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Impact of increased temperatures on the geochemical behaviour of trivalent actinides in aquatic systems

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IMPACT OF INCREASED TEMPERATURES ON THE GEOCHEMICAL BEHAVIOR OF TRIVALENT ACTINIDES IN AQUATIC SYSTEMS

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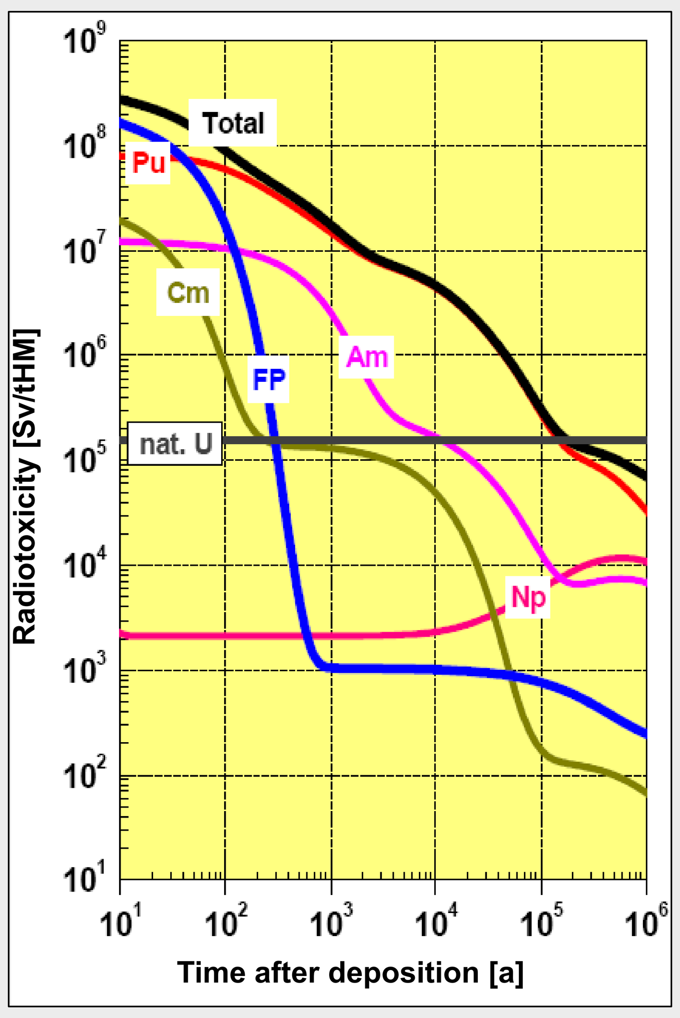
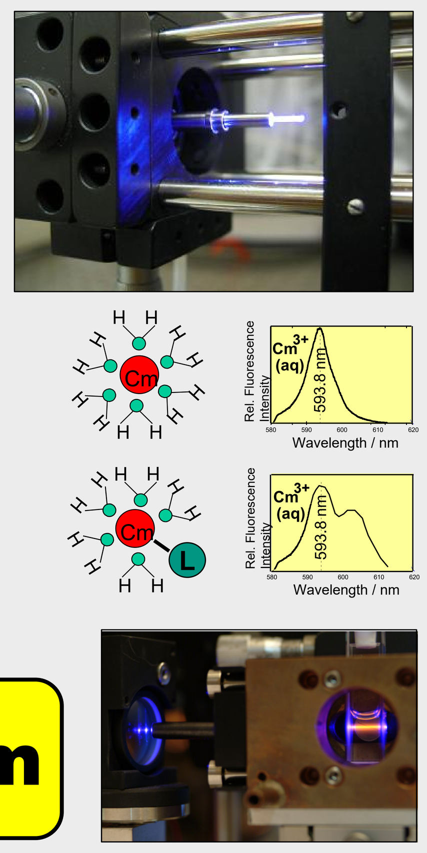
Introduction



