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Uranium(VI) Uptake by Synthetic Calcium Silicate Hydrates

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2nd International Workshop
MECHANISMS AND MODELLING OF WASTE/CEMENT INTERACTIONS
Le Croisic, October 12-16 , 2008

Lay-out

- Introduction

- Batch sorption studies:

    Sorption isotherms

- Spectroscopic investigations:
    Time-resolved Laser Fluorescence Spectroscopy
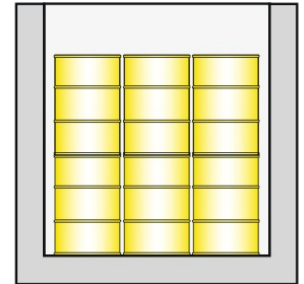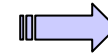
- Conclusions

Safety barrier systems of cementitious repositories

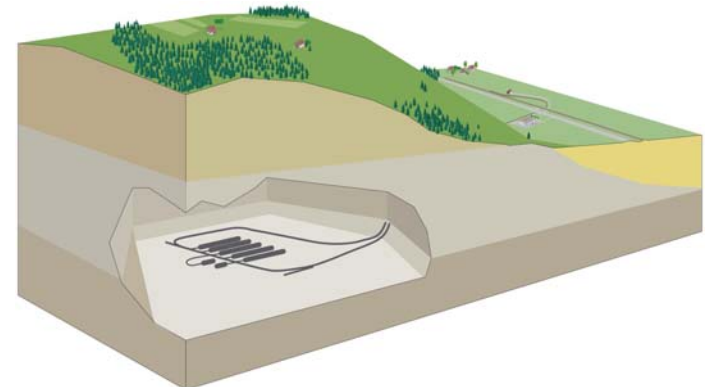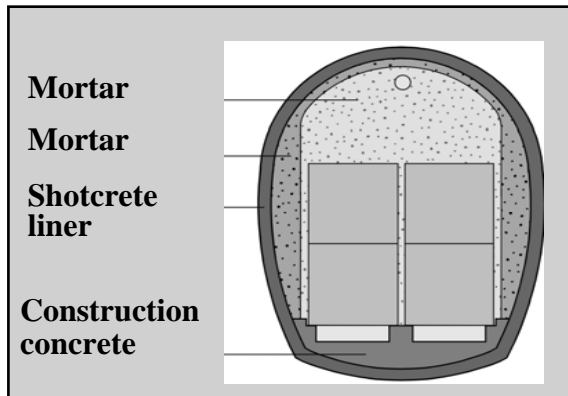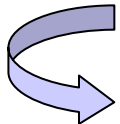## Disposal of Low- and intermediate level radioactive waste

Cementitious materials are used for conditioning of the waste and for the construction of the engineered barrier system
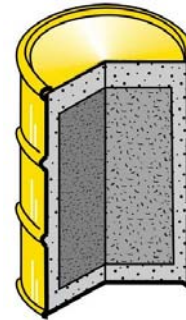
Waste solidification

Container: concrete, mortar, steel

Mortar

Mortar

Shotcrete liner

Construction concrete

Deep geological repository

C-S-H phases in cement

Fresh cement	Altered cement			
Gypsum Portlandite (40%) Monosulfo–aluminate Ettringite Aluminate Ferrite CSH gels (50)%	Monosulfo-aluminate Ettringite Aluminate Ferrite CSH gels	Ettringite Ferrite CSH gels	CSH gels	Silica gel rich in Fe/Al

(Atkinson et al., 1988, Berner, 1990; Adenot & Richet, 1997)
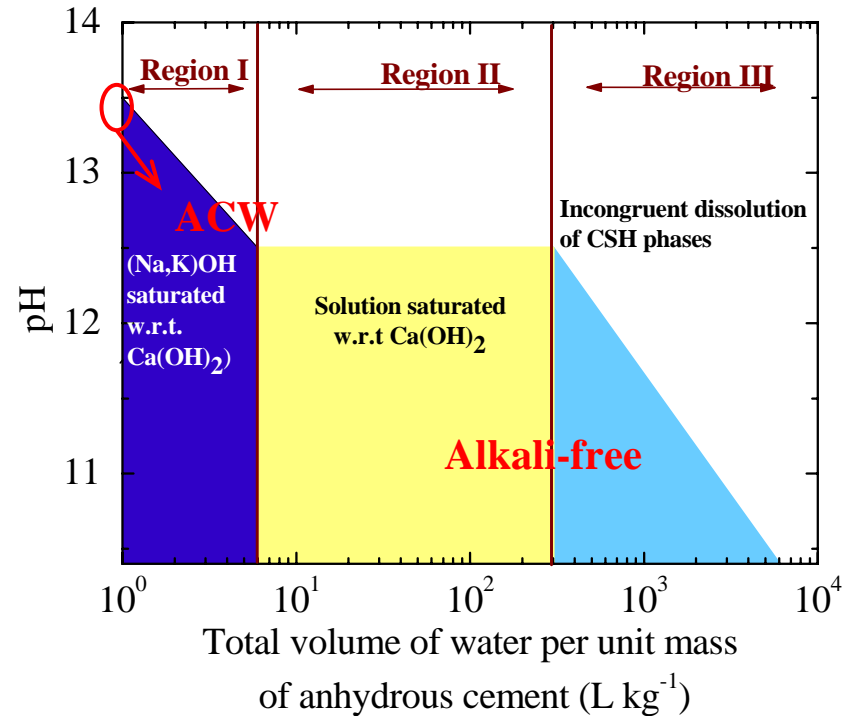
Calcium Silicate Hydrate (C-S-H) phases play an important role throughout the evolution of cement

