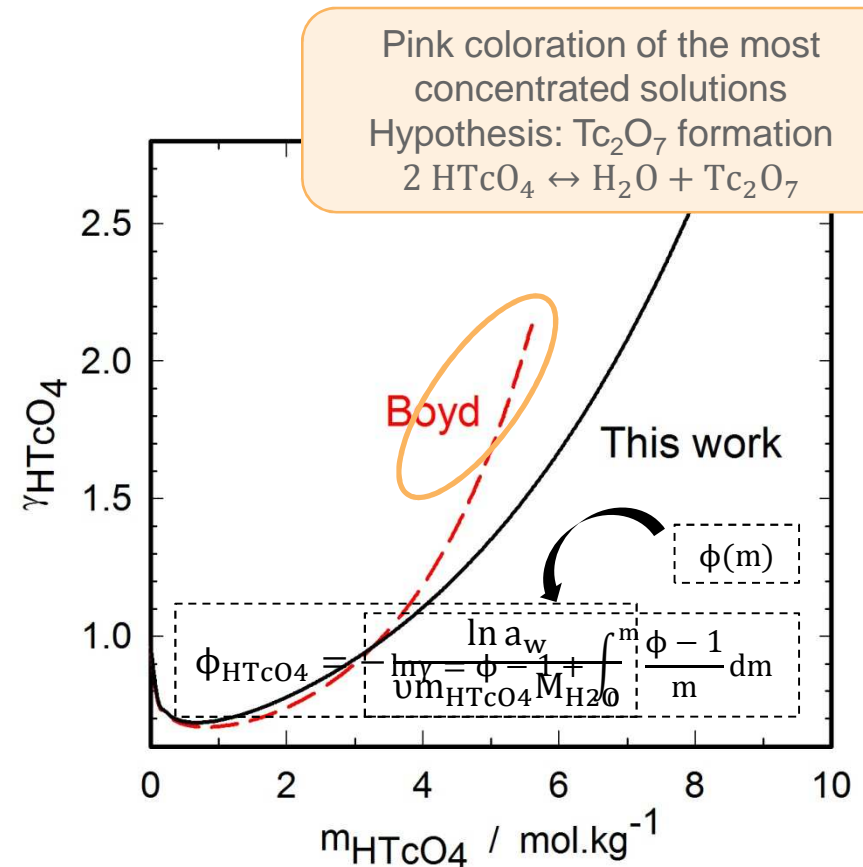


Pertechnetate acid HTcO_4 binary data = triplet $(\Phi_{\text{HTcO}_4}, \gamma_{\text{HTcO}_4}, m_{\text{HTcO}_4})$

New variation of $\gamma = f(m)$

- Boyd's data available in the literature
- New a_w measurements
- New variation implemented in the models

$$\gamma_{\text{HTcO}_4} = \frac{\nu_{\text{HTcO}_4} \gamma_{\text{HTcO}_4}^{\text{bi}} m_{\text{HTcO}_4}^{\text{bi}}}{\nu_{\text{HTcO}_4} m_{\text{HTcO}_4} + \nu_{\text{HNO}_3} m_{\text{HNO}_3} + \nu_{\text{UO}_2(\text{NO}_3)_2} m_{\text{UO}_2(\text{NO}_3)_2}}$$



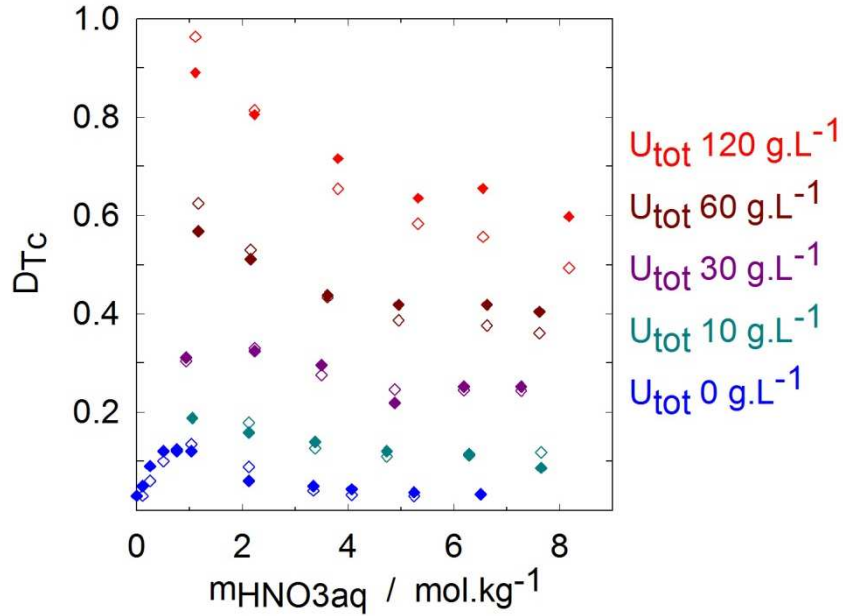
Boyd, G.E., Inorganic Chemistry, 1978. **17**(7): p. 1808-1810.

