Hydrolysis of uranium(VI), neodymium(III) and cerium(III/IV) by thermal decomposition of urea

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Outline

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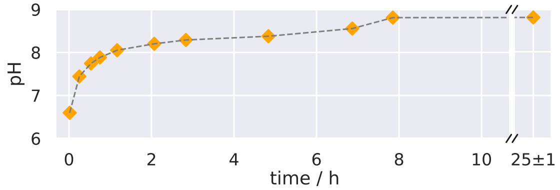
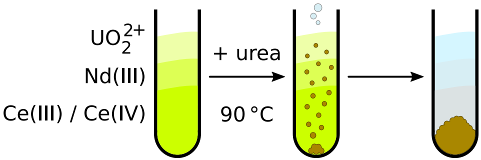
Decomposition of urea

Urea decomposition leads to ammonia and bicarbonate formation[1]:

$$CO(NH_2)_2 + H^+ + 2\,H_2O \longrightarrow HCO_3^- + 2\,NH_4^+$$



👉 The resulting pH increase is used to trigger the hydrolysis of UO_2^{2+}, Nd^{III}, Ce^{III} and/or Ce^{IV} cations.



Reaction follow-up via

- pH, UV/Vis and ICP-MS of supernatant

Characterisation of precipitates by

- XRD and SEM

[1] Soler-Illia et al. 1999. DOI: 10.1021/cm9902220.

Metal compositions and hydrolysis conditions

Conditions adopted from a study on Th hydrolysis[2].

Metal precursors:

$UO_2(NO_3)_2 \cdot xH_2O \rightarrow UO_2^{2+}$

$Nd(NO_3)_3 \cdot 6\,H_2O \rightarrow Nd^{III}$ (Am^{III} surrogate)

$Ce(NO_3)_3 \cdot 6\,H_2O \rightarrow Ce^{III}$ (Pu^{III} surrogate)

$(NH_4)_2[Ce(NO_3)_6] \rightarrow Ce^{IV}$ (Pu^{IV} surrogate)

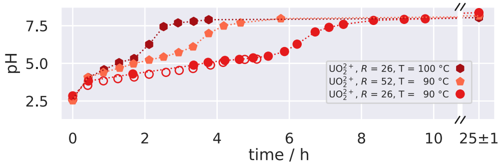
- $c(M^{n+}) = 0.05\,\mathrm{mol\,L^{-1}}$
- c(urea): $1.30\,\mathrm{mol\,L^{-1}}$ or $2.60\,\mathrm{mol\,L^{-1}}$
- R(urea): 26 or 52 $\quad R(\mathrm{urea}) = \frac{n(\mathrm{urea})}{n(M^{n+})}$
- T: 90 °C or 100 °C

molar metal fraction				R(urea)	T
UO_2^{2+}	Nd^{III}	Ce^{III}	Ce^{IV}		/ °C
1.00				26	100
1.00				26, 52	90
	1.00			26	90
		1.00		26	90
			1.00	26	90
0.90	0.10			26, 52	90
0.75	0.25			26, 52	90
0.80		0.20		26	90
0.80			0.20	26	90
0.55	0.25	0.20		26	90
0.55	0.25		0.20	26	90

[2] Wangle et al. 2018. DOI: 10.1515/ract-2017-2871.

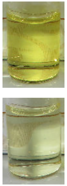
Influence of *R*(urea) and *T* on UO_2^{2+} hydrolysis

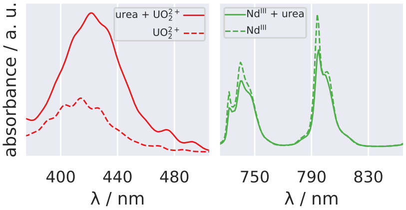
$c(UO_2^{2+})$ = 0.05 mol L^{-1}, *R*(urea) of 26 (90 ℃, 100 ℃) and 52 (90 ℃)



- precipitation of UO_2^{2+} between pH 4.0 and 5.3
- at 90 ℃ doubling urea leads 2× faster precip.
- *T* increase to 100 ℃ precip. in ≈ $\frac{1}{4}$ of time

larger influence of *T* on kinetics than *R*(urea)

