Plutonium speciation in aqueous solution studied by Pu L_3 and M_5 edge high-energy resolution XANES

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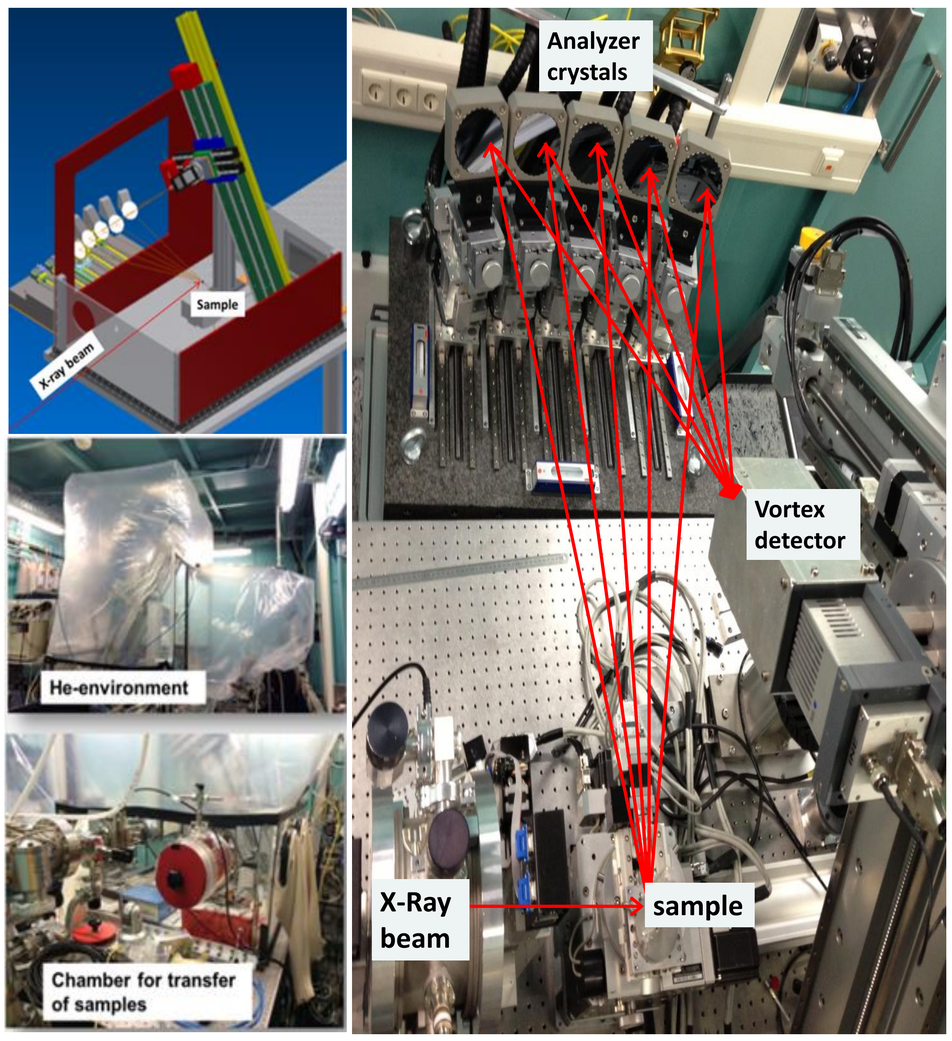
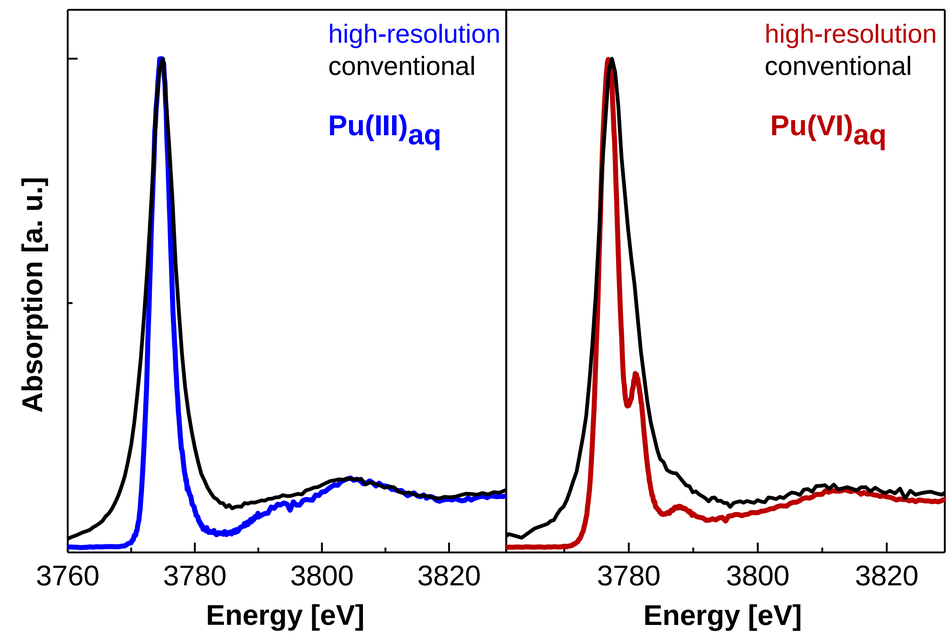
BACKGROUND