Moeyaert, P., et al. The Journal of Chem. Therm., 2015. **85**(0): p. 61-67.

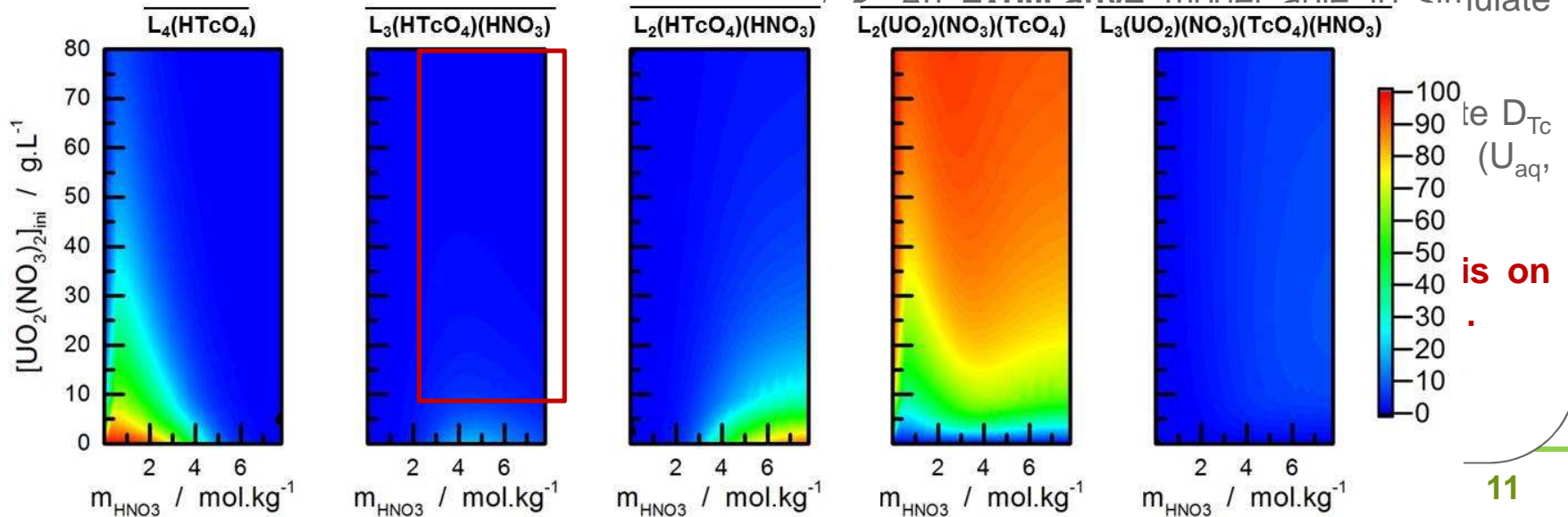
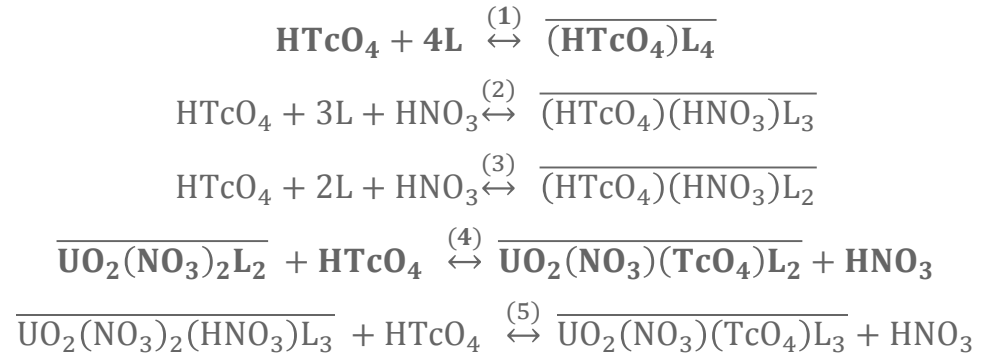
Moeyaert, P., et al. The Journal of Chem. Therm., 2015. **91**(0): p. 94-100.