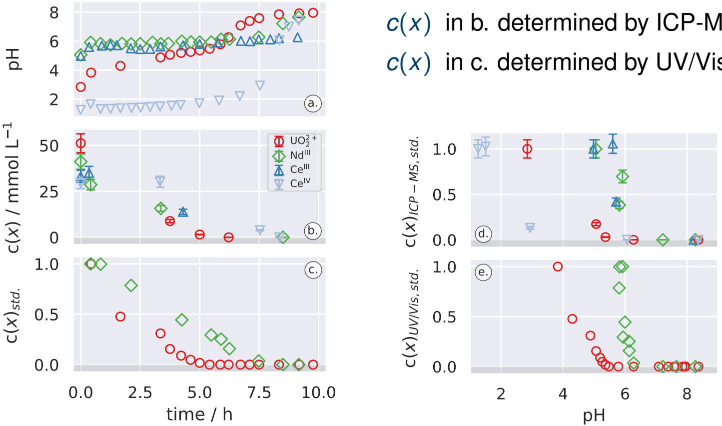




- $A(UO_2^{2+})_{max}$ at 414 nm, urea addition caused A_{max} shift to 421.5 nm indicating a $UO_2[CO(NH_2)_2]_2^{2+}$ complex
- no complexation for Nd^{III} observed
- $A(Ce^{III})_{max}$ at 265 nm (shoulder up to 340 nm) overlaps with $A(NO_3^-)$ at 220 nm; Ce^{IV} has broad *A* up to 500 nm

Hydrolysis pH of individual cations

UO_2^{2+}, Nd^{III}, Ce^{III} and Ce^{IV} ($c(M^{n+})$ = 0.05 mol L^{-1}, R(urea) = 26, T = 90 °C)



$c(x)$ in b. determined by ICP-MS

$c(x)$ in c. determined by UV/Vis

The following precipitation regions could be assigned to the individual cations:

Ce^{IV}: pH 1.3 to 2.9

UO_2^{2+}: pH 4.0 to 5.3

Ce^{III}: pH 5.2 to 6.7

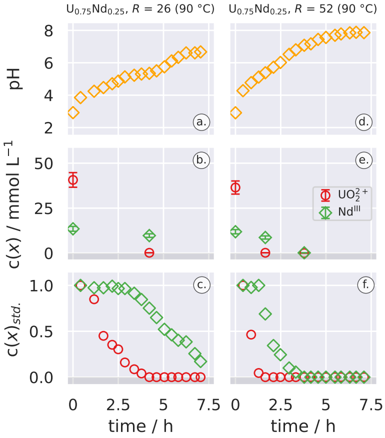
Nd^{III}: pH 5.2 to 6.7

👉 overlapping precipitation pH region for Nd^{III} and Ce^{III}

Hydrolysis of binary UO_2^{2+}/Nd^{III} compositions

Influence of urea content ($c(M^{n+})$ = 0.05 mol L^{-1}, *R*(urea): 26 and 52, *T* = 90 °C)

25 mol% Nd^{III}, *R*: 26/52

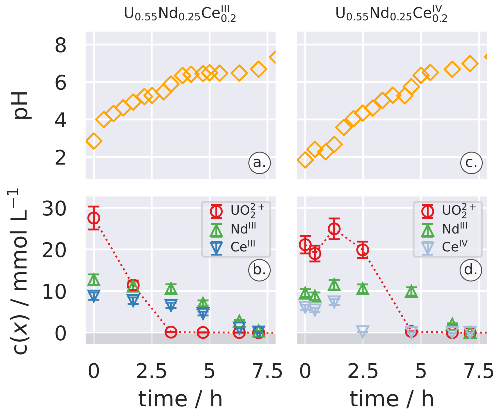


- hydrolysis of both cations about twice as fast when doubling the urea content from a *R* of 26 to 52
- more slowly precip. with *R* of 26 shows a partial overlapping precip. region for UO_2^{2+} and Nd^{III}
- urea content of *R* = 52 less favourable for a co-precipitation
- behaviour independent of the dopant content, similar obervations made for Nd content of 10 mol%

☞ better incorporation of Nd phase into ADU for precipitation with *R* of 26?

