SeO$_3^{2-}$ ADSORPTION ON CONDITIONED NA-ILLITE:
XAS SPECTROSCOPY, KINETICS, SURFACE
COMPLEXATION MODEL AND INFLUENCE
OF COMPACTION

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INTRODUCTION
A comprehensive study was undertaken to describe the adsorption of SeO$_3^{2-}$ on conditioned Na-illite in both dispersed and compacted state. Illite du Puy was chosen as reference clay mineral because of possibilities of comparison with literature data from Bradbury and Baeyens [1] who used the same material to model adsorption of metal and radionuclide cations.

EXPERIMENTAL CONCEPT
Firstly, SeO$_3^{2-}$ surface complexes on conditioned Na-illite du Puy were qualified using X-ray absorption spectroscopy (XAS) analysis. X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray absorption fine structure (EXAFS) data were collected of selenite standard solutions and illite sorption suspensions (pH 3-6) in order to elucidate the molecular coordination environment of selenite ions on illite clay.

Secondly, a kinetic and surface complexation study was made on the adsorption of selenite to dispersed illite using batch measurements. Adsorption kinetics were studied over a period of about 100 days. The adsorption mechanism at short (< 7 days) equilibration times was elucidated by a combination of sorption plots at trace concentrations as a function of pH, and of sorption isotherms over a wide concentration range at different background electrolyte concentrations.

Finally, the sorption data obtained on dispersed systems were compared to sorption data obtained on consolidated systems to assess the effect of compaction on the sorption properties of illite. Illite consolidation was achieved using a newly-developed capillary method.

RESULTS AND INTERPRETATION
All sorption samples had XANES and EXAFS spectra which closely resembled the spectrum of HSeO$_3^-$, indicating they had a similar molecular structure with asymmetric first coordination shell oxygen positions (figure 1A). In the Fourier-transformed spectra (figure 1B) additional features at longer Se distances and different from the HSeO$_3^-$ standard were observable which could point to an inner-sphere sorption complex on the clay platelet edges. The new peak in the RSFs could be fitted by an aluminium atom located at 3.1±0.1 Å of the central Se absorber but the weak backscattering properties associated with Al currently hinder the unambiguous interpretation of the spectra.

The adsorption as a function of time revealed a two-step adsorption process: after an initial fast (< 30 min) adsorption step, a constant log K$_q$ value is reached and maintained up to about 7 days. Hereafter a slow increase in log K$_q$ is observed which exhibits a linear character as a function of the logarithm of time. Several rate laws could be used to provide a good model fit to the data. The Elovich and diffusion-based rate laws provided the best fits to the experimental data.
Figure 1: (A – left) Se K-edge EXAFS spectra for illite sorption samples and HSeO$_3^-$, (B - right) Fourier transformed Se K-edge EXAFS spectra. Open squares denote experimental data, while solid lines represent the best fit to the data.

Figure 2: Sorption edges (A - left) and sorption isotherms (B - right) showing the effect of pH, Se(IV) concentration and ionic strength on the adsorption of Se(IV) on Na-illite du Puy.

The SeO$_3^{2-}$ sorption as a function of pH (figure 2A) showed a so-called “sorption edge” which is characteristic for anion sorption on oxide surfaces. Adsorption was maximal (log $K_D = 1.5-2.0$) in the neutral-to-acid pH range and decreased sharply from pH 6.0 to pH 8.5. Sorption isotherms (figure 2B) at pH 4.0 were linear on a log-log scale, indicating Freundlich-type behaviour, and independent of the electrolyte concentration. This latter feature is inherent to inner-sphere sorption, which confirmed results from EXAFS analysis. SeO$_3^{2-}$ sorption modelling was performed using the quasi-mechanistic model from Bradbury and Baeyens [1] in which two amphoteric surface hydroxyl sites with different acidity are used to fully describe illite titration behaviour. Monodentate inner-sphere surface complexes (including ligand exchange) provided a good model fit to both the experimental sorption edge and sorption isotherm data.

Data from sorption edges and sorption isotherms on consolidated systems agreed very well with data on dispersed systems, indicating that the degree of compaction (up to 9000 g l$^{-1}$) reached with the capillary method did not affect either the sorption properties of illite nor the surface complexation mechanisms of Se(IV).

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References
[1] Bradbury, M.H., Baeyens, B. Modelling titration data and the sorption of Sr(II), Ni(II), Eu(III) and U(VI) on Na-illite, ISSN 1019-0643, 71 pp., PSI Nuclear Energy and Safety Research Department - Laboratory for Waste Management, Villigen, Switzerland (2005)