CEA Thesis L. Abiad

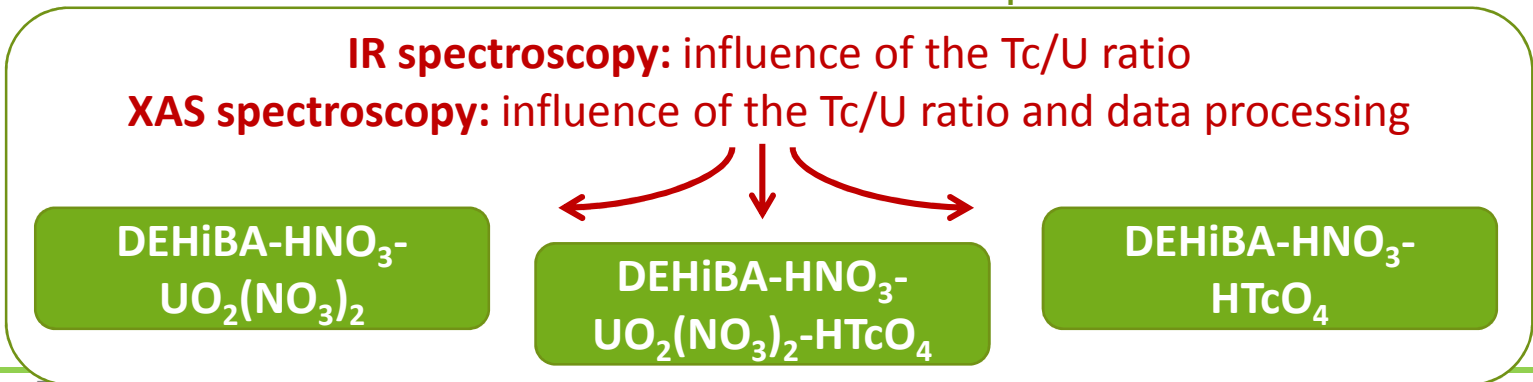
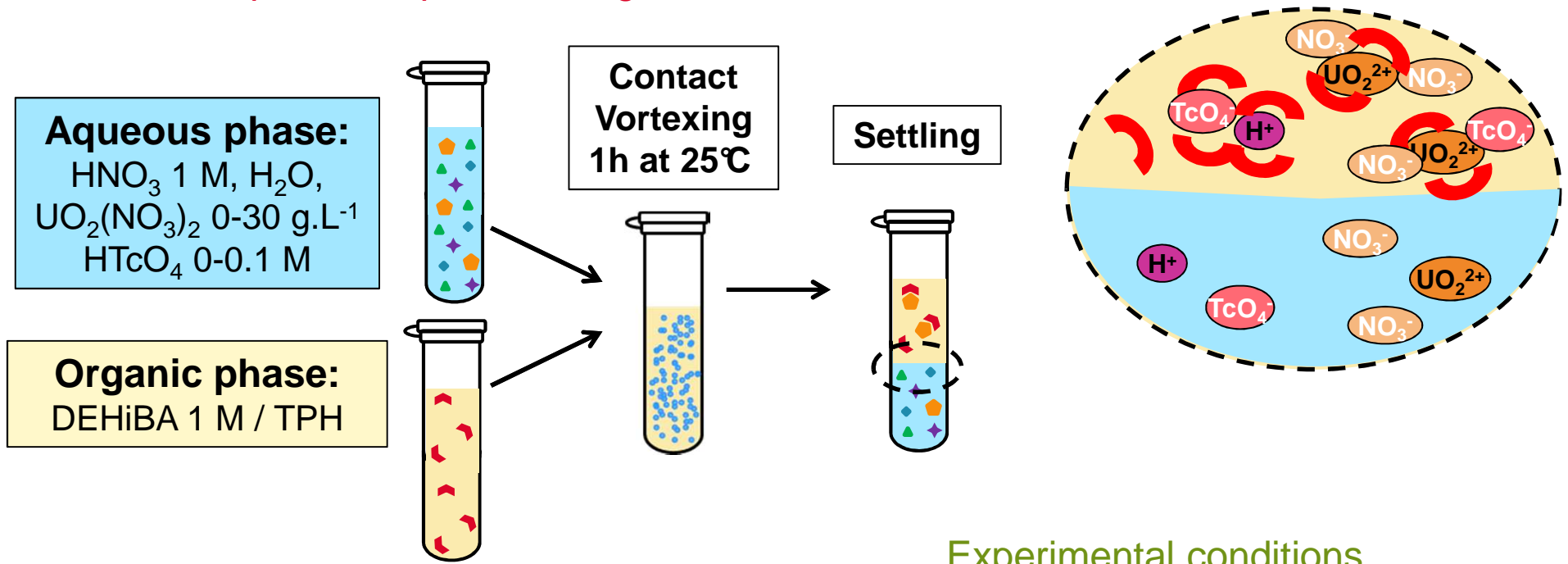
TECHNETIUM EXTRACTION MODELING RESULTS



