Supporting information

Sorption and Redox Speciation of Plutonium at the Illite Surface

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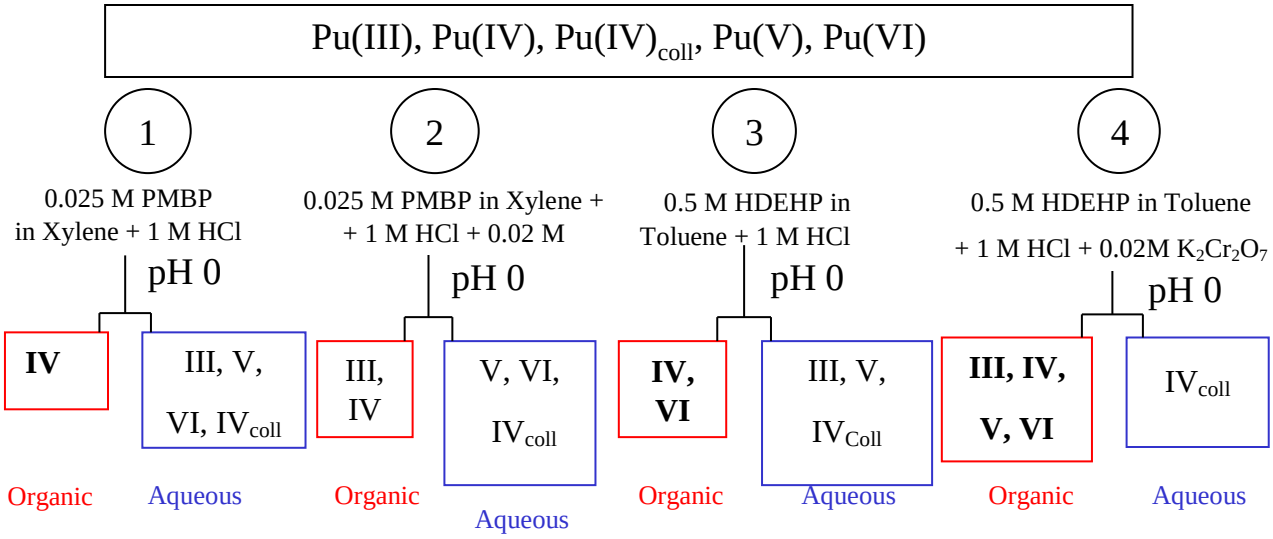
1. Extraction method



Pu(IV) = Extraction 1 (organic)

$Pu(IV)_{coll}$ = Extraction 4 (aqueous)

Pu(III) = Extraction 2 (organic) - Pu(IV)

or

Pu(III) = Extraction 1 (aqueous)- Extraction 2 (aqueous)

Pu(VI) = Extraction 3 (organic) - Pu(IV)

Figure S1. Schematic presentation of the experimental procedure for redox state analysis of Pu in solution by the liquid-liquid extraction method.

2. Thermodynamic calculations

Table S1. Relevant aqueous reactions for the calculations of Pu sorption and speciation in the present study. Thermodynamic constants are taken from the NEA-TDB[1] and refer to the value at infinite dilution. In case of gaps in the available database for Pu, data for analogues are used (i.e. Eu(III), Np(IV), Np(V) and U(VI) for the respective Pu redox states). Although available for Pu, the formation constants for $PuOH^{2+}$ and $Pu(OH)_{4(aq)}$ are taken from Eu(III) and Np(IV) to ensure the consistency between aqueous speciation and surface complexation modeling, i.e. to avoid additional corrections of the literature parameters for the 2 SPNE SC/CE model.