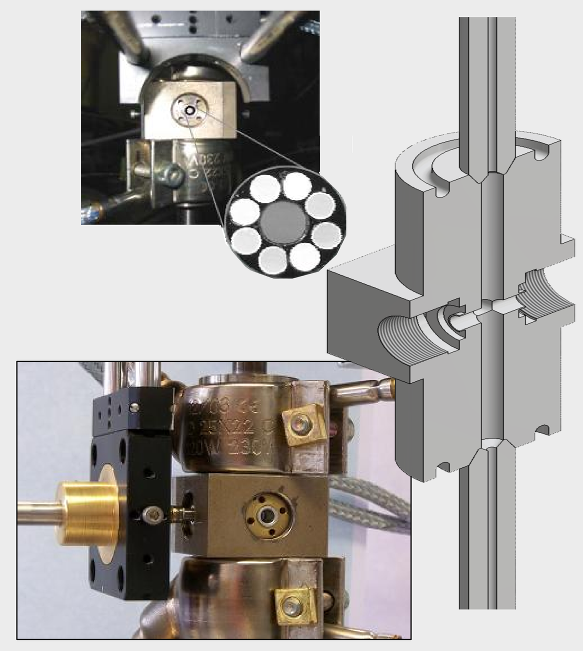
Due to their long half lifes and their radiotoxicity, actinides are of major importance for the long term safety of a nuclear waste repository. An important safety issue is the retention and migration of the actinides in the aquifer of the surrounding host rock of the repository. Therefore, their geochemical behavior under repository conditions must be understood for the Safety Case of a nuclear waste repository. Hereby, elevated temperatures are of interest under near field conditions.

TRLFS

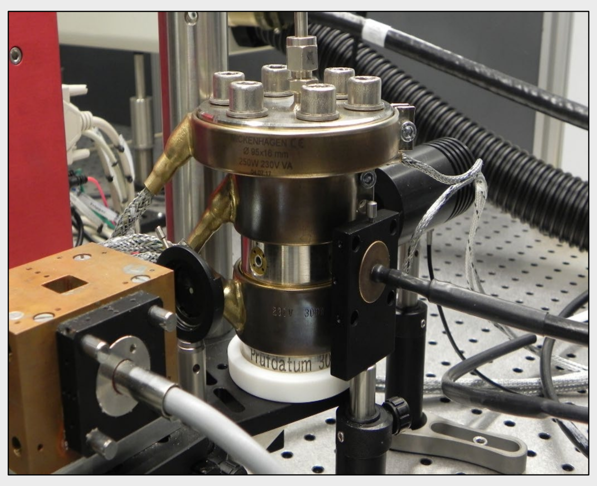


- *Detection limit* of Cm(III) in the sub-micro molar concentration range
- *In situ measurement* without disturbing the chemical equilibrium
- *Emission spectra and fluorescence lifetimes* for the characterization of Cm(III) complexes
- *Measurement in different media:*
  - Aqueous and organic solution
  - Suspension
  - Solid phase
  - Mineral surfaces

High-temperature cells

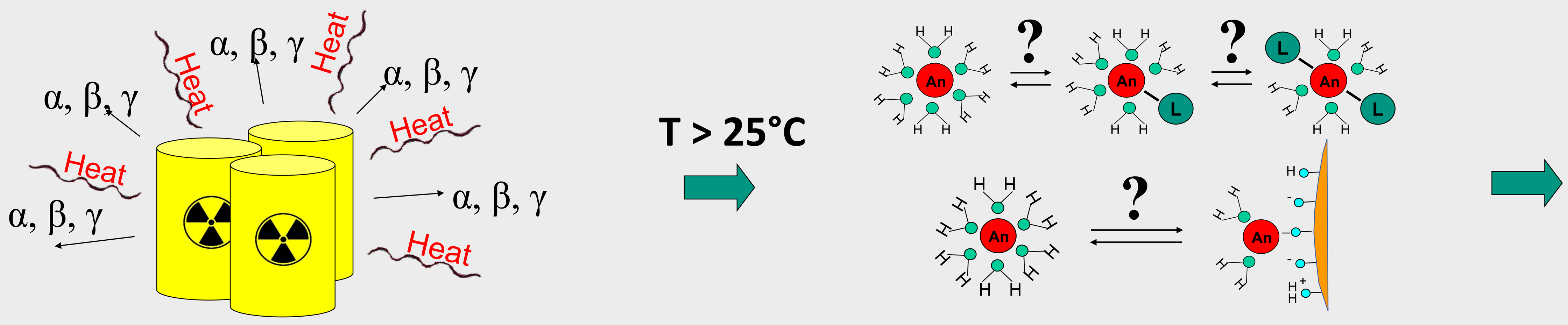


- *Body*: Ti - 0.2wt.% Pd; 4 optical quarz windows
- *Tubings*: TiPd (hot regions), PEEK (cold regions)
- V_{sample}: ~ 2 ml
- T_{max}: 200 °C
- P_{max}: 40 bar
- *Optical fibre*



- *Body*: Stainless steel; 2 optical quarz windows
- *Tubings*: Steel (hot regions), PEEK (cold regions)
- T_{max}: 200 °C
- P_{max}: 40 bar
- P_{max}: 40 bar
- *Variable sample holder*

Why studies at elevated T ?



