

Review of the SR-Site sorption database for the SR-PSU assessment; preliminary results

Michael Ochs, BMG Engineering Ltd

The sorption database has been reviewed for the SR-Site data and process report. The literature on experimental sorption data that had become available since the publication of TR-04-18 was screened, and no new data were found that were inconsistent with the data sources used for TR-04-18. Therefore, the selection done for TR-04-18 was considered still relevant.

It is also in the process of being reviewed in the frame of the presently on-going preparation of the SR-PSU data report. For many RN, no new relevant data have become available in the meantime, to our knowledge. Where new data have become available, the selection made in TR-04-18 is still relevant in nearly all cases.

A comparison of K_d values selected for SR-Site (SKB 2010) and SR-PSU (data report, in preparation) is given in the following table. Changes in recommended values proposed in SR-PSU are marked in colour:

red: lower values are proposed for SR-PSU in comparison to SR-Site

green: higher values are proposed for SR-PSU in comparison to SR-Site

Explanations are given in the following. These are taken from the SR-PSU data report; it should be noted that this report is in a draft state and the data presented are suggestions that have not yet been qualified.

Radionuclide (oxidation state)	K_d (m ³ /kg)		Upper K_d limit (m ³ /kg)		Lower K_d limit (m ³ /kg)	
	SR-Site	SR-PSU	SR-Site	SR-PSU	SR-Site	SR-PSU
Ac(III)	8	8	233	233	0.3	0.3
Ag(I)	n.a.	pending	15	1	0	pending
Am(III)	61	61	378	378	10	10
¹⁴ C, carbonate species	0	pending	0	pending	0	pending
¹⁴ C, CH ₄ , organic acids	0	0	0	0	0	0
Cd(II)	0.3	0.30	13.3	13.3	0.007	0.007
Cl(-I)	0	0	0	0	0	0
Cm(III)	61	61	378	378	10	10
Cs(I) GEKO/QI		0.11		0.60		0.018
Cs(I) MX-80	0.093		0.56		0.015	
Cs(I) Deponit Ca-N	0.086		0.52		0.014	
Cs(I) Milos	0.090		0.54		0.015	
Eu(III)	8	8	93	93	0.8	0.8
Ho(III)	8	8	93	93	0.8	0.8
I(-I)	0	0	0	0	0	0
Mo(VI)	0	0	0	0	0	0
Nb(V)	3	3	45	45	0.2	0.2
Ni(II)	0.3	0.30	3.3	3.3	0.03	0.03
Np(IV)	63	63	1113	700	4	4
Np(V)	0.02	0.02	0.2	0.2	0.004	0.004
Pa(IV, V)	3	3	45	45	0.2	0.2
Pb(II)	74	74	457	457	12	2.4

Pu(III)	100	61	984	378	10	10
Pu(IV)	63	63	1111	700	4	4
Pu(V)	0.02	0.02	0.2	0.2	0.002	0.002
Pu(VI)	3	3	28	18	0.3	0.3
Ra(II) GEKO/QI		0.005		0.031		0.0009
Ra(II) MX-80	0.0045		0.027		0.00075	
Ra(II) Deponit Ca-N	0.0042		0.025		0.00070	
Ra(II) Milos	0.0044		0.025		0.00073	
Se(-II)	0	0	0	0	0	0
Se(IV)	0.04	0.04	0.4	0.4	0.003	0.003
Se(VI)	0	0	0	0	0	0
Sn(IV)	63	63	1784	700	2.3	2.3
Sr(II) GEKO/QI		0.005		0.031		0.0009
Sr(II) MX-80	0.0045		0.027		0.00075	
Sr(II) Deponit Ca-N	0.0042		0.025		0.00070	
Sr(II) Milos	0.0044		0.025		0.00073	
Tc(IV)	63	63	1784	700	2.3	2.3
Tc(VII)	0	0	0	0	0	0
Th(IV)	63	63	700	700	6	6
U(IV)	63	63	1113	700	3.6	3.6
U(VI)	3	3	18	18	0.5	0.5
Zr(IV)	4	4	103	103	0.1	0.1

