

## Effects of data scatter and inconsistency in sorption modeling

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### Introduction

Surface Complexation Models (SCM) can describe sorption processes at the mineral-fluid interface on a scientific, quasi-thermodynamic basis. The effect of parameter uncertainty in blind predictions is illustrated by the example of Np(V) sorption onto hematite.

### Neptunium sorption model set-up

The Diffuse Double Layer (DDL) model was chosen as SCM submodel to keep the number of parameters at a minimum. From the surface species reported so far,  $=\text{FeOH}_2^+$ ,  $=\text{FeO}^-$ ,  $=\text{FeONpO}_2$ ,  $=\text{FeONpO}_2(\text{HCO}_3)_2^{2-}$ ,  $=\text{FeOHCO}_2$ , and  $=\text{FeOCO}_2^-$  were selected with their normalized DDL reaction constants  $\log K_n$ , taken from the RES<sup>3</sup>T database (Brendler *et al.*, 2003).

### Blind prediction

The modeling was performed with the FITEQL code, version 3.2. The predictions were evaluated by comparison with the experimental results by Kohler *et al.* (1999), comprising of 52 data points for the Np(V) sorption at varied pH, ionic strength, solid/liquid ratio, Np content, and  $P_{\text{CO}_2}$ . When focusing on the conventional distribution coefficient  $K_D$  the maximum deviation for all data subsets is less than one order of magnitude, a spreading considered to be reasonable in performance assessment applications.

### Uncertainty analysis

Because the protolysis constants cannot be varied independently, the point of zero charge (PZC) and  $\Delta pK$  were calculated based on experimental  $pK_1$  and  $pK_2$ . Consequential we generated 20 independent  $pK$  data sets with the aid of Gaussian-distributed random numbers. None of these parameter sets did deliver unacceptable blind predictions for the distribution coefficients.

### Conclusion

The formally large scatter of  $pK$  values as extracted from literature is actually not critical. Even the use of inconsistent values from other electrostatic models will yield similar results. For well-defined mineral systems, provided a suitable database is accessible, the SCM approach seems to be promising.

### References

Brendler V. *et al.* (2003), *J. Cont. Hydrol.*, **61**, 281-291.  
Kohler M. *et al.* (1999), *Radiochim. Acta*, **85**, 33-48.

## Evolution of the sorption studies on a Spanish bentonite during 8 years of the FEBEX project

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Compacted bentonite is used as an engineered barrier in radioactive waste repositories because it is a material of low permeability and high sorption capability for many solutes. Radionuclide transport through the compacted bentonite is a diffusion-controlled process retarded by sorption. For the performance assessment calculations of a repository,  $K_d$  and apparent and effective diffusion coefficients of relevant radionuclides in bentonite are necessary.

In the Full-scale Engineered Barrier EXperiment in crystalline host rock (FEBEX project), a series of laboratory experiments were planned to determine the above mentioned parameters for several radionuclides of interest and, in particular, for the elements used in the “mock-up” and “in-situ” tracer tests (rhenium, selenium, europium, thorium, uranium, neodymium and cesium).

Regarding sorption studies, during FEBEX I, simply batch sorption tests on the natural FEBEX clay were carried out to determine distribution coefficients ( $K_d$ ), considering different solid to liquid ratios. At the light of the sorption results, and comparing the  $K_d$  values obtained by the batch technique with those obtained by diffusion studies, the question whether or nor the sorption behaviour is the same in dispersed and compacted systems was opened. Under repository conditions, the solid to liquid ratio will be high (4:1) and, furthermore the material will be compacted. For this reason, it was considered necessary to obtain  $K_d$  values by means of experiments under conditions as similar as possible to those expected in the repository. Special experimental cells were designed, in the the second phase of the project, to obtain  $K_d$  values of several elements directly in the compacted clay. The results and the limitation of this technique will be discussed in this work.

Finally, since the “ $K_d$ -approach” does not allow extrapolating laboratory results to different environments, and limits the description of the processes occurring in the medium to an empirical parameter, a new approach based on the mechanistic description of sorption was also undertaken in FEBEX II. The advantages of this approach will be supported by data obtained during the almost a decade of the project.