Structure of C-S-H phases

C-S-H, C/S = 2/3   C-S-H, C/S = 5/4

⬤ Ca   ⬤ O   ⬤ OH   ⬤ H_2O

Garbev et al., 2008
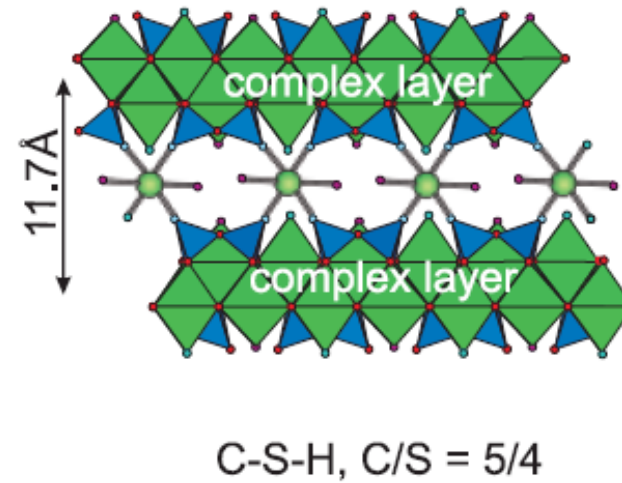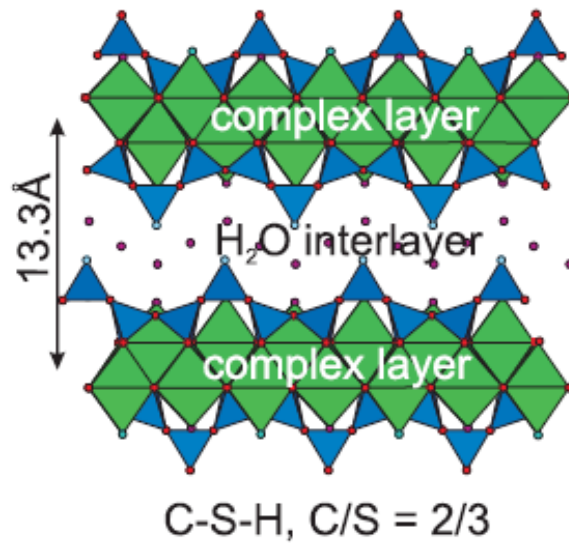
Recrystallisation of C-S-H phases from ⁴⁵Ca uptake
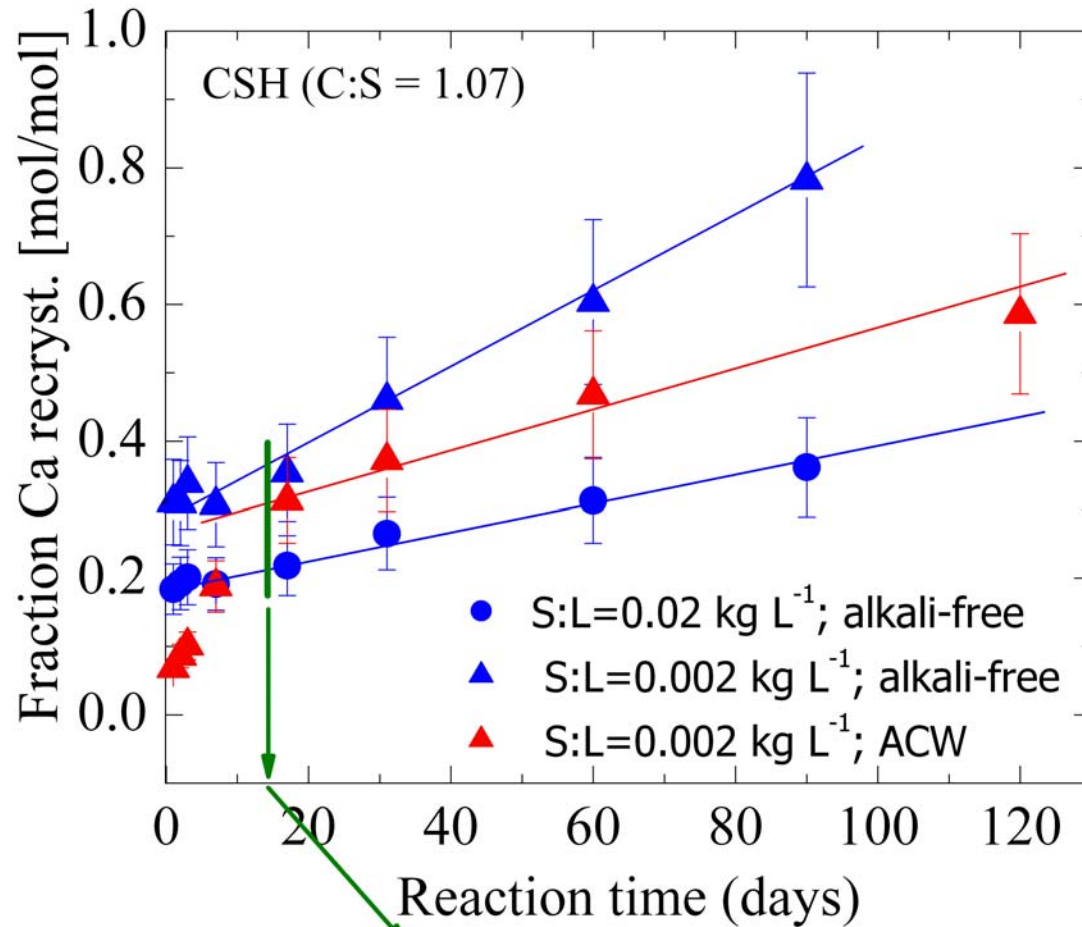
Assumption:

$$\frac{\left[^{45}Ca\right]_{sol}}{\left[Ca\right]_{sol}} = \frac{^{45}Ca_{recryst.solid}}{Ca_{recryst.solid}}$$

CSH (C:S = 1.07)

- ● S:L=0.02 kg L^{-1}; alkali-free
- ▲ S:L=0.002 kg L^{-1}; alkali-free
- ▲ S:L=0.002 kg L^{-1}; ACW