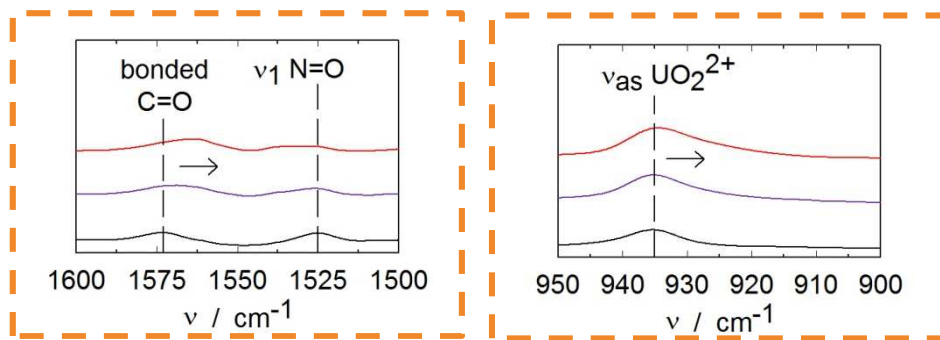
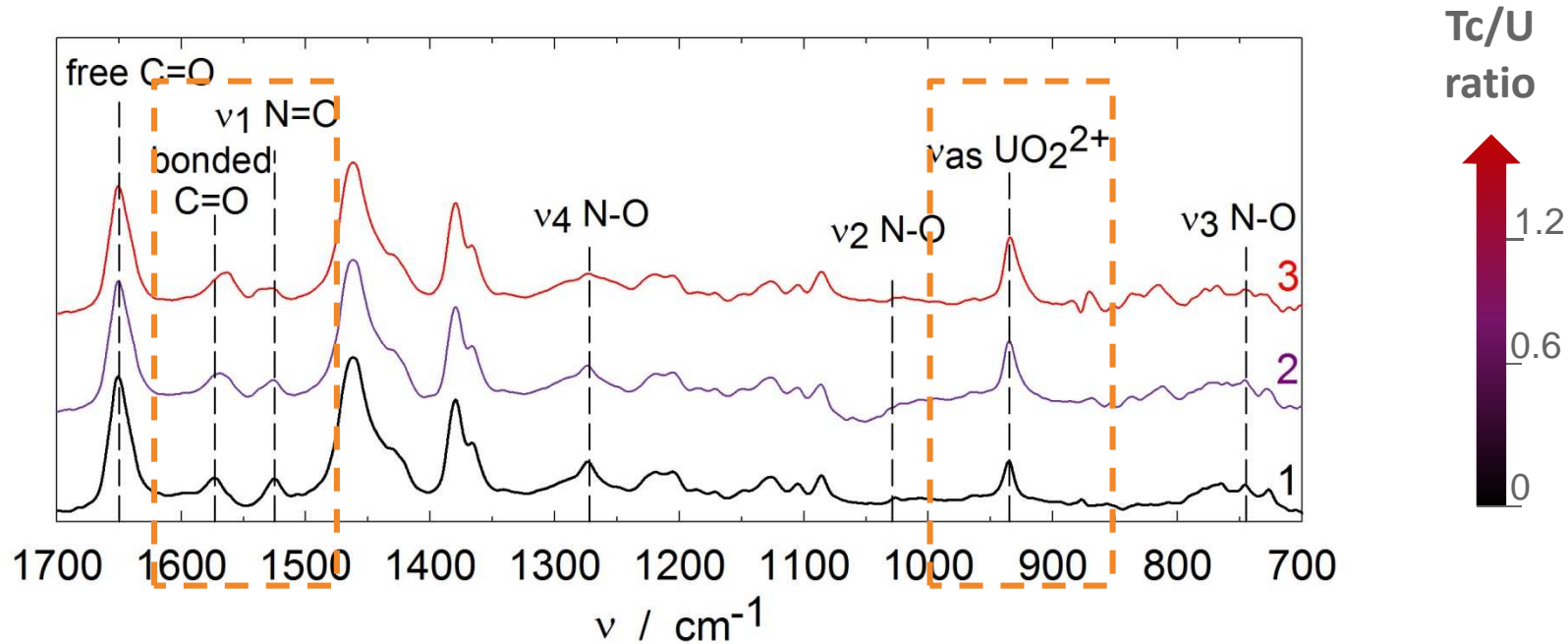
Main extraction mechanisms:



