Sorption

SSM preliminary review of Sr-Site

Presented by: Matt Randall NNL
Structure

• Bedrock sorption
  • Principally SKB R-10-48 “Bedrock Kd data and uncertainty assessment for application in SR-Site geosphere transport calculations
  • Some underlying references

• Bentonite sorption
  • SKB TR-04-18. “SR-Can, Data and uncertainty assessment, Migration parameters for the bentonite buffer in KBS-3 concept”

• Primary focus on methodology
• Bedrock sorption
Solute transport conceptualised as advective flow along a migration path

- Retention caused by matrix diffusion and equilibrium sorption onto rock matrix microstructures

Sorption assumed to be represented by a constant $K_d$, with the inherent assumptions:

- Equilibrium sorption process.
- The water chemistry, mineralogy, and physical state of the in situ rock are identical to those in experiments (extrapolation techniques used to achieve this) and do not vary in time and space (flowpath averaging).
- Linear sorption - radionuclide concentration low enough
Reference Rock type

• Sorption values (in the form of constant $K_d$) supplied for unlatered matrix rock
  • Forsmark reference rock type: granite to granodiorite, metamorphic, medium-grained, SKB rock code 101057)
  • Dominant rock type within the candidate rock volume
  • Most Sorption data are for this rock type

| 28.46 Quartz, 27-41 plagioclase, 0.2 – 36%K-Feldspar, 0.8-8.2% biotite, CEC ~1 cmoles/kg, 0.02 |

Additional sorption on fracture coatings (e.g. clay minerals, co-precipitation with calcite or barite) not considered - Considered cautious approach

May have been useful to include a summary of the site specific rock mineralogy within Kd report – to make it more self contained
Variability

- Uncertainty in spatial variability of material properties is handled in SR-Site by stochastic simulations - distribution of Kd is randomly sampled. As an addition to probabilistic simulations, deterministic calculations are performed using a central *best estimate* value of Kd.

- Spatial and temporal variability and uncertainty of groundwater chemical composition is considered to be a sub-component of overall Kd data uncertainty.

  - Calculations made for the elements where it is possible to approximately estimate the influence of groundwater composition (specifically Cs, Sr, Ra, and possibly Ni) indicate that the impact of variable/uncertain groundwater composition is claimed to be relatively minor in comparison to the overall empirical data uncertainty and therefore does not need to be considered in detail. For these solutes, Kd uncertainty distributions are given for the most *unfavourable* hydrochemical conditions expected during repository groundwater evolution.
Kd derivation approach

• In the Kd data compilation, a number of *transfer factors* were used to account for various biases in the underlying measurement data derived from laboratory experiments.

• $f_A$
  • A surface area normalisation transfer factor which accounts for the difference in sorptive surface area amongst different size fractions used in laboratory investigations. - the ratio of the sorptive surface area of a reference size fraction (2-4mm) of crushed rock relative to the actual size fraction used in the experiment. This allows data obtained for different size fractions to be converted into a mutually compatible form that can then be pooled before extrapolation to in situ conditions.

• $f_m$
  • A mechanical damage transfer factor which accounts for differences between the sorptive surface area of the reference size fraction of crushed rock and undisturbed rock in situ.

• $f_{cec}$
  • A transfer factor which accounts for differences between the cation exchange capacity (CEC) of the site specific rock type and that used in laboratory experiments.

• $f_{chem}$
  • A transfer factor which accounts for differences between the groundwater chemistry under application conditions in situ and that used in laboratory investigations.
Experimental Data

- Kd data taken from a mixture of sources including the Forsmark and Laxemar site investigations and literature data. Supplemented by use of chemical analogues

- Forsmark
  - Cs, Sr, and Am/Eu 950 data points each, crushed rock samples from eight different borehole sections featuring three distinct rock types.
  - Ni, Ra, Np(V), and U(VI) 200 data points each, crushed rock samples from two borehole sections representing a single rock type.

- Laxemar
  - Cs, Sr, and Am/Eu 1,038 data points each crushed rock samples from five different borehole sections featuring four distinct rock types.
  - Ni, Ra, Np(V), and U(VI), 100 data points each, crushed rock samples from one borehole section representing a single rock type.