	Reaction	Log K		
Redox	$PuO_2^{2+} + e^- = PuO_2^+$	15.82		
	$PuO_2^{2+} + 4\ H^+ + 2\ e^- = Pu^{4+} + 2\ H_2O$	33.27		
	$PuO_2^{+} + 4\ H^+ + e^- = Pu^{4+} + 2\ H_2O$	17.45		
	$Pu^{4+} + e^- = Pu^{3+}$	17.69		
	Reaction	Available for Pu	Value used	Analogue
Hydrolysis	$AnO_2^{2+} + H_2O = AnO_2OH^+ + H^+$	-5.50	-5.50	
	$AnO_2^{2+} + 2\ H_2O = AnO_2(OH)_2 + 2\ H^+$	-13.20	-13.20	
	$AnO_2^{2+} + 3\ H_2O = AnO_2(OH)_3^- + 3\ H^+$		-20.25	U(VI)
	$AnO_2^{+} + H_2O = AnO_2OH + H^+$		-11.30	Np(V)
	$An^{4+} + H_2O = AnOH^{3+} + H^+$	0.60	0.60	
	$An^{4+} + 2\ H_2O = An(OH)_2^{2+} + 2\ H^+$	0.60	0.60	
	$An^{4+} + 3\ H_2O = An(OH)_3^{+} + 3\ H^+$	-2.30	-2.30	
	$An^{4+} + 4\ H_2O = An(OH)_4 + 4\ H^+$	-8.50	-8.30	Np(IV)
	$An^{3+} + H_2O = AnOH^{2+} + H^+$	-6.90	-7.20	Eu(III)
	$An^{3+} + 2\ H_2O = An(OH)_2^{+} + 2\ H^+$		-15.10	Eu(III)
	$An^{3+} + 3\ H_2O = An(OH)_3 + 3\ H^+$		-26.20	Eu(III)
Chloride	$AnO_2^{2+} + Cl^- = AnO_2Cl^+$	0.23	0.23	
	$AnO_2^{2+} + 2\ Cl^- = AnO_2Cl_2$	-1.15	-1.15	
	$An^{4+} + Cl^- = AnCl^{3+}$	1.80	1.80	
	$An^{3+} + Cl^- = AnCl^{2+}$		0.24	Eu(III)
	$An^{3+} + 2\ Cl^- = AnCl_2^{+}$		-0.74	Eu(III)

Table S2. Site protolysis,[2] surface complexation constants and cation exchange parameters (logK) for the 2 SPNE SC/CE model used in this study for Np(IV/V),[3,4] Eu(III)[5] and Pu(III/IV/V). "An" refers to Np, Pu or Eu. Source is given for each constant between brackets. The asterisk (*) denotes presently determined constants for Pu(IV). The surface site density is $[\equiv S]_{tot} = 2\times10^{-3}$ mol/kg and the cation exchange capacity is $[X]_{tot} = 0.225$ eq/kg.[2] "na" refers to non-available values. Only the reactions and constants relevant for the present study are tabulated.

	Reaction	Np(IV/V)	Eu(III)	Value used for Pu(III/IV/V)
Surface	$\equiv SOH + H^+ = \equiv SOH_2^+$			4.0[(2)]
	$\equiv SOH = \equiv SO^- + H^+$			-6.2[(2)]
	$\equiv SOH + AnO_2^+ = \equiv SO\text{-}AnO_2 + H^+$	-2.0[(3)]		-2.0
	$\equiv SOH + AnO_2^+ + H_2O = \equiv SO\text{-}AnO_2OH^- + 2\ H^+$	-10.3[(3)]		-10.3
	$\equiv SOH + An^{4+} = \equiv SO\text{-}An^{3+} + H^+$	na		na
	$\equiv SOH + An^{4+} + H_2O = \equiv SO\text{-}AnOH^{2+} + 2\ H^+$	na		9.9*
	$\equiv SOH + An^{4+} + 2\ H_2O = \equiv SO\text{-}An(OH)_2^+ + 3\ H^+$	6.4 ± 1.2[(4)]		5.9*
	$\equiv SOH + An^{4+} + 3\ H_2O = \equiv SO\text{-}An(OH)_3 + 4\ H^+$	0.7 ± 1.0[(4)]		0.1*
	$\equiv SOH + An^{4+} + 4\ H_2O = \equiv SO\text{-}An(OH)_4^- + 5\ H^+$	-5.7 ± 1.2[(4)]		-6.4*
	$\equiv SOH + An^{3+} = \equiv SO\text{-}An^{2+} + H^+$		3.1[(5)]	3.1
	$\equiv SOH + An^{3+} + H_2O = \equiv SO\text{-}AnOH^+ + 2\ H^+$		-4.4[(5)]	-4.4
	$\equiv SOH + An^{3+} + 2\ H_2O = \equiv SO\text{-}An(OH)_2 + 3\ H^+$		-12.7[(5)]	-12.7
Exchange	$X\text{-}Na + AnO_2^+ = X\text{-}AnO_2 + Na^+$			0[(3)]
	$3\ X\text{-}Na + An^{3+} = X_3\text{-}An + 3\ Na^+$			1.9[(5)]
	$4\ X\text{-}Na + An^{4+} = X_4\text{-}An + 4\ Na^+$			na

