Electronic Supporting Information

Americium incorporation into studtite: a theoretical and experimental study

Saptarshi Biswas,^a Samuel J. Edwards,^a Zheming Wang,^b Hang Si,^c Luis León Vintró,^d Brendan Twamley,^a Piotr M. Kowalski^{*c} and Robert J. Baker^{*a}

a. School of Chemistry, University of Dublin Trinity College, Dublin 2, Ireland. Email: bakerrj@tcd.ie b. Pacific Northwest National Laboratory, MSIN K8-96, P.O. Box 999, Richland, WA 99352, United

States.

 c. Institute of Energy and Climate Research, IEK-6: Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Strasse, 52428 Jülich, Germany.
d. School of Physics, University College Dublin, Belfield, Dublin 4, Ireland



Fig S1. Powder XRD patterns of studtite at different pH and the product of Am extruded studtite; Black bars studtite (PDF 16-0206), red bars metastudtite (PDF 16-0207).



Fig S2. Gamma spectroscopy results from Am incorporation (top); solid after treatment with water (middle) and water layer (bottom).



Fig. S3. Raman spectra for the precipitates from Am co-precipitation and contacting reactions.

Further computational information

To understand the binding of Am into the structures of studtite and metastudtite, the projected electronic density of states of different oxygen atoms, namely americinyl (O_{yl}), peroxo (O_{peroxo}) and water (O_w) have been computed and are reported in the panels of Figure S4. The calculations were done on DFT+U ground states charge densities (see main text for details). In order to realistically describe the orbitals in solids (i.e. to use realistic projectors), we constructed the projectors using a maximally localized Wannier functions approach [1,2]. These results were produced in similar fashion as in our recent studies of mixed uranium oxides [3] and result in realistic prediction of the band gaps (~2 eV).

For the case of Am(V), the associated states form in the band gap (region between -2 eV and 2 eV); these states compose of oxygen americinyl and peroxo p states and Am f states. In the case of Am(III) this is a purely 5f state and has much lower energy than that which forms in Am(III), indicating the enhanced stability of Am(III). We note also that the band gap state in metastudtite has a lower energy than in studtite, which contributes to stronger binding of Am(V) in the former phase.



Fig. S4. The partial electronic density of states for studtite (left) and metastudtite (right) with: (a) Am(V) and (b) Am(III). The color lines represent the contributions from p states of different oxygen atoms (americinyl (O_{yl}, red), peroxo (O_{peroxo}, green) and water (O_w, blue)) and Am 5f (f, brown). The black solid line represents the total density of state.

M-O bond (Å)	Am-ST	Np-ST	Am-MST	Np-MST
M(VI)-O _{yl}	1.79	1.79	1.79	1.78
M(VI)-O _w	2.38	2.39	2.38	2.41
M(VI)-O _{peroxo}	2.41	2.40	2.41	2.40
M(V)-O _{yl}	1.89, 2.09 (OH)	1.87, 2.10 (OH)	1.96, 2.05 (OH)	1.90, 2.01 (OH)
$M(V)$ - O_w	2.36	2.41	2.38	2.41
M(V)-O _{peroxo}	2.41	2.41	2.40	2.42
M(IV)-O _{yl}	2.16	2.16	2.20	2.21
M(IV)-O _w	2.38	2.38	2.40	2.40
M(IV)-O _{peroxo}	2.40	2.42	2.39	2.40
M(III)-O _{yl}	2.32 (H ₂ O), 2.49 (H ₂ O)	2.15 (OH), 2.41 (H ₂ O)	2.35 (OH), 2.42 (H ₂ O)	2.34 (OH), 2.43 (H ₂ O)
M(III)-O _w	2.39	2.37	2.41	2.45
M(III)-O _{peroxo}	2.44	2.36	2.45	2.48

Table S1. Structural information from the computed incorporation of M = Am and Np (*M*-O bonds)



Fig. S5. Experimental and fitted Raman spectrum of Am + studtite after leaching experiments.

Further emission data



Fig. S6. Time-resolved luminescence spectra of Am-incorporated studtite at 10 K at different delay times (λ_{ex} =415 nm).

References

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