Supplementary information

A luminescence line-narrowing spectroscopic study of the uranium(VI) interaction with cementitious materials and titanium dioxide

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Estimate of the Förster distance for U(VI) sorbed onto C-S-H phases (adapted fromVisser et al[1])

The Förster distance was calculated following a procedure described by Hink et al. 2003[2]: The Förster distance can be calculated using the following equation:

$$R_0 = 0.2108 \cdot \left(\kappa^2 \cdot \Phi_0 \cdot n^4 \cdot J\right)^{1/6} \quad (1)$$

In which κ^2, is the orientation factor, Φ_0, the quantum efficiency of the sorbed UO_2^{2+}, n is the refractive index and J, the degree of spectral overlap between donor fluorescence spectrum (F_D, its spectrum normalized so that the integral is equal to one), and acceptor absorption spectrum (scaled to its maximum molar extinction coefficient, ε, in units of M^{-1} cm^{-1}), given here in terms of wavelength λ (in units of nm):

$$J = \int_0^\infty F_D(\lambda) \cdot \varepsilon(\lambda) \cdot \lambda^4 d\lambda \quad (2)$$

Parameters:

The parameters used to calculate the Förster distance for UO_2^{2+} in a C-S-H matrix, were taken from luminescence experiments with UO_2^{2+} in matrixes similar to the C-S-H matrix described in the literature. The Förster distances obtained with the present calculations are therefore **only rough approximations**.

Molar extinction coefficient (ε): 20 - 25 dm^3 mol^{-1} cm^{-1}
(For uranyl sorbed on colloidal silica and in silica glasses, measured with λ_{ex} = 337 nm at room temperature[3, 4]).

Dipole orientation factor (κ^2): 0.48 (Visser and Rolinski, 2010. Basic Photophysics. http:// www.photobiology.info.)

Refractive index (n): 1.55 (Plombierite or 14Å Tobermorite, a crystalline analog of C-S-H phases[5])

Quantum yield (Φ_0): 0.7 (Uranyl in silica glasses measured with λ_{ex} = 337 nm[4])

The Förster distance, R_0, was calculated with the help of an Excel spreadsheet provided by Visser et al[1]. J was calculated from the overlap between the normalized UO_2^{2+} excitation spectrum and a normalized UO_2^{2+} luminescence spectrum recorded at an excitation wavelength λ_{ex} = 476 nm (Figure 1). This calculation results in a value for the Förster distance of **R_0 = 10.98Å or 1.1 nm**.

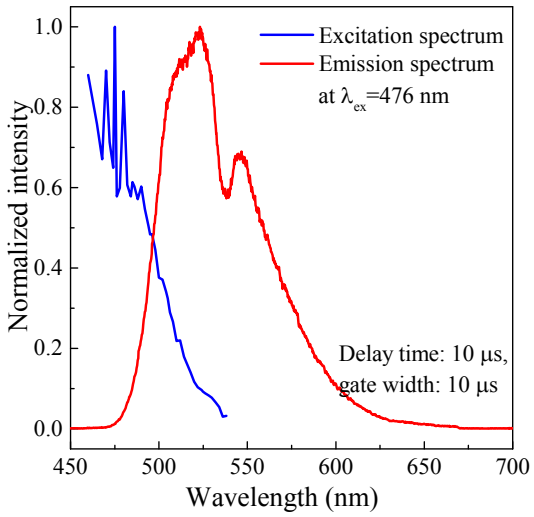

Figure 1: Excitation spectrum and luminescence spectrum recorded at λ_{ex} = 476 nm of UO_2^{2+} sorbed on a C-S-H phase.

Estimate of the Förster distance for U(VI) sorbed onto rutile

The same calculation procedure as in the case of the C-S-H phases was applied. Compared the the calculations for UO_2^{2+} in a C-S-H matrix, only the refractive index was adapted. The other parameters were not changed due to a lack of relevant literature data. The Förster distances obtained with the present calculations are therefore **only rough approximations**.

The following parameters were used:

Parameters:

Molar extinction coefficient (ε): 20 - 25 dm^3 mol^{-1} cm^{-1}
(A value for the molar extinction coefficient of UO_2^{2+} sorbed on rutile could not be found in the literature. The same vale as for UO_2^{2+} sorbed on C-S-H phases was adopted as a rough approximation.

Dipole orientation factor (κ^2): 0.48 (Visser and Rolinski, 2010. Basic Photophysics. http:// www.photobiology.info.)

Refractive index (n): 2.8[6]

Quantum yield (Φ_0): 0.7
(A value for the molar extinction coefficient of UO_2^{2+} sorbed on rutile could not be found in the literature. The same vale as for UO_2^{2+} sorbed on C-S-H phases was adopted as a rough approximation.)

This calculation results in a value for the Förster distance of **R_0 = 6.93Å or 0.69 nm**.

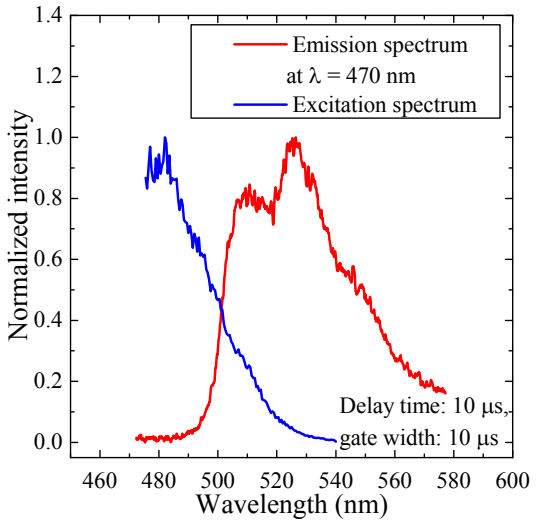

Figure 2: Excitation spectrum and luminescence spectrum recorded at λ_{ex} = 460 nm of UO_2^{2+} sorbed on rutile.

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