Sorption equilibration time of isotherms = 2 weeks

Batch sorption experiments
Sorption tests

Experimental set-up

Aerosil-300   **CaO** UO_2^{2+}

H_2O
ACW   →   ageing   →

equilibration

sampling of
supernatant   centrifugation

N$_2$ atmosphere

C:S ratio: 0.5 – 1.60

S:L ratio: 5.0 g/L (batch sorption tests)
1.0 g/L (TRLFS measurements)

$[U(VI)]_{added}$: 10^{-3} M – 10^{-7} M

Ageing time: 2 weeks

Equilibration time:
2 weeks (batch sorption tests)
1 – 14 days (TRLFS measurements)

TRLFS / measurements

Alpha counting / ICP-OES analysis
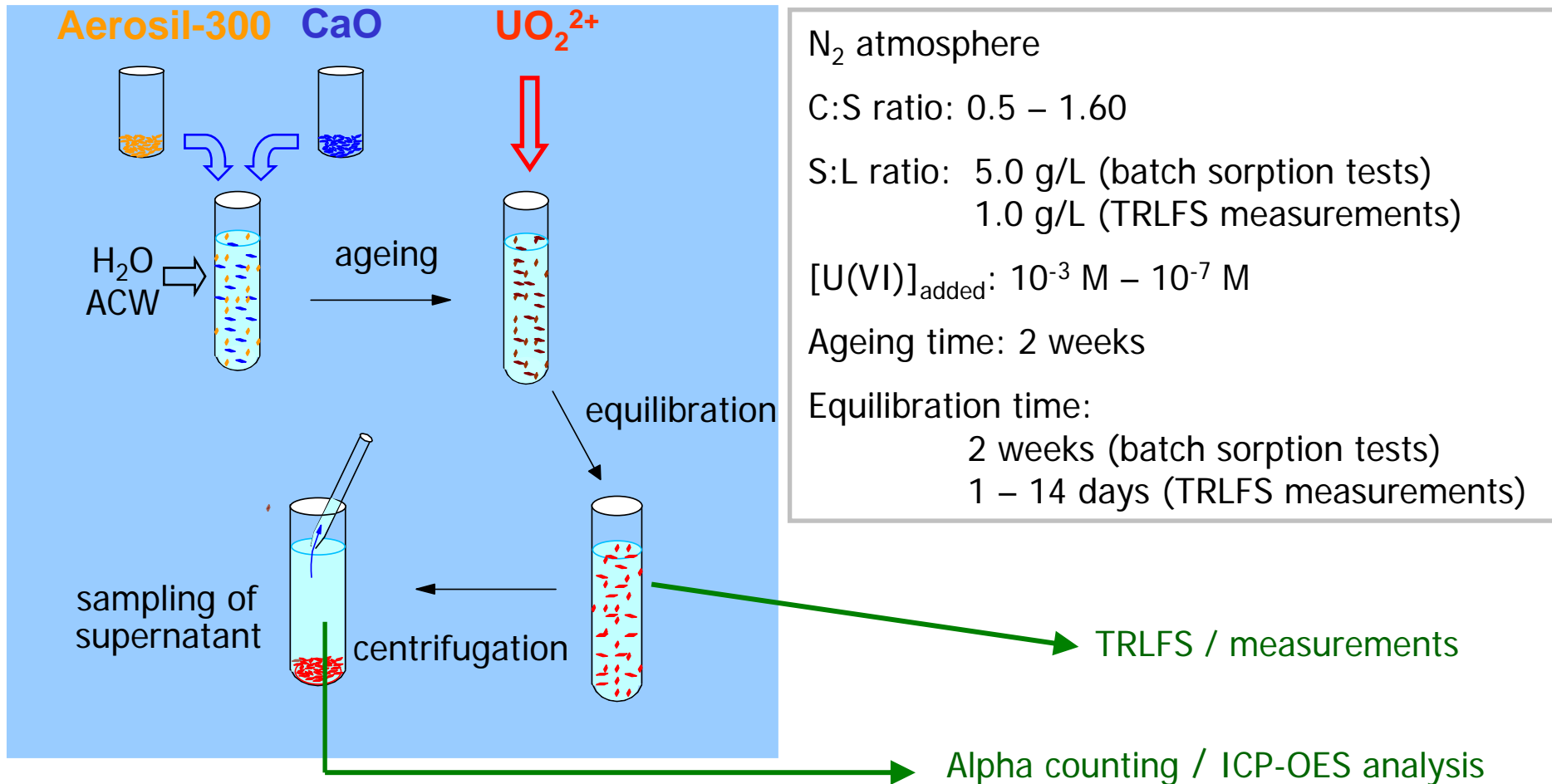
Batch sorption experiments
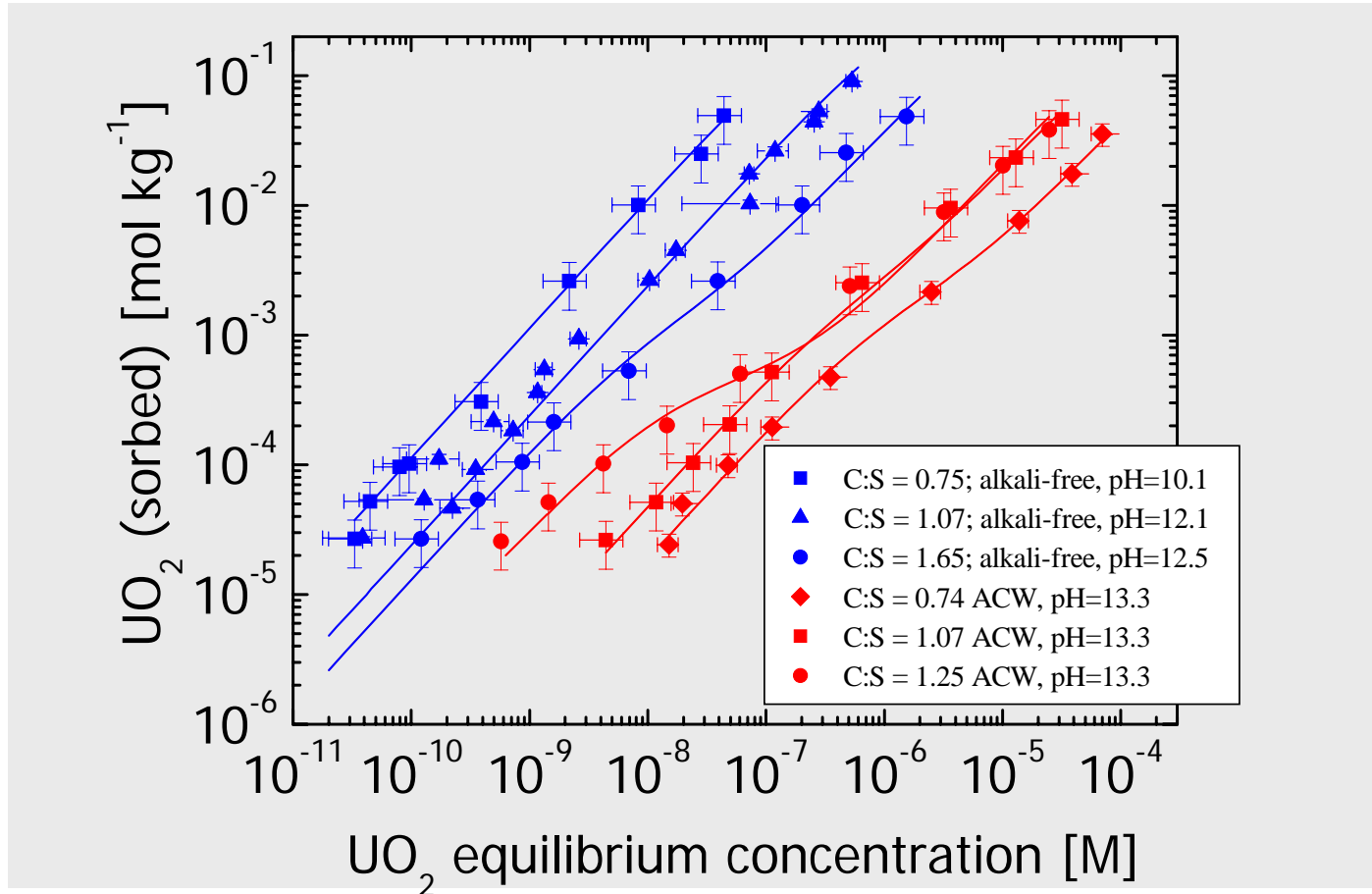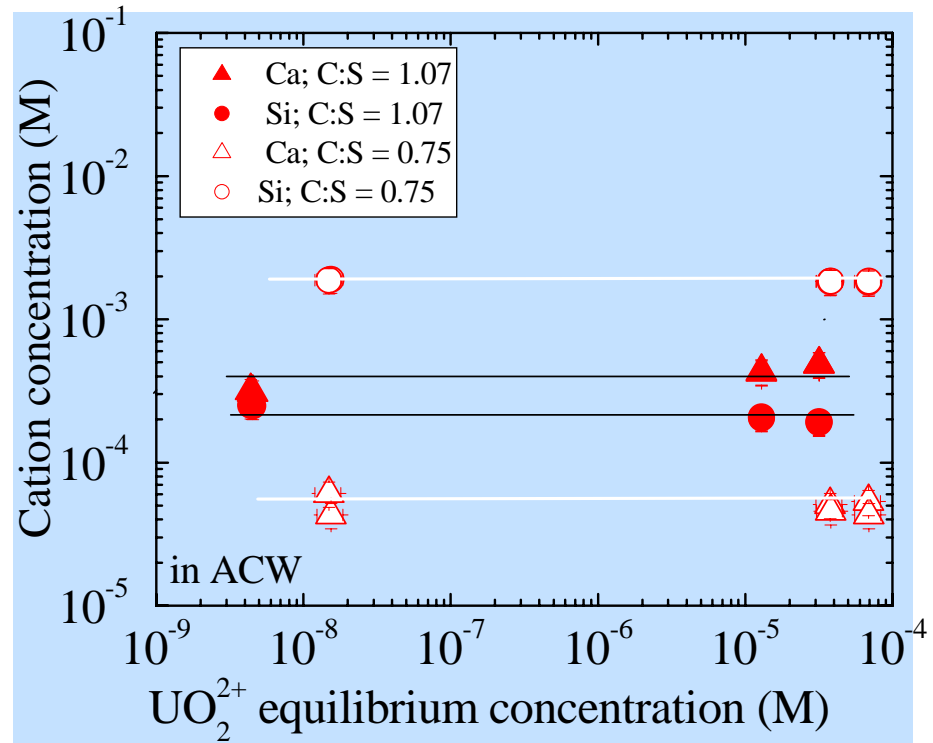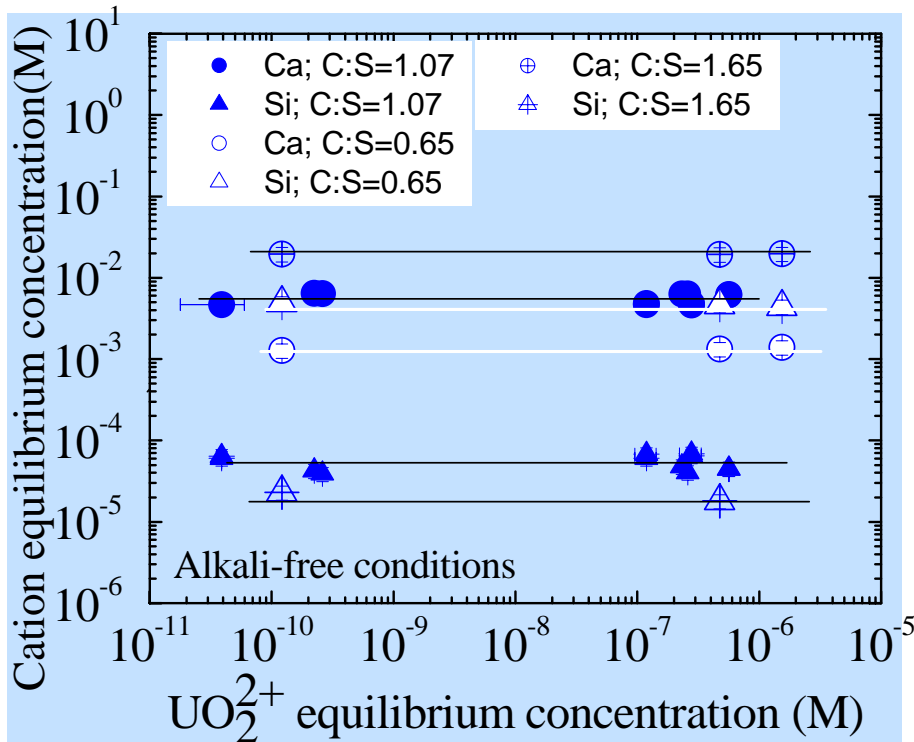## Sorption isotherms

