Application of the Tikhonov regularization method to the detection of U-Si neighbours in soddyite using EXAFS spectroscopy

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Our EXAFS study on U(VI) sorption on kaolinite indicated that U forms inner-sphere complexes with [SiO_4] tetrahedra [1]. Soddyite, $(UO_2)_2(SiO_4)x2H_2O$, is a natural mineral with monodentate and bidentate coordination of the UO_2^{2+} moiety to [SiO_4] with U-Si distances of 3.80 and 3.15 Å, respectively [2]. Before using the Tikhonov regularization method [3] for the EXAFS analysis of the U(VI)/kaolinite samples, we investigated the possibility of detecting U-Si pairs in simulated and experimental U L_3-edge EXAFS spectra of soddyite.

As a first step in our simulation, we calculated three partial radial atomic distribution functions (RDFs) for U-O, U-Si, and U-U in the *r* - range of 1.5 - 4.6 Å using the crystal structural data of soddyite given in Table 1. The program FEFF8.20 [4] was used to calculate scattering phase and amplitude functions. These functions and the RDFs were used to calculate four theoretical U L_3-edge EXAFS spectra $\chi(k)$. Three $\chi(k)$ were calculated using only the RDF of U-O, U-Si, or U-U. The fourth $\chi(k)$, which simulates the experimental $\chi(k)$, was calculated by combining all three RDFs. Then, four theoretical $\chi(k)$ and one experimental $\chi(k)$, which was measured at 15 K, were analyzed by the Tikhonov regularization method. The regularization parameters were α = 0.7 and β = 0.3 for all calculations. The resulting RDFs (Tikhonov solutions) for the pair U-Si are shown in Fig.1.

We conclude the following based on the results shown in Fig.1:

1) The theoretical RDF(U-Si) agrees with the experimental one;
2) The pairs U-O, U-Si, and U-U contribute additively to the RDF(U-Si);
3) The monodentate U-Si at 3.80 Å cannot be derived from the RDF(U-Si) due to the interference with U-U at 3.85 Å.
4) The bidentate U-Si at 3.15 Å can be identified in the theoretical and experimental RDFs.
5) For the detection of U-Si in an unknown structure, e.g., U/kaolinite, it is necessary to remove the contributions of U-O and U-U from $\chi(k)$ before calculating the RDF(U-Si) or to perform special calculation experiments with the contributions from U-O and U-Si in $\chi(k)$.

Fig.1.RDF (Tikhonov solution) for the U-Si pair calculated from:

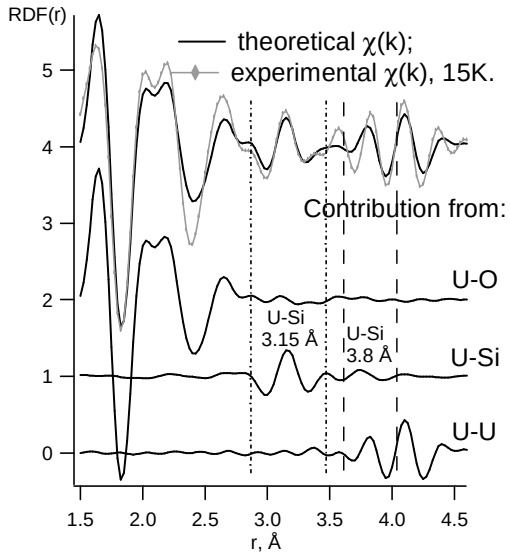

Table1: Structural parameters for the calculation of the model RDFs :

	N	r, Å	σ^2, Å^2
RDF U-O	2	1.78	0.002
	5	2.38	0.010
RDF U-Si	1	3.15	0.004
	2	3.80	0.004
RDF U-U	2	3.85	0.002

References:

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