IR and XAS spectroscopies investigations



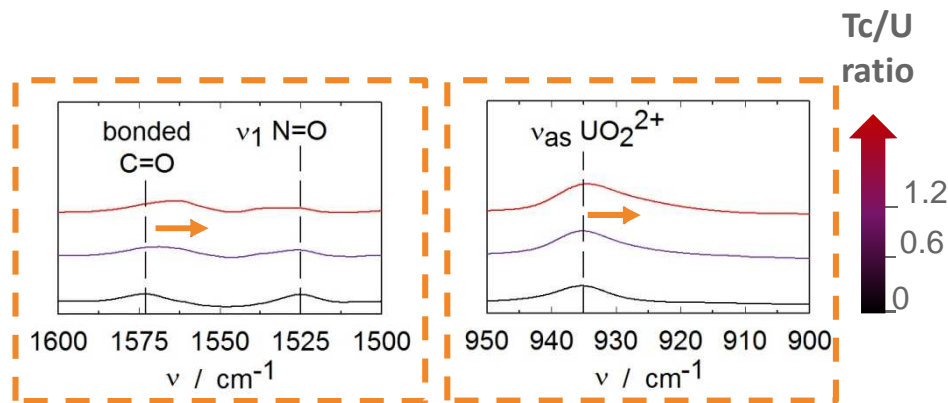
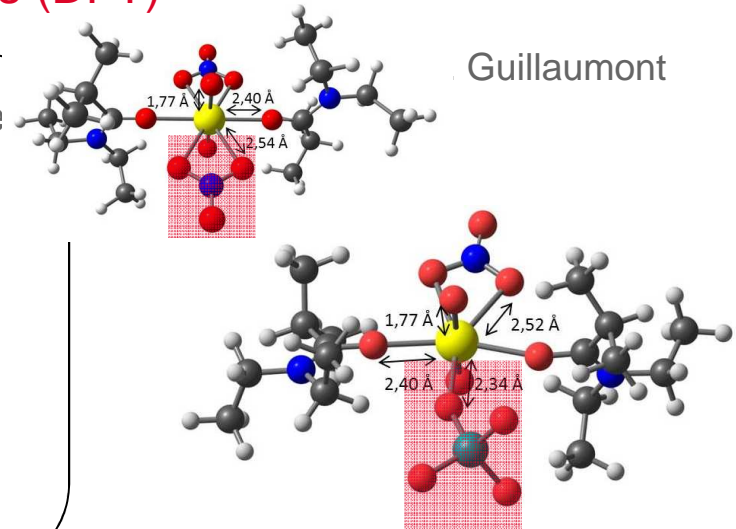
IR spectroscopy



- Bonded C=O and UO_2 stretch shifted to lower frequencies when $[Tc] \nearrow$
- Changes in the intensity and in the shape of the nitrate v_1 N=O stretch when $[Tc] \nearrow$
- ➔ **Changes are occurring in the U(VI) inner coordination sphere when uranium and technetium are co-extracted**