Non-linear sorption: 2-site langmuir isotherm: Site 1: 1.5×10^{-3} mol/kg; site 2: >0.6 mol/kg

Effect of U(VI) speciation (pH) and C:S ratio (aqueous Ca concentration)

Batch sorption experiments
Sorption isotherms

Solution composition is independent of the U(VI) sorption

Batch sorption experiments
summary of the observations

- C-S-H phases have a high recrystallisation rate providing opportunities for incorporation (SS formation)

- U(VI) sorption on C-S-H phases:

  – Is non-linear

  – Depends on the U(VI) aqueous speciation (influence of pH)

  – Depends on the C-S-H composition (Ca concentration?)

Can these observations be described by a solid solution model?

Batch sorption experiments
Requirements to model solid – solutions :
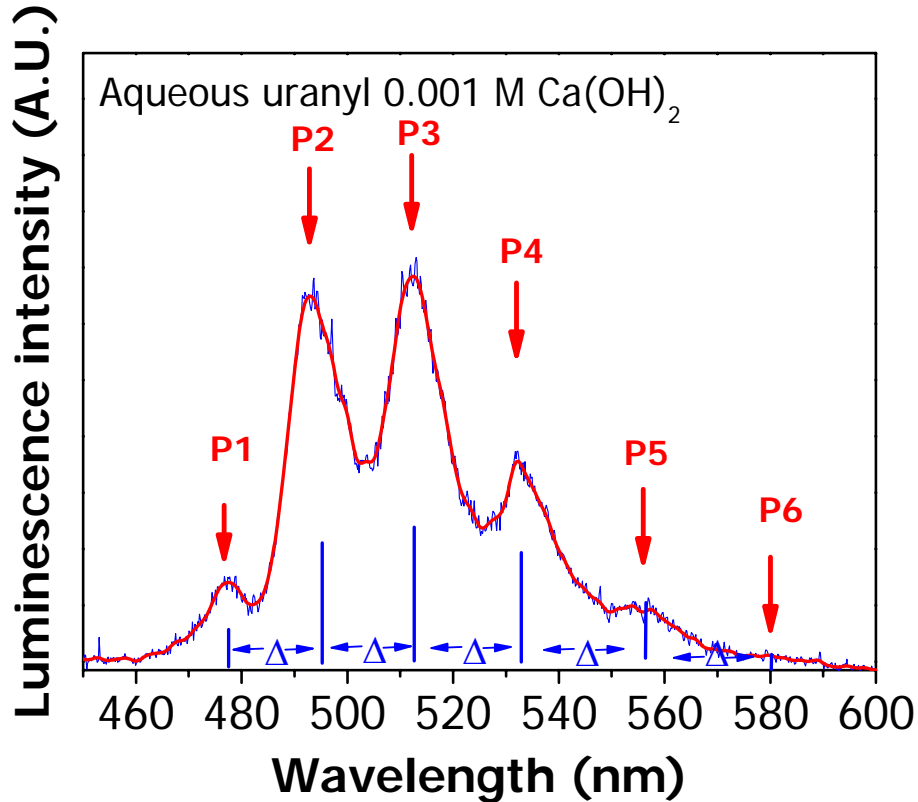
- ❖ Mixing model: ideal or non-ideal

- ❖ Amount of recrystallized solid

  - ➢ From recrystallisation experiments with ^{45}Ca

- ❖ End-members and end-member stoichiometries:

  - ➢ C-S-H end-members: (see e.g. presentations of D. Kulik and B. Lothenbach, S. Churakov,...)

  - ➢ U(VI) containing end-members ??

    ⟹ Indications from spectroscopic investigations (EXAFS, **TRLFS**,...)