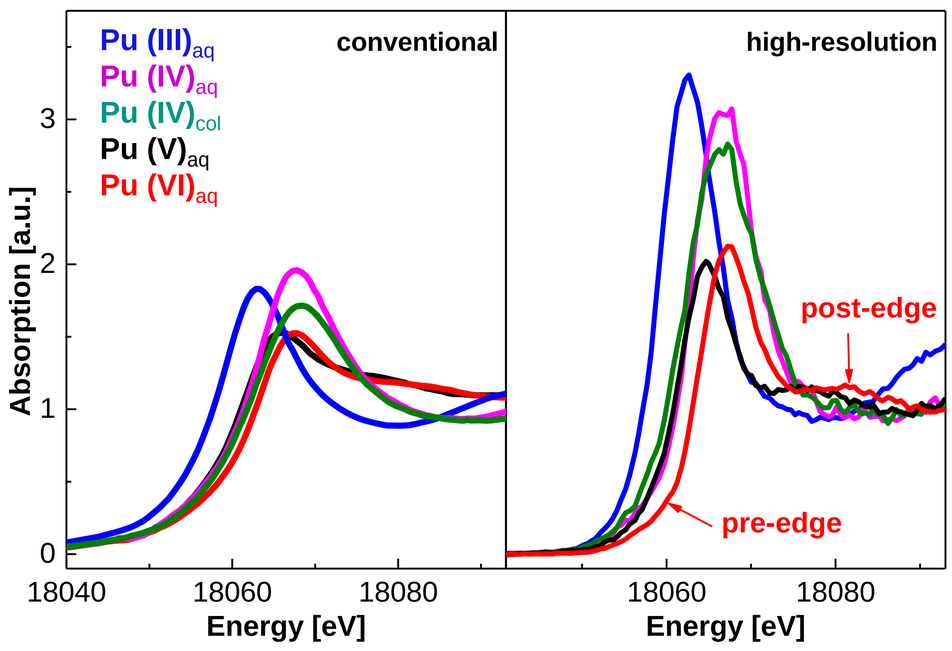
Plutonium (Pu): one of the main radiotoxic elements in Spent Nuclear Fuel
Pu may coexist in four oxidation states: Pu(III), Pu(IV), Pu(V) and Pu(VI)
Precise and reliable experimental techniques are required for Pu speciation



