

  ROBL-CRG	Experiment title: EXAFS investigation of sorbed selenium oxyanions onto hematite	Experiment number: 20-01-718	
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Report:

A thorough investigation of the Se(VI) sorption processes onto hematite was carried out by X-ray Absorption Spectroscopy. 2 g.L⁻¹ hematite samples with different pH values (3.5-6.0), different ionic strengths (0.01-0.1M NaCl) and Se(VI) concentration (1 × 10⁻⁴, 2.5 × 10⁻⁴ and 5 × 10⁻⁵ M) were prepared under CO₂-free conditions (cf. Table 1).

Table 1. List of EXAFS samples for the Se(VI)/hematite binary system.

Sample	pH	[Se ^{VI}] _{initial} (μmol L ⁻¹)	Ionic strength (mol L ⁻¹)	%Se(VI) sorbed	Surface loading [mg Se kg _{solid} ⁻¹]
1	6.0	250	0.1	4.8	475
2	5.0	250	0.1	15.4	1525
3	3.5	50	0.1	85.9	1697
4	3.5	100	0.1	66.3	2620
5	4.0	250	0.1	30.6	3025
6	3.5	250	0.1	33.7	3325
7	3.5	250	0.01	43.8	4325

After 3 days of shaking to reach sorption equilibrium, the samples were ultracentrifuged during 30 minutes at 187,000 × g. The wet pastes were transferred into sample holders, which were covered with Kapton tape and flash-frozen in liquid N₂. Great care was taken to exclude O₂ during sample transport and storage by keeping them in liquid N₂. At the beamline, they were rapidly (2 min) transferred to a closed-cycle He cryostat (with a large fluorescence exit window and a low vibration level (CryoVac), where they were kept at 15 K during the XAS measurements (fluorescence mode). The XANES spectra are shown in Figure 1.

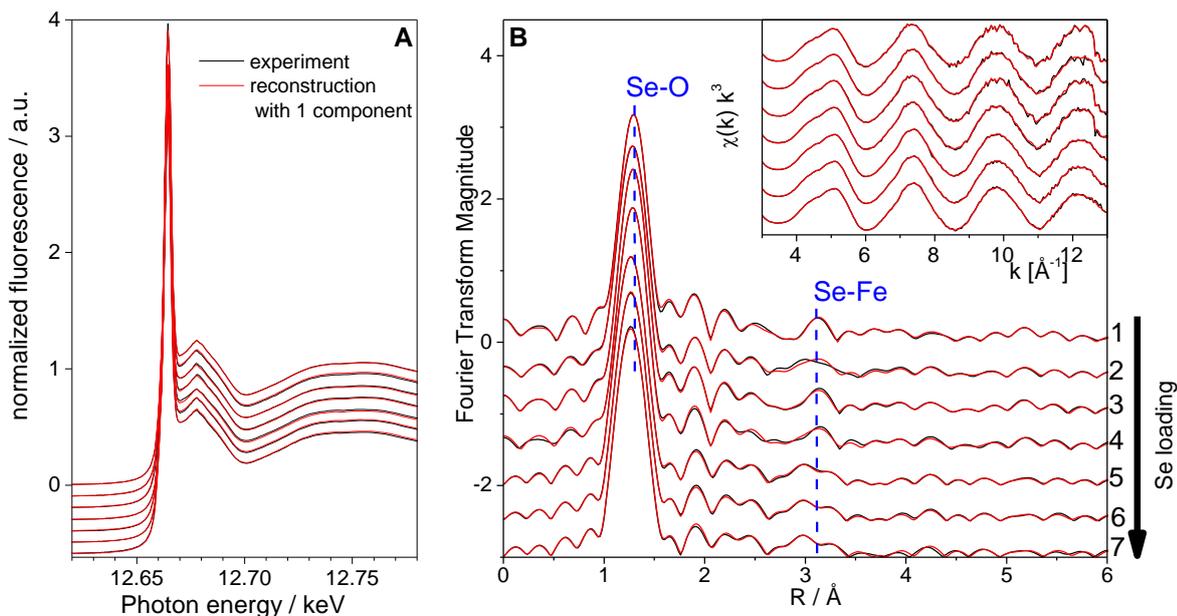


Figure 1. Se K-edge XAS results of Se(VI) sorbed hematite. (A) XANES spectra and their reconstruction by 1 principal component. (B) Fourier Transform EXAFS spectra and their reconstruction by 2 principal components, k^3 -weighted chi spectra as insert. The numbers and arrow indicate sample numbers and increasing surface loading, respectively, according to Table 1.

The XANES edge energy of 12.663 keV as well as the strong white-line intensity (Figure 1A) are in line with Se(VI), demonstrating the absence of redox processes at the hematite surface across the investigated pH and Se-loading range.

The Fourier transform magnitude shown in Figure 1B is dominated by a strong peak at about 1.3 Å (not corrected for phase shift), arising from the typical four O atoms in the coordination sphere of selenate. Further ripples out to about 3 Å arise from tri- and four-legged multiple scattering (MS paths) within the tetrahedral SeO_4 unit. Especially the samples at lowest loadings show another peak slightly above 3 Å, which is still above the background noise, indicative of an Se-Fe path. A detailed factor analysis was performed to investigate whether there are statistically significant trends within the data set. The analysis revealed that two principal components are required to reconstruct the spectra (see red lines in Figure 1B and insert) and based on a minimum of the Malinowski indicator value for 2 (not shown). When fitting the two most extreme spectra, only spectrum 1 with the lowest Se loading could be fitted with an Se-Fe path at 3.41 Å, while this was not possible for spectrum 7 with the highest loading (data not shown). Note that the 3 and 4-legged multiple scattering contributions from the O coordination shell were fitted in order to obtain correct coordination numbers for the Se-Fe path.

The Se-Fe distance observed for low loading is 3.41 Å which is in line with a bidentate, binuclear corner-sharing (CS) complex. This observed coordination number for the Se-Fe path of 0.4 arises from the sum signal of two different complexes: (a) the outer-sphere complex with a coordination number of 0, which does not show Se-Fe interactions but only the Se-O backscattering from the coordination shell and (b) the binuclear corner-sharing complex with a coordination number of 2. The fraction of the binuclear complex is therefore $0.4/2 = 0.2$, while the fraction of the outer-sphere complex is 0.8.

From EXAFS data, Se(VI) sorbs prevalently as outer sphere complex. When the Se loading decreases by about one order of magnitude, also a small percentage of a corner-sharing inner sphere sorption complex becomes visible.