General approach

In the current work with the Data Report for SR-PSU (in preparation), the K_d values selected in Ochs and Talerico (2004) and SKB (2010) are considered to be applicable to the present conditions within the discussed uncertainties. Similarly, no new information has emerged in the pertinent literature published after Ochs and Talerico (2004) that would motivate a modification of the applied conversion procedures and uncertainty factors. While new thermodynamic sorption models addressing both ion exchange as well as surface complexation have been developed for several RN, these models are typically parameterised only for simple systems (e.g. pure montmorillonite in contact with an inert electrolyte solution) are not applicable to more complex porewater compositions containing carbonate and other strong ligands (see discussions in NEA 2012). Ideally, the derivation of K_d values for safety analyses would be based on sorption models that are parameterised for similar conditions. However, the available experimental database is not sufficient to permit such an approach (NEA 2012).

New experimental data

With regard to the underlying source data used for the derivation of K_d values, the selections made in Ochs and Talerico (2004) are generally still considered to be valid. For many RN, no new relevant data have become available in the meantime, to our knowledge. The cases where new potentially relevant source data have been determined that were not considered in Ochs and Talerico (2004) and SKB (2010) are discussed in the following

- In case of Ni, Tertre et al. (2005) measured sorption edges on montmorillonite (obtained from MX-80) in 0.025 M and 0.5 M NaClO₄ solution. Their data show approximately the same trend as the data on SWy-1 by Baeyens and Bradbury (1997) but indicate slightly lower sorption. Similarly, Ochs and Talerico (2004) also noted that the sorption isotherm by Bradbury and Baeyens (2003) on MX-80 gave a lower K_d for Ni than their SWy-1 data. Since Ochs and Talerico (2004) conservatively based the recommended K_d for Ni on the

MX-80 source data, the additional data by Tertre et al. (2005) do not motivate any re-evaluation. Rather, they support the original, conservative choice of source data. More recently, Akafia et al. (2011) also measured Ni sorption on smectite (SWy-2). Their data fall within the range delineated by the data of Baeyens and Bradbury (1997) and Tertre et al. (2005).