Hydrolysis of ternary U/Nd/Ce compositions

Ce^{III} vs. Ce^{IV} ($c(M^{n+})$ = 0.05 mol L^{-1}, R(urea) = 26, T = 90 °C)



55 mol% UO_2^{2+}, 25 mol% Nd^{III} and 20 mol% Ce^{III}:

- simultaneous precipitation of Nd^{III} and Ce^{III}
- small fraction of *Ln* phase might be incorporated into the ADU phase

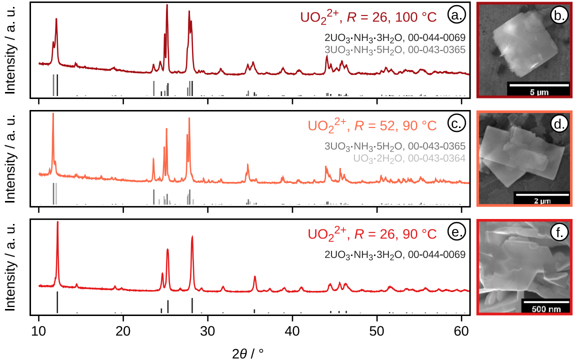
55 mol% UO_2^{2+}, 25 mol% Nd^{III} and 20 mol% Ce^{IV}:

- individual precipitation of Ce^{IV}, UO_2^{2+} and Nd^{III}
- most likely formation of three different phases

👍 better precipitate homogeneity anticipated for composition prepared with Ce^{III} than with Ce^{IV}

Characterisation of UO_2^{2+} precipitates

XRD pattern and SEM micrographs



R(urea) = 26, T = 100 ℃

- $2\,UO_3 \cdot NH_3 \cdot 3\,H_2O$ hexagonal
- $3\,UO_3 \cdot NH_3 \cdot 5\,H_2O$ orthorhombic

R(urea) = 52, T = 90 ℃

- $3\,UO_3 \cdot NH_3 \cdot 5\,H_2O$ hexagonal
- $3\,UO_3 \cdot 2\,H_2O$ orthorhombic

R(urea) = 26, T = 90 ℃

- $2\,UO_3 \cdot NH_3 \cdot 3\,H_2O$ hexagonal

$a = b = 1.410(4)$ Å, $c = 1.451(4)$ Å

The stoichiomety of the ADU phase depends on the $\frac{n(NH_3)}{n(UO_2^{2+})}$ ratio during precipitation.[3]

[3] Cordfunke. 1962. DOI: 10.1016/0022-1902(62)80184-5; Manna et al. 2017. DOI: 10.1016/j.net.2016.09.005.

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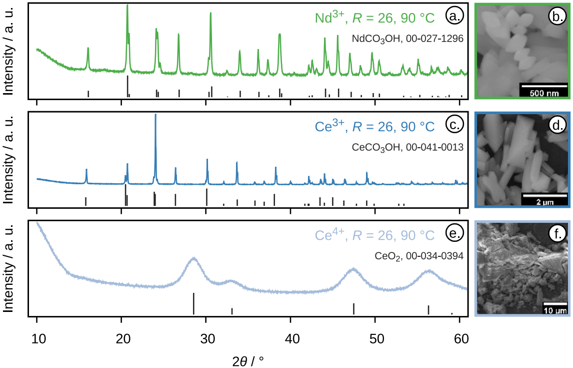
Characterisation of single component precipitates

XRD pattern and SEM micrographs (hydrolysis conditions: *R*(urea) = 26, *T* = 90 ℃)



Nd^{III} precipitate

- $NdCO_3OH$ orthorhombic

  $a = 5.03(4)$ Å, $b = 8.49(8)$ Å, $c = 7.33(6)$ Å

Ce^{III} precipitate

- $CeCO_3OH$ orthorhombic

  $a = 5.00(2)$ Å, $b = 8.50(4)$ Å, $c = 7.31(2)$ Å

Ce^{IV} precipitate

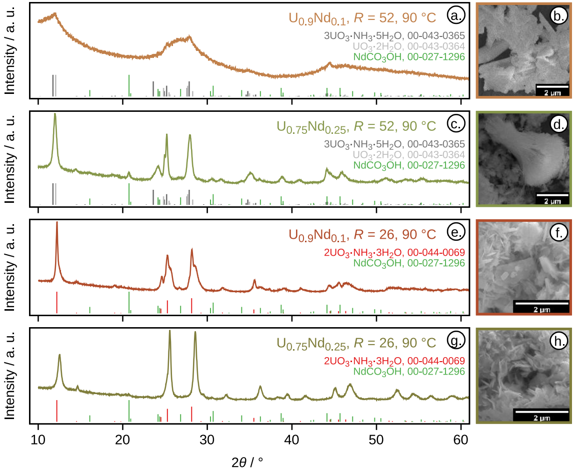
- nanocrystalline CeO_2
  (mean crystallite size of 7 nm)

Lattice parameter of crystalline monophasic compositions correspond to references.[4]

[4] Debets and Loopstra. 1963. DOI: 10.1016/0022-1902(63)80027-5; Dexpert and Caro. 1974. DOI: 10.1016/0025-5408(74)90106-8; Akinc and Sordelet. 1987. DOI: 10.1111/j.1551-2916.1987.tb00087.x.