Table S3. SIT parameters (ε(i,k)) used in the present study, taken from the NEA-TDB[1] for Pu or the corresponding analogue (as in Table S1). "na" refers to non-available values (set equal to 0).

i	k	ε(i,k)
H^+	Cl^-	0.12
Na^+	Cl^-	0.03
Na^+	OH^-	0.04
PuO_2^{2+}	Cl^-	0.22
PuO_2OH^+	Cl^-	na
$PuO_2(OH)_3^-$	Na^+	-0.09
PuO_2Cl^+	Cl^-	0.22
PuO_2^+	Cl^-	0.09
Pu^{4+}	Cl^-	0.40
$PuOH^{3+}$	Cl^-	0.20
$Pu(OH)_2^{2+}$	Cl^-	0.10
$Pu(OH)_3^+$	Cl^-	0.05
$PuCl^{3+}$	Cl^-	0.62
Pu^{+3}	Cl^-	0.23
$PuOH^{2+}$	Cl^-	-0.04
$Pu(OH)_2^+$	Cl^-	-0.06
$Pu(OH)_3$	Cl^-	0.00
$Pu(OH)_3$	Na^+	-0.17
$PuCl^{2+}$	Cl^-	0.191
$PuCl_2^+$	Cl^-	0.129

3. Results and discussion

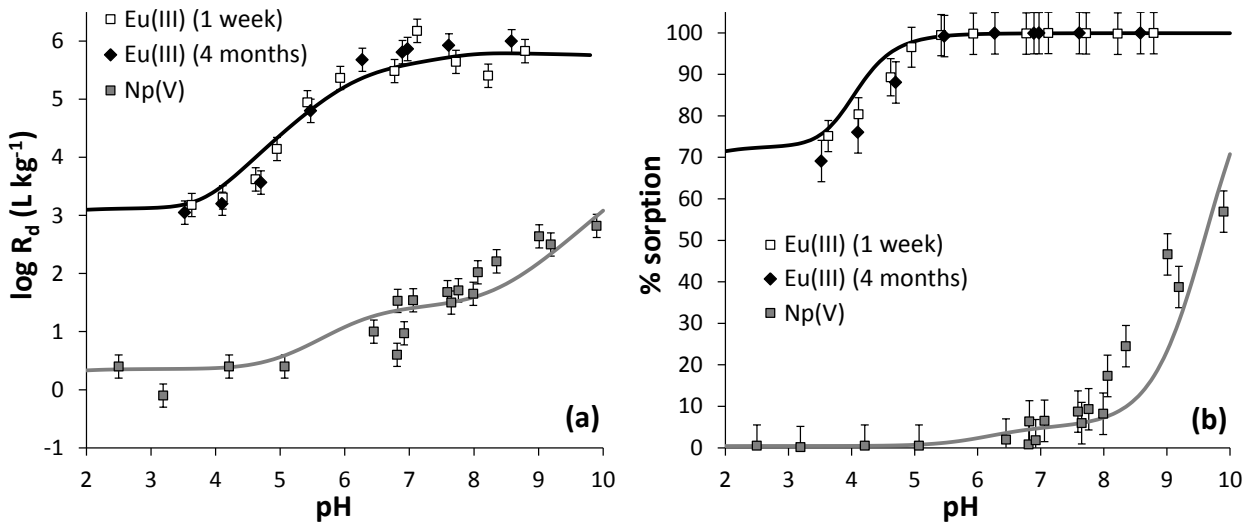


Figure S2. Sorption data for Np(V),[6] and present ones for Eu(III) (measured after 1 week and 4 months equilibration time) on illite presented as (a) log R_d (and error of ± 0.2 is assumed) and (b) percentage sorption for 2 g L^{-1} of illite (and error of ± 5% is assumed). Curves are model results with previously reported constants for the 2 SPNE SC/CE model, tabulated in Table S2.[3,5] No significant aging effect is observed for Eu(III) under our experimental conditions.