- Audit trail ok, although convoluted at times. Source data and experimental methods not easily found
Experimental data

- Long term experiments – up to 180 days
- Suggested this could be due to CO₂ outgassing
- Could have significant impact on Kd

“Owing to large uncertainties concerning the interpretation of time dependencies in the laboratory data, no attempt has been made to model or filter the data with regard to sorption contact time.”
Sorption of Am on 101057

• Increase in Kd over time suggesting either equilibrium not reached or impact of pH drift
Use of analogues

- Chemical analogues used where data not available

<table>
<thead>
<tr>
<th>Analogue species</th>
<th>Representing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(I)</td>
<td>Ag(I)*</td>
</tr>
<tr>
<td>Am(III)/Eu(III)</td>
<td>Ho(III), Sm(III), Pu(III), Ac(III), Cm(III)</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Cd(II)*</td>
</tr>
<tr>
<td>Pu(IV)</td>
<td>Np(IV), U(IV), Th(IV), Zr(IV)<em>, Sn(IV)</em>, Tc(IV)*</td>
</tr>
<tr>
<td>Non-sorbing</td>
<td>Cl(-I), I(-I), C(IV,-IV), Tc(VII), Mo(VI)</td>
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</tbody>
</table>

- Pu(IV) used as an analogue for all +4 radionuclides but
  - Questionable whether it is suitable
  - Pu data taken from non site-specific sources
  - Assumptions regarding presence of Pu(IV) in experiments
Radium

- Considered background measured radium
- Some correlation with barium – although “weak”
- Consideration of radiobarite solid solution formation in interpreting laboratory studies
- Site specific data used to derive Kd values, while the Finnish data were used as a consistency check
- Effect of ionic strength has been quantified by introducing a chemistry transfer factor to account for ion-exchange competition (Ba analogue) – though deemed to be low impact
  - “no more than a factor of about 2.4 shift of the best estimate Kd value for the range of salinities encountered during the temperate phase relative to the least favourable groundwater composition at 3,000 y”
  - Although more impact seen in site specific experiments?
Uranium

- Used site specific and literature values
  - Best estimate $1.06 \cdot 10^{-4}$
  - Lower $5.53 \cdot 10^{-6}$
  - Higher $2.05 \cdot 10^{-3}$
Conclusions

• Very systematic and complete presentation of $K_d$ derivation

• General assumptions of “$K_d$” – linearity, equilibrium etc reasonable for safety assessment calculations

• Identified areas of interest
  • Experimental data – extent, control of geochemical conditions, varying conditions
  • Potential for compounded cautiousness: correction factors, neglect of fracture minerals
  • “Uncertainty” encapsulates a lot of variables
  • Lack of thermodynamic modelling to support $K_d$ measurements
• Bentonite sorption
Introduction

• Most sorption measurements are carried out in dilute suspensions - no reliable sorption measurements in compacted material. Also extremely difficult to obtain pore solution from compacted systems

• Approach is to take data from experimental systems and apply “conversion factors”
Bentonite properties

- Similar BET surface areas for loose and compacted MX-80 bentonite
- Differences in sorption due to the aqueous rather than the solid phase
- The focus is thus on an accurate characterisation of bentonite porewaters under repository conditions.
  - Thermodynamic modelling used to predict porewaters
  - Some discrepancies between MX-80 bentonite composition in this derivation and that quoted in TR-10-15 (Design, production and initial state of the buffer)
Derivation of data

- Experimental data for dispersed systems extrapolated to the compacted system through a combination of various “conversion factors”
  - Sorption capacity/CEC
  - pH
  - Speciation
  - Presence of competing ions, particularly carbonate.
- Differences in speciation between sorption experiment conditions and predicted repository conditions were evaluated via thermodynamic modelling.
- Consistency/errors associated with thermodynamic modelling?
Experimental data

- A relatively small number of batch sorption datasets considered.
- Rationale was to use
  - Systematic sets of high quality data
  - Where possible data obtained from MX-80 bentonite
  - Other bentonites considered, as well as data from experiments with montmorillonite
- Experimental details well documented
Availability of data

- Experimental measurements used for Am, Cs (plus thermodynamic modelling), Pb, Np(V), Ni(plus thermodynamic modelling), Se, Th, U(VI)

- Chemical analogues or assumptions of zero sorption for other radionuclides, significantly
  - Thorium used as analogue for U(IV), Np(IV), Pu(IV), Sn(IV), Tc(IV)
  - Calcium used as analogue in thermodynamic models
Uncertainties

- Attempted to identify, separate and treat consistently the various contributions to uncertainty,
- Acknowledging that the available datasets are not sufficient to allow the calculation of statistical uncertainties.
  - CEC: factor of 1.4 on $K_d$ value;
  - pH: factor of 2.5 on $K_d$ value;
  - Speciation and competitive ligands: factor of 1.4 on $K_d$ value.
- Clearly semi-quantitative.
- Sensitivity factor for pH may be too low?