Characterisation of binary UO_2^{2+}/Nd^{III} precipitates

XRD pattern and SEM micrographs (hydrolysis conditions: *R*(urea): 26 and 52, *T* = 90 °C)



UO_2^{2+}/Nd^{III} precipitates, *R*(urea) = 52

- 10 mol% Nd: amorphous ADU fraction
- 25 mol% Nd: ADU and $NdCO_3OH$ phases

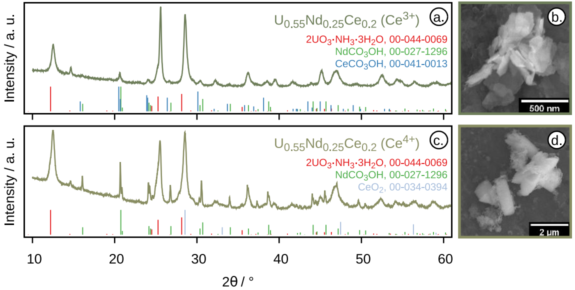
UO_2^{2+}/Nd^{III} precipitates, *R*(urea) = 26

- 10 mol% Nd: *Ln* incorporated in ADU phases
- 25 mol% Nd: *Ln* incorporated in ADU phase, reflection at 20.7° barely visible at close look

☞ no additional *Ln* phases in doped ADU prepared by internal gelation observed

Characterisation of ternary U/Nd/Ce precipitates

XRD pattern and SEM micrographs (hydrolysis conditions: *R*(urea) = 26, *T* = 90 °C)



- more emphasised *Ln* phase, but lower ADU content in precipitates (64.2 wt% and 66.3 wt%) as compared to binary *Ln*/U precipitates
- $2\,UO_3 \cdot NH_3 \cdot 2\,H_2O$ reflections shifted towards higher 2θ, more pronounced for Ce^{III} than Ce^{IV}
- three individual phases visible for composition prepared with Ce^{IV} in (c.) $CeO_2 \rightarrow$ broadening
- significantly lower intensity of *Ln* phase in (a.) suggests partial incorporation of lanthanides into ADU for the composition prepared with Ce^{III}

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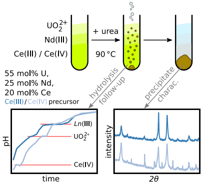
Conclusions

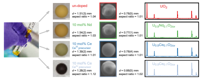
- Complexation of uranyl and urea demonstrated by UV-VIS.
- UO_2^{2+} hydrolyses pH determined for 90 ℃ and 100 ℃.
- Nd^{III}, Ce^{III}, Ce^{IV} hydrolysis pH determined for 90 ℃, confirmed for *Ln*/UO_2^{2+} mixtures.
- Larger influence of temperature than urea content on its decomposition kinetics.
- Precipitation with *R*(urea) of 26 led to monophasic ADU compound and incorporation of the *Ln* phase(s) originating from trivalent *Ln* precursors into the ADU phase.
- Ce^{III} is more suitable than Ce^{IV} for the preparation of Ce-doped ADU, a better precipitate homogenity was observed and a smaller pH difference has to be overcome to complete the precipitation of U and Ce.

Published work



C. Schreinemachers et al.: Hydrolysis of uranyl-, Nd-, Ce-ions and their mixtures by thermal decomposition of urea. In: European Journal of Inorganic Chemistry (submitted). DOI: 10.1002/ejic.202100453

C. Schreinemachers et al.: Data of uranyl-, Nd-, Ce-hydrolysis and their mixtures induced by thermal decomposition of urea. (Version 1.0.0) [Data set], License: CC BY-NC. 2021. DOI: 10.5281/zenodo.3841374



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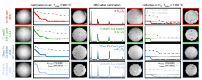

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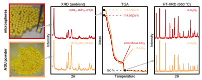

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GEN IV integrated oxide fuels recycling strategies

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economie
FOD Economie, K.M.O., Middenstand en Energie

project: ASOF - Advanced Separation for
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