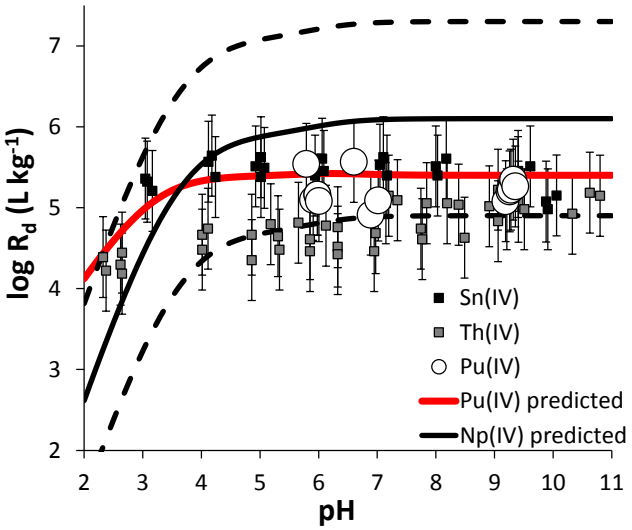


Figure S3. Comparison between experimental sorption data for Pu(IV) (i.e. our data for pH > 6) and other tetravalent elements to illite (Th(IV) and Sn(IV)[2,3]) in 0.1 M $NaClO_4$ versus the pH and the predicted sorption of Np(IV)[4] and Pu(IV) (present work) with the 2 SPNE SC/CE model. Dashed lines show the confidence interval on the surface complexation constants of Np(IV).

4. Experimental results

Table S4. Data recorded after one week and one year equilibration time of Pu with illite. R_d values are given in L kg^{-1}.

$[Pu]_{tot}$ (M)	pH (1 week)	pH (1 year)	pe (1 week)	pe (1 year)	log R_d (1 week)	log R_d (1 year)
8×10^{-11}	3.06	3.04	5.8	8.4	3.1	4.0
8×10^{-11}	3.65	3.66	5.2	9.1	3.8	4.9
5×10^{-10}	4.24	4.26	6.1	7.7	3.9	5.1
1×10^{-8}	4.27	4.28	7.3	6.2	3.6	4.2
1×10^{-10}	4.33	4.30	6.0	7.5	3.9	4.6
3×10^{-9}	4.08	4.30	8.2	6.8	3.6	4.8
8×10^{-11}	4.28	4.35	5.6	9.1	3.8	4.9
8×10^{-10}	4.02	4.37	8.7	6.9	3.6	4.5
8×10^{-9}	4.15	4.38	8.1	6.2	3.6	4.2
8×10^{-11}	5.22	5.15	4.2	7.7	3.9	5.6
8×10^{-11}	5.78	5.41	3.7	7.5	3.9	5.3
8×10^{-11}	6.32	5.79	3.4	7.1	4.0	5.5
8×10^{-11}	6.67	5.91	3.1	6.8	4.0	5.1
1×10^{-10}	6.92	5.98	3.2	5.0	4.3	5.2
3×10^{-10}	6.84	6.01	3.5	5.1	4.4	5.1
8×10^{-11}	7.82	6.60	2.5	5.9	4.8	5.6
1×10^{-8}	7.02	6.89	3.8	4.2	4.0	4.9
8×10^{-11}	8.55	7.02	1.8	5.1	4.6	5.1
8×10^{-10}	9.97	9.19	0.9	2.5	5.2	5.1
1×10^{-8}	9.97	9.26	0.2	2.3	5.4	5.2
8×10^{-11}	9.97	9.28	0.4	2.4	5.4	5.2
3×10^{-9}	9.97	9.32	0.4	2.4	5.3	5.3
8×10^{-9}	9.97	9.36	0.3	2.3	5.7	5.3

Table S5. Results of Pu redox state analysis in solution on contact with illite ($[Pu]_{tot} = 10^{-8}$ M).

Time	pH	pe	% sorption	%Pu(III)	%Pu(IV)	%Pu(V)
1 week	4.27	7.3	89	3	2	92
1 week	7.02	3.8	95	7	77	20
1 week	9.97	0.2	100	2	98	0
1 year	4.28	6.2	97	22	85	0
1 year	6.89	4.2	99	5	96	1
1 year	9.26	2.3	100	4	99	0

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