Temp in the near-field can reach up to 200°C

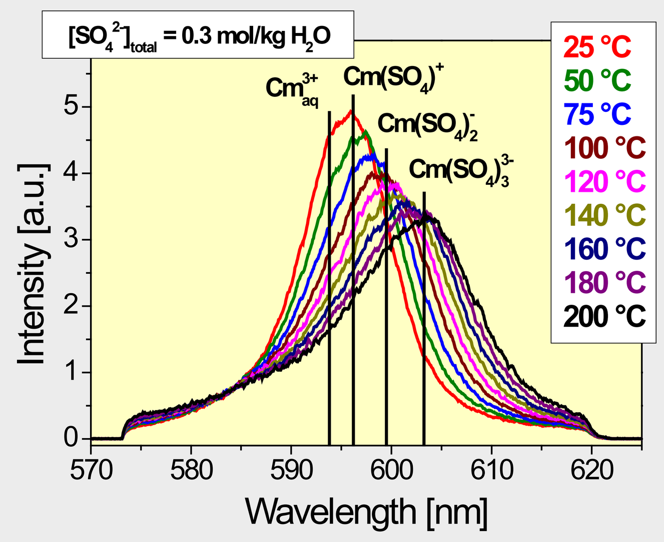
Chemistry at increased temperatures?

Thermodynamic data needed

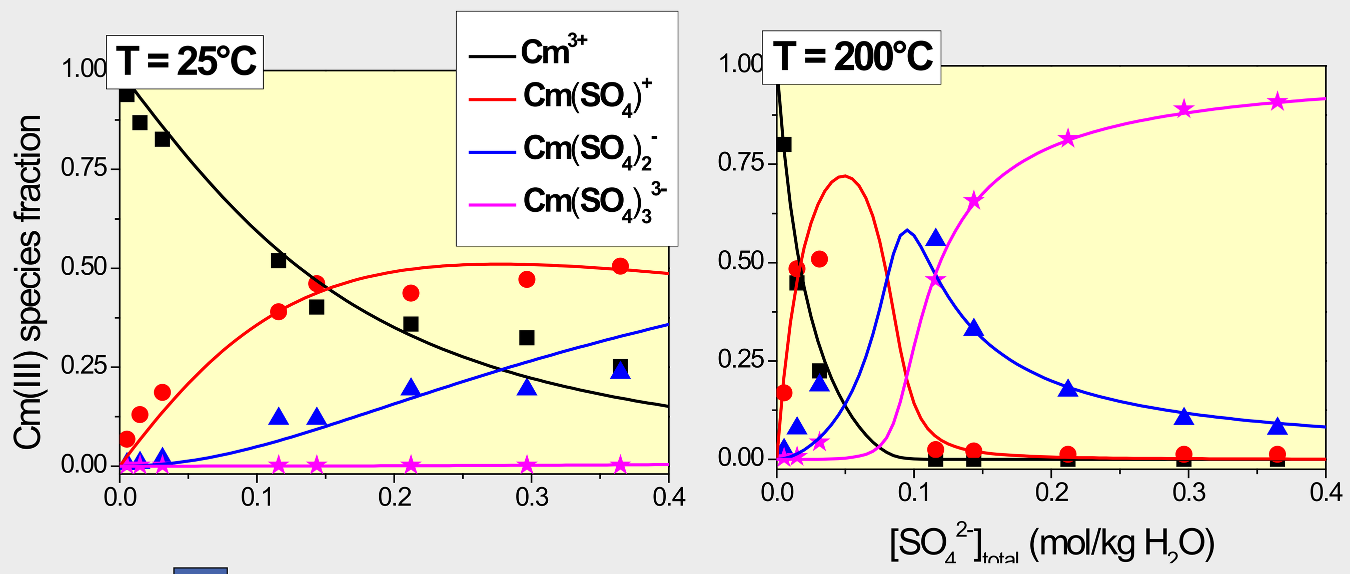
$\Delta_r H^0_m$ | log $K(T)$ | $\Delta_r S^0_m$ | $\Delta_r C^0_{p,m}$ | $\Delta_r G^0_m(T)$

Safety case of a nuclear waste repository

Inorganic ligands – Sulphate, Nitrate, Chloride, Fluoride



- *Exemplary Emission Spectra for the Cm(III)-SO_4^{2-}–System*
  - Strong redshift with increasing T
  - Peak deconvolution reveals chemical speciation
  - Strong favoring of the formation of complexes species at elevated T



- *Extrapolation of conditional data to reference state conditions (I_m = 0)*
  - Specific Ion Interaction Theory (SIT) & Van't Hoff Equation