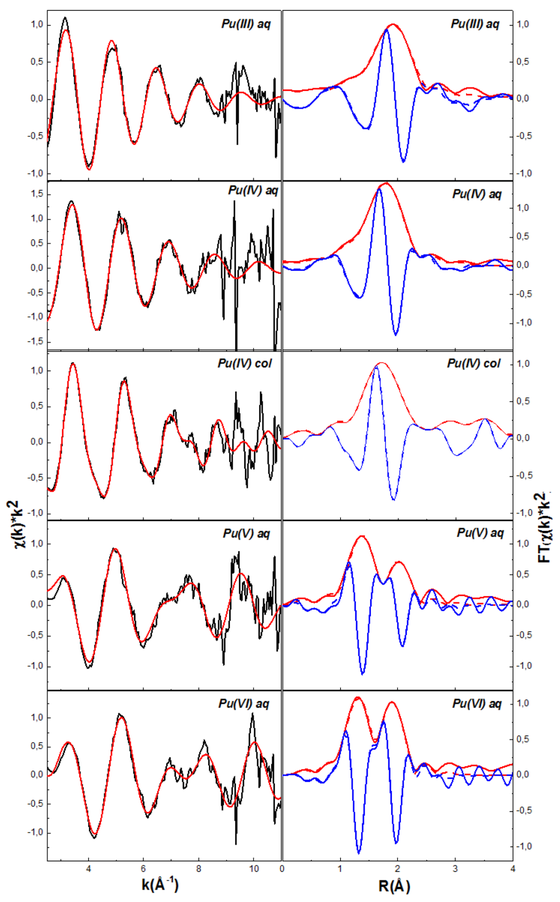
Pu M_5 edge XANES



Pu L_3 edge XANES



EXAFS



Specie	Scattering path	Coordination number, N	Average distance, R(Å)	shift of E_0, ΔE_0(eV)	Debye-Waller factor, σ^2(Å)^2
$Pu(III)_{aq}$	Pu-O	10.5 ± 1	2.48 (1)	-3.2 (8)	0.01 (2)
$Pu(IV)_{aq}$	Pu-O	11.2 ± 0.5	2.34 (1)	-4.4 (5)	0.01 (1)
$Pu(IV)_{col}$	Pu-O Pu-Pu	8.3 ± 1 11.7 ± 3.7	2.29 (1) 3.66 (3)	0.3 (2) -9 (5)	0.01 (3) 0.01 (3)
$Pu(V)_{aq}$	Pu-O ax Pu-O eq	2.0 ± 0.4 2.7 ± 0.3	1.82 (2) 2.50 (1)	5.2 (7) 5.2 (7)	0.0003 (2) 0.0003 (2)
$Pu(VI)_{aq}$	Pu-O ax Pu-O eq	1.7 ± 0.2 3.6 ± 0.4	1.74 (1) 2.39 (1)	5.5 (9) 2.5 (9)	0.0006 (5) 0.0004 (5)

EXPERIMENT

I NE – Beamline

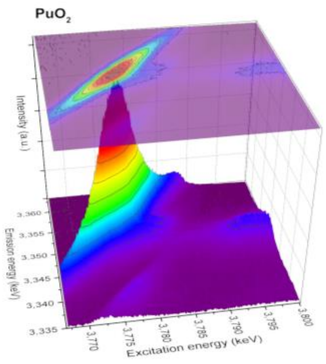
Five-analyzer crystal Johann spectrometer Commissioned in 2013

Pu L_3 HR-XANES
Crystals - Si (777)
Bragg angle θ = 75.7^0
Lα_1 = 14282 eV

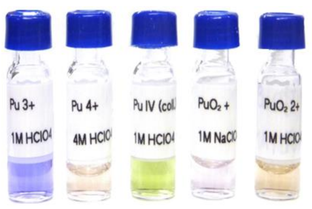
Pu M_5 HR-XANES
Crystals - Si (220)
Bragg angle θ = 75.18^0
Mα_1 = 3340 eV

[Pu] ~ 15-50 mM
Aqueous, colloidal Pu(IV)
$HClO_4$ / $NaClO_4$

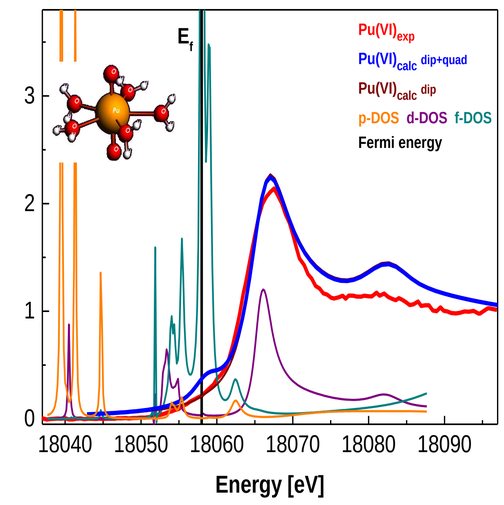
Pu M_5 edge RIXS



Pu oxidation states electrochemistry (INE)



FEFF 9.6 L_3 edge calculation Pu (VI) perchlorate



CONCLUSIONS

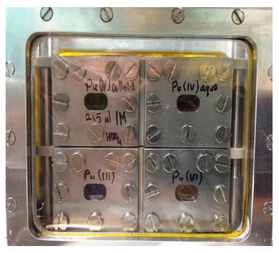
Pu L_3 and M_5 edge high-resolution XANES measured for the first time

All spectra have better energy resolved features: in Pu(VI) L_3 and M_5 edges high-resolution spectra

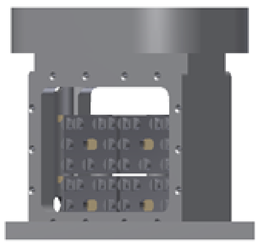
M_5 edge XANES gives new insights into Pu electronic structure

High-energy resolution XANES technique favours detection of minor contributions of Pu in oxidation states mixture

Cell for M edge An XANES
3D model



2x2 chamber cell (13µm Kapton) with aqueous Pu



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ANKA