ROBL-CRG	**Experiment title:** **EXAFS investigation of sorbed selenium oxyanions onto anatase**	**Experiment number**: 20-01-704
Beamline: BM 20	**Date of experiment**: from: 24.11.2010 to: 27.11.2010 (9 shifts)	**Date of report**: 31.1.2011 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: Andreas Scheinost	

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Report:

For the first time, the mechanism leading to the retention of selenium(VI) and selenium(IV) onto pure anatase (a polymorph titanium dioxide TiO_2 with a tetragonal structure), as well as the nature of the sorbed species were elucidated by using XAS spectroscopy. Defined amounts of 0.1 M Se(VI) and Se(IV) stock solution (0.1 M NaCl, pH 4) were added to suspensions of TiO_2. To avoid an activation of anatase photocatalytic properties (Sanuki et al., 1999), all bottles were covered by aluminum foil. The starting suspensions consisted of 5×10^{-5} M Se, in NaCl 0.1 M as background electrolyte. The pH-dependence sorption of selenium(VI) and selenium(IV) onto anatase was studied from pH 3.5 to 5.0 and from pH 3.5 to 8.0, respectively. To check whether the Se(IV) surface loading or the ionic strength had an influence on the nature of the sorbed surface complexes (at constant pH), additional samples with a lower initial concentration of 10^{-5} M Se and a lower ionic strength (NaCl 0.01 M) were also prepared. After 3 days of stirring to reach sorption equilibrium, the samples were ultracentrifuged during 1 h at 285000 g and the slurries loaded as a wet paste in a sample holder, which was then sealed with Kapton tape. Great care was taken to exclude O_2 during sample transport and storage by keeping them in liquid N_2. At the beamline, they were rapidly (2 min) transferred to the closed-cycle He cryostat, where they were kept at 15 K for the XAS measurements. XANES and EXAFS spectra of Se reacted anatase were recorded on the Se K edge (E_0 = 12 658 keV) in fluorescence mode at the Rossendorf Beamline at ESRF (Grenoble, France). Corrections of energy and fluorescence deadtime as well as averaging of scans (4 to 12 depending on Se loading) were performed with SixPack, while data reduction steps and shell fitting were performed with WinXAS 3.1. The theoretical scattering phases and amplitudes were calculated using the scattering code FEFF8.2.

Fig. 1 shows the results of EXAFS measurements conducted on samples of selenium(VI) and selenium(IV) adsorbed onto anatase at pH 3.5, i.e. the Fourier transform magnitude corresponding to radial structure functions (RSF). Concerning Se(IV), there is clear evidence of two shells in the RSF: a Se–O shell (fit with ~3 O_2 at 1.69 Å) and a Se–Ti shell (fit with ~2 Ti at 3.38 Å). The best assignment of the bonding environment for selenite onto anatase is a bidentate binuclear surface complex. Neither the pH nor the selenium surface loading had an influence on the geometry of the sorbed surface species (data not shown).

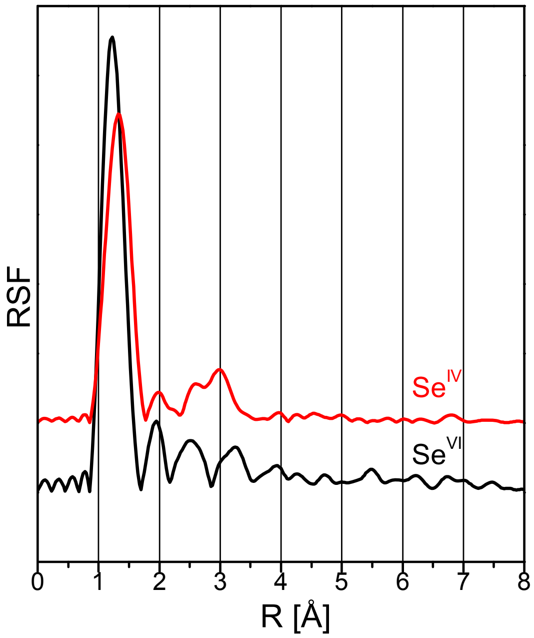

Fig. 1. Fourier transforms of Se(VI) (black) and Se(IV) (red) sorbed onto anatase at pH 3.5.

In the selenium(VI) reacted anatase sample (Fig. 1), the data could be fitted with approximately four O atoms at a distance of ~1.64 Å. The lack of second shell Se-Ti distance evidences that the sorption of selenate onto anatase proceeds via the formation of outer-sphere complexes.

Our findings are in good agreement with previous studies of selenium oxyanions adsorption on other minerals. Indeed, selenium(IV) has consistently been observed to form bidentate binuclear bridging complexes onto goethite (Hayes et al., 1987; Manceau and Charlet, 1994; Missana et al., 2009; Peak and Sparks, 2002; Su and Suarez, 2000), HFO (Manceau and Charlet, 1994), hematite (Catalano et al., 2006), Hydrous Aluminum Oxide (Peak, 2006) and γ-Al_2O_3 (Elzinga et al., 2009). Concerning selenium(VI), Elzinga et al. (2009) also evidenced by EXAFS the formation of non-protonated outer-sphere surface complexes during selenium(VI) sorption onto hydrated γ-Al_2O_3 surface (pH range 4-7.6).This study will also help to constrain the stoichiometries used during the surface complexation modeling of these two binary systems.

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