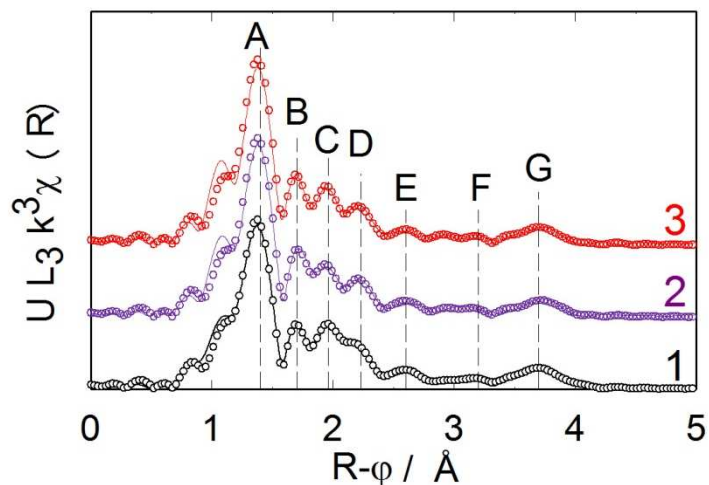
IR spectroscopy combined with theoretical calculations (DFT)

- Optimisation of the $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$ complex structure
- Vibrational frequencies calculation for $\text{UO}_2(\text{NO}_3)_2\text{L}_2$ and $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$ complexes
- ➔ **Confirmation that changes are occurring in the U(VI) inner coordination sphere when uranium and technetium are co-extracted**
- ➔ **Calculated $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$ structure is used as support for XAS data processing**

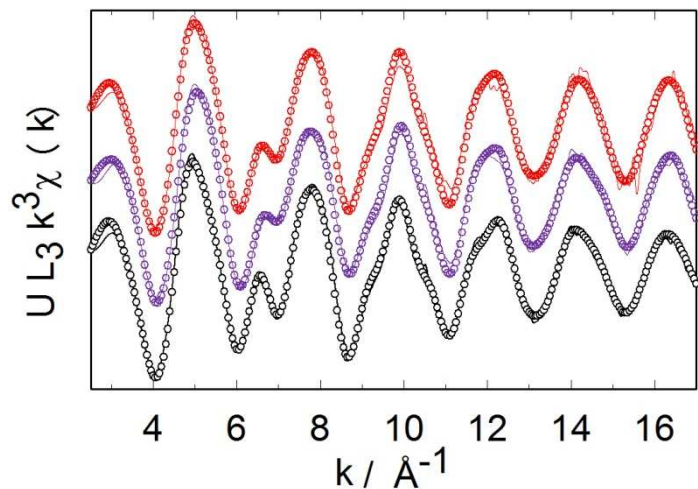


		v / cm ⁻¹	
		Bonded v C=O	ν _{as} UO ₂ ²⁺
exp	Type of vibration		
	$\text{UO}_2(\text{NO}_3)_2\text{L}_2$	1573	935
		v / cm ⁻¹	
		Bonded v C=O	ν _{as} UO ₂ ²⁺
calc	Type of vibration		
	$\text{UO}_2(\text{NO}_3)_2\text{L}_2$	1587	933
	$\text{UO}_2(\text{NO}_3)(\text{TcO}_4)\text{L}_2$	1576	930

XAS spectroscopy



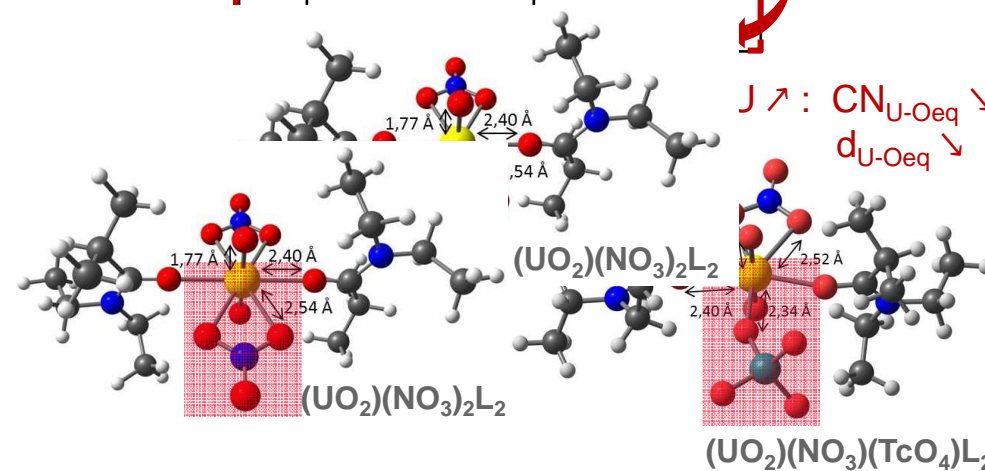
Fourier transform of the k^3 -weighted EXAFS spectra at uranium L_3 edge for U-Tc complexes