Ligand	Species	log β^0_n (25°C)	log β^0_n (200°C)	$\Delta_r H^0_m$ / kJ mol^{-1}	$\Delta_r S^0_m$ / J mol^{-1} K^{-1}	$\Delta_r C^0_{p,m}$ / J mol^{-1} K^{-1}
Sulphate	$Cm(SO_4)^+$	3.45 ± 0.13	7.55 ± 0.91	40 ± 2	68 ± 6	280 ± 12
	$Cm(SO_4)_2^-$	4.57 ± 0.57	11.06 ± 1.00	70 ± 8	147 ± 13	430 ± 27
	$Cm(SO_4)_3^{3-}$	3.40 ± 1.50	13.43 ± 1.23	132 ± 15	333 ± 22	-
Nitrate	$Cm(NO_3)^{2+}$	1.29 ± 0.06	2.08 ± 0.24	1.8 ± 1.0	30.5 ± 3.5	170 ± 20
	$Cm(NO_3)_2^+$	0.93 ± 0.12	2.88 ± 0.45	10.8 ± 3.0	53.0 ± 10.0	250 ± 50
Chloride	$Cm(Cl)_2^-$	-0.81 ± 0.35	2.83 ± 0.09	55 ± 5	169 ± 6	40 ± 10
Fluoride	$Cm(F)^{2+}$	3.69 ± 0.05	5.26 ± 0.15	23 ± 5	148 ± 5	-
	$Cm(F)_2^+$	6.88 ± 0.15	10.27 ± 0.13	52 ± 7	306 ± 16	-

Organic ligands – Small Mono- & Dicarboxylic Acids

$(CH_{3/2})_n$-COOH: Formate(n=0), Acetate(n=1), Propionate(n=2)

HOOC-$(CH_2)_n$-COOH: Oxalate(n=0), Malonate(n=1), Succinate(n=2)

Ligand	Species	log β^0_n (20°C)	log β^0_n (90°C)	$\Delta_r H^0_m$ / kJ mol^{-1}	$\Delta_r S^0_m$ / J mol^{-1} K^{-1}
Formiate	$Cm(Form)^{2+}$	2.11 ± 0.07	2.49 ± 0.09	11 ± 1	79 ± 2
	$Cm(Form)_2^+$	-	4.13 ± 0.16	42 ± 9	201 ± 26
Acetate	$Cm(Ac)^{2+}$	3.12 ± 0.32	3.25 ± 0.10	3 ± 13	70 ± 37
	$Cm(Ac)_2^+$	4.60 ± 0.35	5.50 ± 0.60	36 ± 28	209 ± 89
Propionate	$Cm(Prop)^{2+}$	3.34 ± 0.07	3.49 ± 0.11	5 ± 1	80 ± 4
	$Cm(Prop)_2^+$	5.11 ± 0.35	6.36 ± 0.27	38 ± 5	225 ± 12
Oxalate	$Cm(Ox)^+$	6.86 ± 0.03	6.76 ± 0.04	-3 ± 1	122 ± 3
	$Cm(Ox)_2^-$	11.54 ± 0.12	11.79 ± 0.16	8 ± 3	248 ± 6
	$Cm(Ox)_3^{3-}$	13.65 ± 0.17	14.19 ± 0.23	18 ± 5	324 ± 9
Malonate	$Cm(Mal)^+$	5.26 ± 0.22	5.50 ± 0.09	9 ± 2	129 ± 5
	$Cm(Mal)_2^-$	3.12 ± 0.17	8.98 ± 0.33	19 ± 5	223 ± 14
	$Cm(Mal)_3^{3-}$	-	10.50 ± 0.52	32 ± 9	286 ± 26
Succinate	$Cm(Succ)^+$	5.13 ± 0.13	5.27 ± 0.25	2 ± 7	106 ± 22
	$Cm(Succ)_2^-$	7.48 ± 0.23	8.53 ± 0.36	36 ± 10	266 ± 32
	$Cm(Succ)_3^{3-}$	-	9.36 ± 0.45	-	-

Conclussion

- *Strong impact of elevated temperatures on the compleation of trivalent actinides with inorganic and organic ligands*
  - **Succesfull application of custom-built high temperature cells for laserspectroscopic studies up to 200 °C**
  - **Almost all ligands show a distinct increase of log $\beta^0_n(T)$ with the temperature**
  - **Complexation reactions are in general endothermic and entropy driven**
  - **Stronger complexation (e.g. chelating liagand) leads to lower rH0m and weaker temperature dependency.**
- *Formation of new complex species at elevated temperatures possible, which need to be considered for the Safety Case of a Nuclear Waste Repository*

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