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Sorption of selenium species onto kaolinite surface: experiments, surface complexation modelling and DFT studies

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Selenium (Se) is a micronutrient that is of fundamental importance to human health. However, it has one of the narrowest ranges between dietary deficiency (<40 µg per day) and toxic levels (>400 µg per day). Therefore, prevention and remediation of Se pollution is a crucial task for human's wellbeing. However, widely scattered occurrence, high mobility and variable oxidation states make it difficult to predict the distribution of Se. At the same time, anthropogenic activities like oil drilling, nuclear waste disposal and agriculture have spread more widely the Se distribution and might expose humans to Se pollutions. To prevent future health hazards, this work presents a way to evaluate the distributions of Se sorption on kaolinite; a common clay mineral in the environment, by surface complexation modelling. Besides, to validate the model, DFT molecular modelling was executed to provide mechanism understanding at molecular level.

Titration, sorption edge and sorption isotherm experiments were performed for the basis of the developed multi-site surface complexation model that includes the wide range of environmental conditions. All the experiments were performed under low oxygen and carbon dioxide groundwater conditions mimicking the conditions deep in bedrock. Mineral dissolution, cation exchange and proton exchange effect that may course experimental errors were calibrated. A computer code PHREEQC (for geochemical calculations) coupled with Python (for work-flow controlling) was developed for all of the fitting and optimization processes. The fitting procedure was performed in an iterative way until a group of parameters that was able to describe all the experimental results was found (Figure 1). The developed model was validated for the Se sorption from strong acid conditions to strong basic conditions.

The strong/weak sorption sites assumed in the surface complexation model and the corresponding sorption site densities were illustrated by DFT molecular modelling. The surface complexation reactions of different Se species at strong/weak sorption sites were examined and corresponding sorption energies were calculated (Figure 2). The probability of sorption reactions, and possible surface charge transfer reactions, on the specific crystalline surfaces were estimated according to the sorption energies.

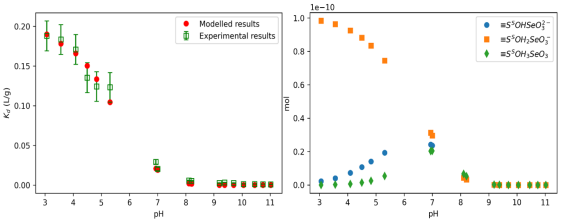

Figure 1. Experimental data and modelling results of sorption edge data (left); the distribution of sorption species on strong sorption of kaolinite predicted by the model.

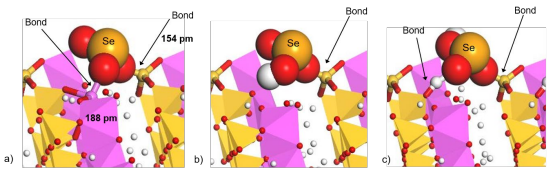

Figure 2. Sorption of SeO_3^{2-} (a), $HSeO_3^-$ (b) and H_2SeO_3 (c) on the kaolinite (120) surface calculated by DFT molecular modelling. Al – pink, H – white, O – red and Si – yellow.