Time-resolved laser fluorescence spectroscopy of uranyl
Fluorescence process

Vibrational relaxation

Non-radiative relaxation e.g. via O-H stretch vibrations

Excitation $\lambda = 266$ nm
ligand σ_μ (axial oxygen $2p$ orbital)-to-metal δ_u ($5f$ orbital) charge-transfer

Fluorescence emission

$\nu=n$

$\nu=2$

$\nu=1$

Time-resolved laser fluorescence spectroscopy

Aqueous uranyl 0.001 M Ca(OH)$_2$
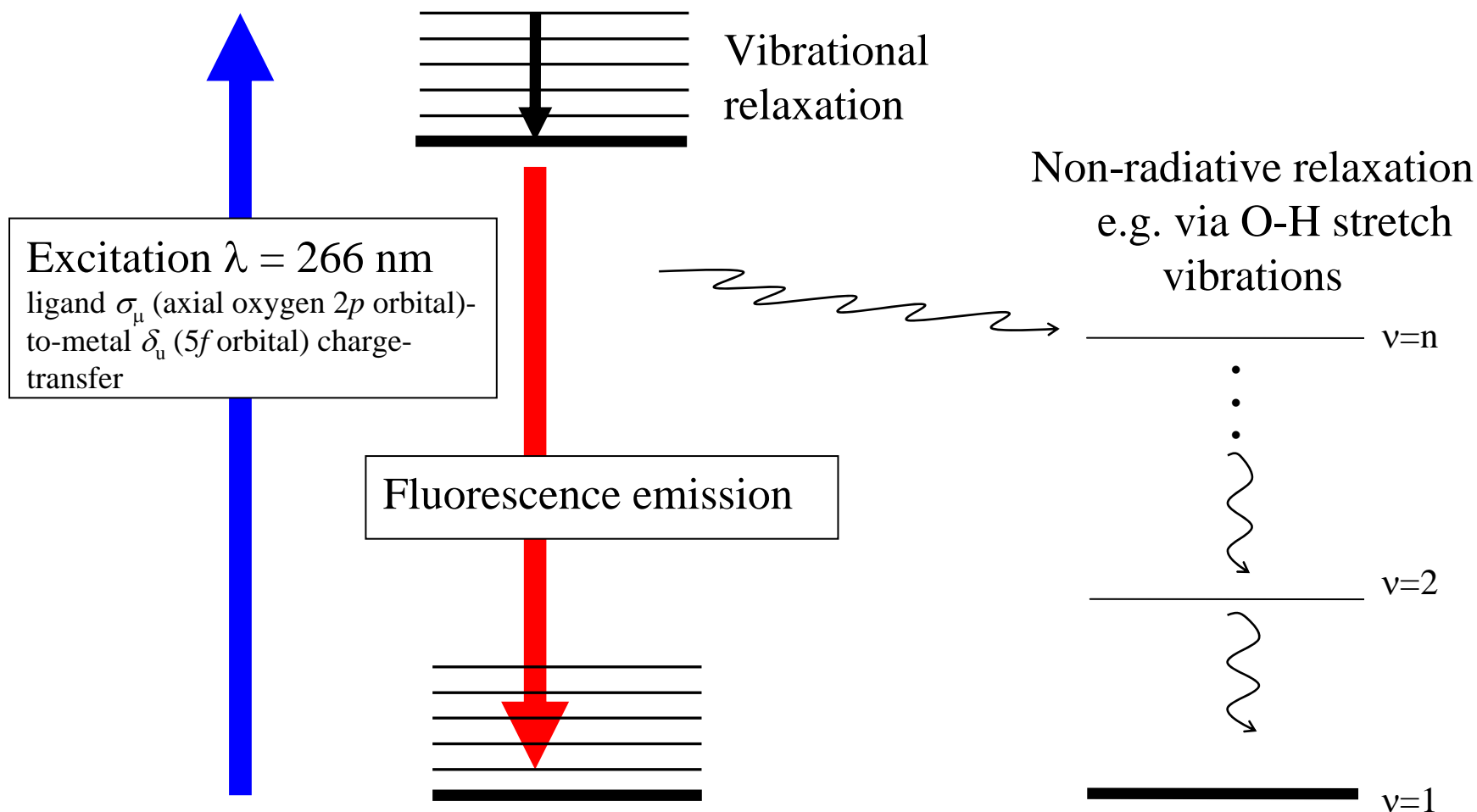
> Uranyl compounds fluoresce above 470 nm with characteristic vibronic progressions originating mainly from the symmetric stretch vibration of the O=U=O moiety (minor contributions from assymetric stretch- and bending vibration)
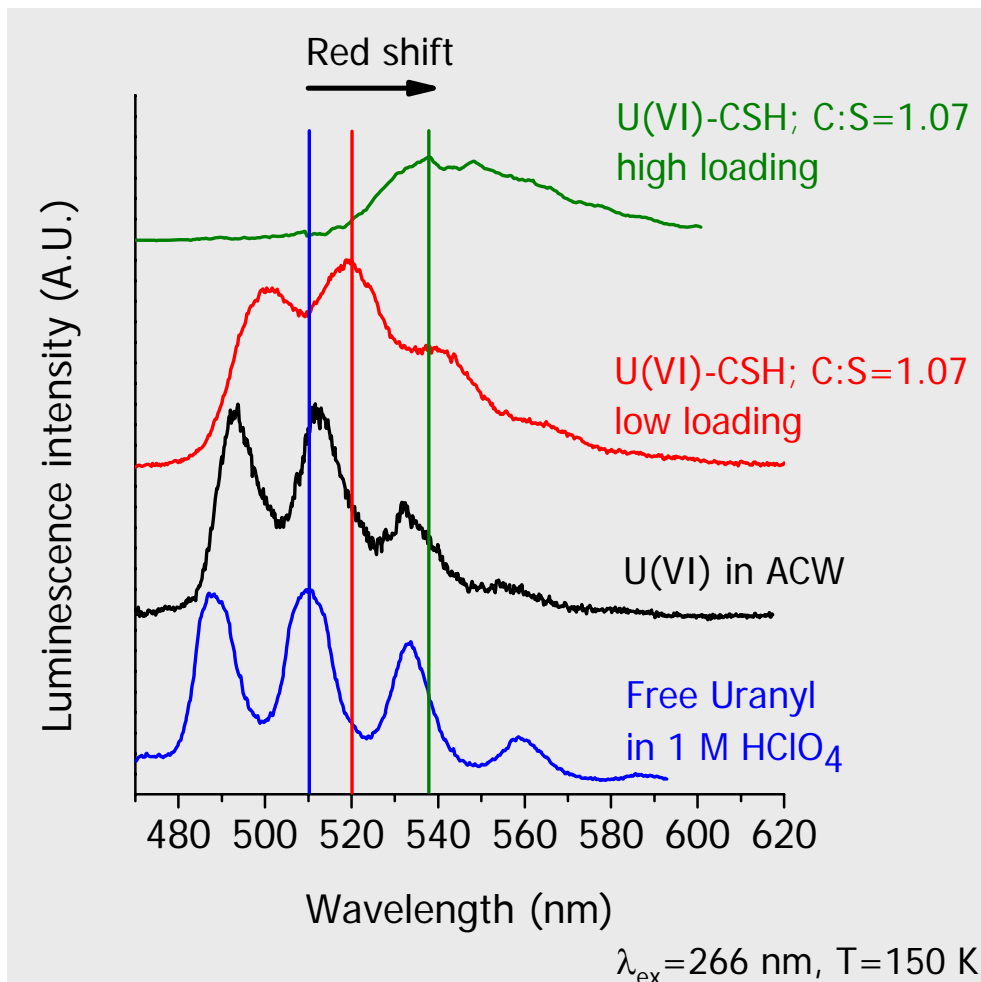
> **The position (↓), spacing (Δ), relative intensities (P_i/P_{i+1}) of the vibronic bands, lifetime, are sensitive to geometry of the uranyl and local chemical environment**