- New experimental data have also become available in case of selenite, Se(IV). Missana et al. (2009) measured several pH edges of selenite on smectite in 0.001 M to 0.5 M background solutions. Their measured K_d values are higher by about factor 5 or more than the data by Bradbury and Baeyens (2003) considered by Ochs and Talerico (2004). Montavon et al. (2009) measured a sorption edge on MX-80 in 0.05 M background solution. At the relevant pH (7.8), these data agree very well with the sorption isotherm by Bradbury and Baeyens (2003). Ochs and Talerico (2004) also did not consider a number of K_d values measured by Shibutani et al. (1994) and Tachi et al. (1999). These data show very large scatter, but their mean is also close to the source value used by Ochs and Talerico (2004). In summary, the mentioned additional data do not give a reason to revise the proposed sorption values. The other potentially relevant oxidation states Se(-II) and Se(VI) were assigned a K_d of zero. No new data were found that would motivate a revision in either case.
- For Mo, no K_d is given in Ochs and Talerico (2004). In SKB (2010), a K_d of zero is assigned, based on an analogy between the molybdate anion (which is the only species of Mo occurring in normal aqueous solutions) and selenate. SKB (2010) did not consider the study of Motta and Miranda (1989) and Goldberg et al. (1996). The two studies investigated the sorption of molybdate on montmorillonite, but do not give a clear picture. Motta and Miranda (1989) measured sorption isotherms at pH < 5 and saw low but significant sorption. On the other hand, Goldberg et al. (1996) observed a steep decrease of sorption with increasing pH and measured no appreciable sorption at pH > 7. On this basis, it is concluded that the K_d of zero selected in SKB (2010) may be conservative, but that a re-evaluation of Mo sorption is not warranted.
- Andra (2005) report a sorption edge for Nb on smectite extracted from MX-80. These data became available after the publication of Ochs and Talerico (2004) and were not considered in SKB (2010). At a similar pH value, this sorption edge gives a K_d similar to the value measured by Ikeda and Amaya (1998), which was considered in Ochs and Talerico (2004). However, their argument of using a conservative estimate due to the scarcity of data is still considered valid, and no re-evaluation to arrive at a higher value seems warranted.
- For Ag, Ochs and Talerico (2004) did not consider the study by Khan et al. (1995), who measured the sorption of Ag on bentonite. While their data are not conclusive, they indicate K_d values in the range of about 0.01-0.4 m³/kg. Considering further the potential effect of chloride on Ag sorption, it is proposed to revise the upper limit of 15 m³/kg given in Ochs and Talerico (2004) down to 1.0 m³/kg. As in Ochs and Talerico (2004), a lower limit of zero and no best estimate is proposed. This work is still ongoing within the SR-PSU project and a final decision on data has not yet been made.
- For Sn (specifically Sn(IV), Sn(II) is not relevant), Ochs and Talerico (2004) did not consider the study by Oda et al. (1999), who measured a sorption edge on untreated Kunigel-V1 bentonite in 0.01 M NaCl. Within the (relatively large) experimental scatter, their dataset is almost identical to the data by Bradbury and Baeyens (2003), which had been considered as potential source data but were not used in the end. Both studies indicate consistently high K_d values of ≈ 1000 m³/kg for about pH 4-7, decreasing to ~ 150 m³/kg at pH 10. Thus, the decision by Ochs and Talerico (2004) to base K_d for Sn on an analogy with Th can be viewed as conservative.
- In case of Pb, some new sorption data (Akafia et al. 2011) have become available after the publication of Ochs and Talerico (2004) and SKB (2010). These data show generally a good agreement with the data by Ulrich and Degueldre (1993), which were selected as source data

by Ochs and Talerico (2004). However, a part of the data by Akafia et al. (2011) indicate lower sorption than the data by Ulrich and Degueldre (1993). A comparison of the experimental conditions indicates that this can be attributed to the difference in initial Pb concentrations, which are significantly lower in case of Ulrich and Degueldre (1993). Assuming that trace concentrations are most representative for the migration of radionuclides in a bentonite barrier, the data by Ulrich and Degueldre (1993) are still regarded as the most representative. However, to acknowledge the data by Akafia et al. (2011), it is proposed to reduce the previously derived lower limit by a factor of five while retaining the best estimate and upper limit values given in Ochs and Talerico (2004).