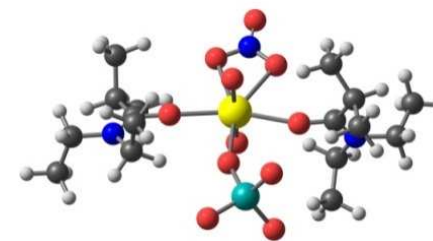
k^3 -weighted EXAFS spectra at uranium L_3 edge for U-Tc complexes



	$CN_{U-O_{eq}}$	$d_{U-O_{eq}} / \text{\AA}$
1	6	2.48
2	5.7	2.47

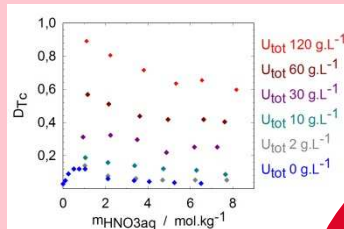
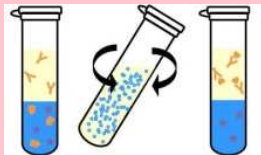
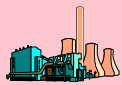


Confirmation of the suggested co-extraction mechanism of U(VI) and Tc(VII)



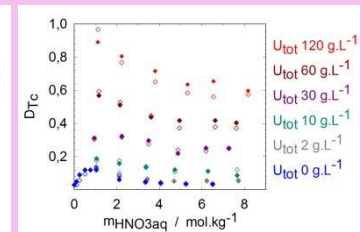
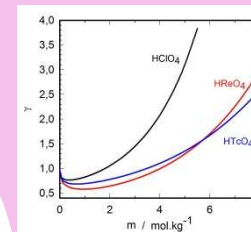
Liquid liquid extraction:

Batch experiments, γ spectrometry, UV-vis, etc



Modeling:

Solving the mass balance by taking into account deviation from ideal behaviour



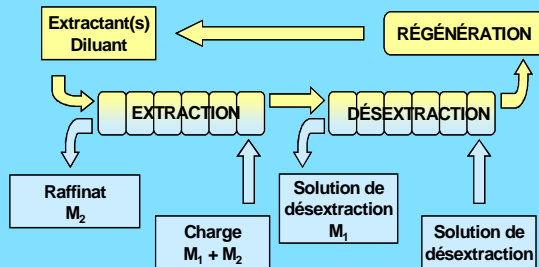
Macroscopic scale

Physico-chemical modeling

Objectives :
D, SF,
recovery %

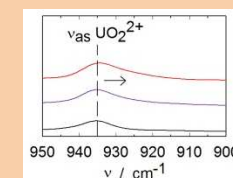
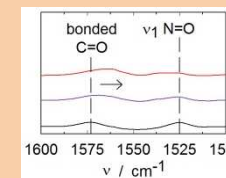
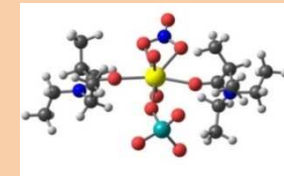
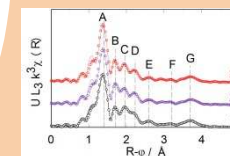
Process modeling

Molecular scale



Process simulation :

Models integrated into the CEA PAREX code



Speciation of organic complexes:

UV-vis, IR, ESI-MS, EXAFS etc.

Moeyaert, P., et al. Inorg. Chem., 2016. Submitted

Aknowledgements

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Dr. Dominique Guillaumont
Dr. Kristina Kvashnina
Pr. Philippe Moisy
Pr. Jean-François Dufrêche



THANK YOU FOR YOUR ATTENTION



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