> O=U=O axial bond length, R_{UO}:
> $R_{UO} = 10650 \cdot [\Delta]^{-2/3} + 57.5$ (Bartlett & Cooney, 1989)

Time-resolved laser fluorescence spectroscopy
Comparison of spectra from sorbed and aqueous uranyl species

Red shift

U(VI)-CSH; C:S=1.07
high loading

U(VI)-CSH; C:S=1.07
low loading

U(VI) in ACW

Free Uranyl
in 1 M $HClO_4$

Luminescence intensity (A.U.)

Wavelength (nm)

λ_{ex}=266 nm, T=150 K

Increasing red shift (lower energy): Indication of weakening of the axial U=O bond, (lower stretch frequency)

Stronger interaction between U(VI) and the equatorial ligands
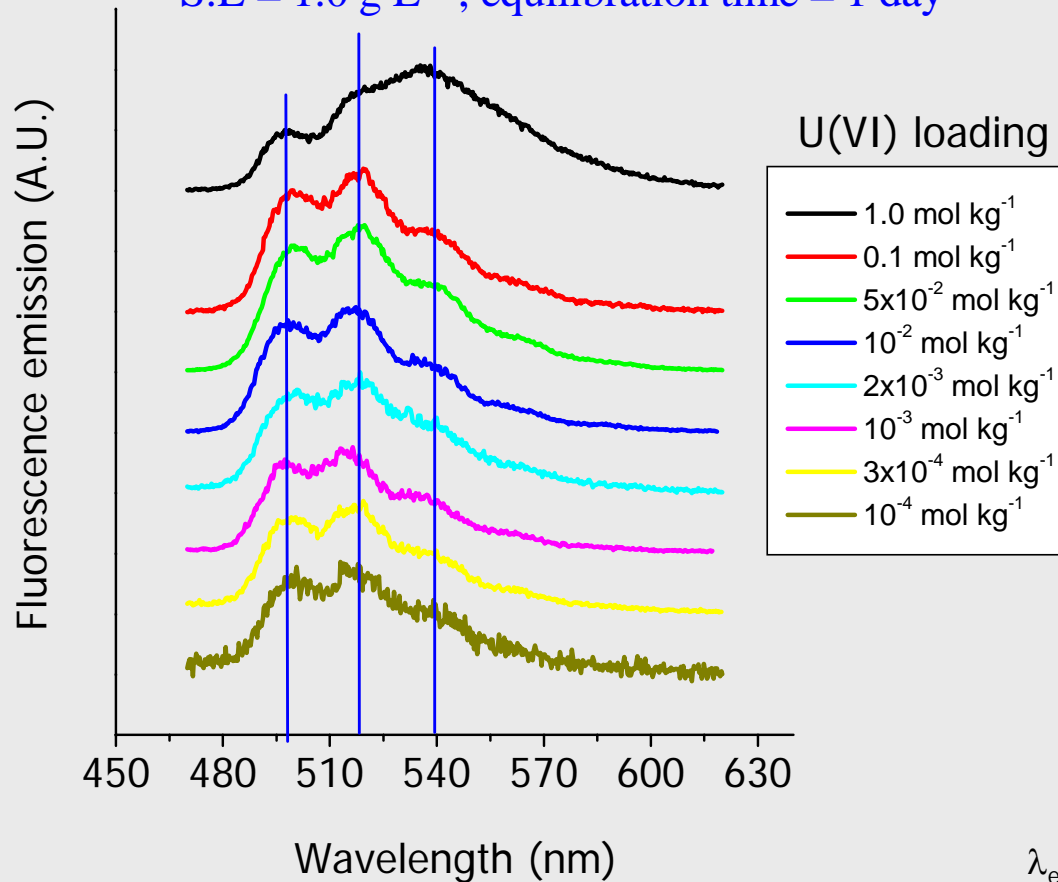
Change in geometry of uranyl moiety
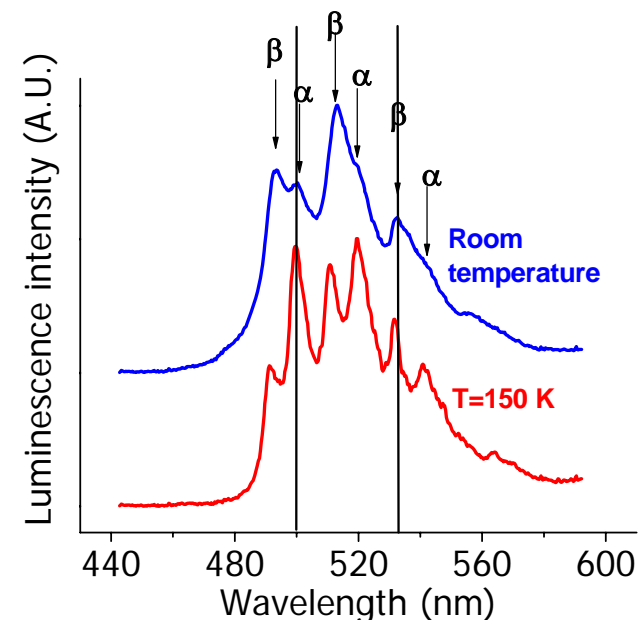
Time-resolved laser fluorescence spectroscopy
Sorption isotherm

U(VI) sorbed on CSH at pH 12.0; C:S = 1.07
S:L = 1.0 g L^{-1}; equilibration time = 1 day

U(VI) loading

- 1.0 mol kg^{-1}
- 0.1 mol kg^{-1}
- 5x10^{-2} mol kg^{-1}
- 10^{-2} mol kg^{-1}
- 2x10^{-3} mol kg^{-1}
- 10^{-3} mol kg^{-1}
- 3x10^{-4} mol kg^{-1}
- 10^{-4} mol kg^{-1}

Fluorescence emission (A.U.)

Wavelength (nm)

λ_{ex}=266 nm, T= 150 K

Time-resolved laser fluorescence spectroscopy
Comparison with spectra of reference compounds

Uranophane α and β
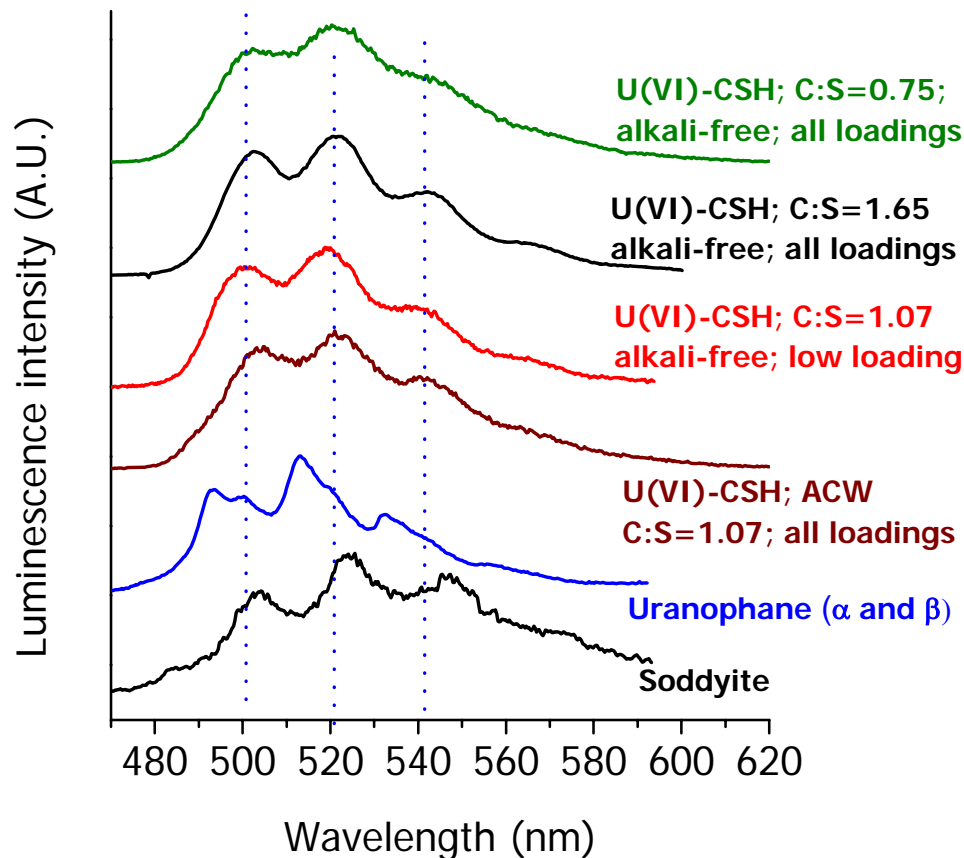
λ_{ex}=266 nm, T=293 K or 150 K

Time-resolved laser fluorescence spectroscopy
Comparison with spectra of reference compounds

	Axial U − O distance (Å)		
	XRD	EXAFS	TRLFS
Soddyite	1.78 (Demartin et al. 1983)	1.77(2)	1.80(5)
K-boltwoodite	1.80 (Burns et al. 1998)	1.80(2)	-
Uranophane α	1.80 (Ginderow, et al. 1988)		1.86(5)
Uranophane β	1.82 (Viswanathan et al. 1986)		1.84(5)
C-S-H (alkali-free)		1.83(2)	1.9(1)
C-S-H (ACW)		1.81(2)	1.9(1)

TRLFS: $R_{UO} = 10650 \cdot [\Delta]^{-2/3} + 57.5$ (Bartlett & Cooney, 1989)

Summary

➢ C-S-H phases have a high recrystallisation rate

➢ U(VI) sorption onto C-S-H phases is non-linear (at least 2 sorbed species)

 - increases with increasing C:S ratio

 - decreases with increasing pH

➢ TRLFS can give indications about possible U(VI) containing end-members:

 - Luminescence spectra of U(VI) sorbed on C-S-H phases are all similar
   → similar geometry of the uranyl moiety (1 sorbed species)
   In contrast to information from batch sorption experiments

 - Geometry of the sorbed uranyl is similar to the uranyl geometry in
   α-uranophane (derived from spectral shape and peak position)

 - Uncertainies on axial oxygen distances is still high
   (Future experiments at 4 K may improve the quality of this kind of
   information)

Acknowledgements

Thank you for your attention