- For Am, new sorption edge data by Bradbury and Baeyens (2006) on Na- and Ca-SWy-1 have become available. The data on Ca-SWy-1 agree well with the data by Gorgeon (1994), which are the source data for the K_d values recommended in Ochs and Talerico (2004) and SKB (2010). In comparison, the data for Na-SWy-1 indicate higher sorption of Am. As the speciation of Am in the experiments by Bradbury and Baeyens (2006) is more straightforward than in case of Gorgeon (1994), it could be argued that the data recommendation should be re-evaluated, which could only lead to a higher recommended K_d . However, in view of the abovementioned difference between the Na- and Ca-forms, it is proposed to retain the more conservative value derived on the basis of the data by Gorgeon (1994).
- Ochs and Talerico (2004) and SKB (2010) base the recommended K_d of Cm on an analogy with Am. Systematic sorption data of Cm have become available from Rabung et al. (2005) for Ca-SWy-1 in simple Ca-electrolyte solution and from Grambow et al. (2006) for MX-80 in synthetic porewaters. The data by Rabung et al. (2005) follow roughly the data by Bradbury and Baeyens (2006) for the Ca-system. The data by Grambow et al. (2006) show a much less pronounced sorption edge; they are similar to the data for Ca-smectite at $\text{pH} \approx 7$, but are by nearly an order of magnitude lower in the range of $\text{pH} 8-10$. Considering the established chemical similarity between Am and Cm and the good agreement between the data by Rabung et al. (2005) and the corresponding data by Bradbury and Baeyens (2006) for Am, the value proposed by Ochs and Talerico (2004) is still considered valid.
- New sorption data for U(VI) by Bradbury and Baeyens (2005) have become available. In comparison to the data by Pabalan and Turner (1997) these data would indicate higher sorption. Thus, the data derived in Ochs and Talerico (2004) may be somewhat conservative.
- For Pa, sorption edge measurements on Na-montmorillonite (SWy-1) by Bradbury and Baeyens (2006) became available after the publication of Ochs and Talerico (2004). These data were also not considered in SKB (2010). They indicate a constant sorption value of about $90 \text{ m}^3/\text{kg}$ over a pH range from 4 to 10.5. This K_d value is more than an order of magnitude higher than the K_d values estimated previously by Ochs and Talerico (2004) on the basis of data for Pa presented in Yu and Neretnieks (1997). However, due to the lacking detail regarding the composition of the bentonite and porewater in the SFR Silo, and hence the speciation of Pa, no re-evaluation of Pa sorption is done and the values proposed in Ochs and Talerico (2004) are accepted as very conservative estimates.
- For all other RN (C, Cl, Sr, Zr, Tc, I, Cs, Ho, Pu, Np, Cd, Eu), no new relevant sorption data have become available.

Handling of comments by Zhou et al. (2009)

In the framework of a review of the safety assessment study SAR-08, Zhou et al. (2009) criticised the fact that the data recommended by Ochs and Talerico (2004) are based on a limited database. There are several reasons for this approach:

- The main reason is the strong dependency of K_d on chemical conditions. This means that K_d values can be directly applied only in case of very similar conditions. In all other cases, it is

required to transfer the literature data to the PA-conditions (NEA 2005) by means of conversion procedures (or thermodynamic models, where available). The main uncertainty of recommended K_d stems from this transfer of sorption data to different conditions (NEA 2005). The respective uncertainties are considered explicitly in Ochs and Talerico (2004). The resulting overall uncertainties in K_d are significantly larger than the scatter of experimental data from different (reliable) sources.

- Because of the dependency of K_d on chemical conditions, it would be a misconception to assume that a compilation of experimental data from different sources would allow a better assessment of uncertainties in source data. This is because most of the apparent scatter observed in comparisons of experimental data is typically due to the variability of conditions rather than to actual uncertainty. When like is compared with like (i.e., data obtained under matching conditions), the scatter is often substantially reduced. Accordingly, Ochs and Talerico (2004) carried out a transparent, quantitative derivation on the basis of selected source data rather than a more qualitative expert estimation on the basis of large data compilation.
- The only datasets considered to be of highest quality are those that are obtained as a function of an important system variable, such as pH (sorption edges), RN concentration (sorption isotherm), or other important solution constituents. The embedding in a series of related data lends additional confidence to the individual data points in terms of both representativeness and absence of bias. Single point measurements or data obtained under a narrow range of conditions are much less useful and more difficult to transfer to different conditions, because no clear trends can be assigned to such datasets. In the present context it is therefore not helpful to 'dilute' state of the art source data (as outlined above) with additional datasets of lesser quality.

Zhou et al. (2009) also comment on the rather high upper limits as well as the best estimate values given for several RN in their tetravalent oxidation state (Tc, Sn, Np, Pu) in Ochs and Talerico (2004) and SKB (2010). In particular, it is pointed out that such high values have not been recommended for earlier safety assessments. Regarding the currently recommended values given in the SR-PSU Data Report (in preparation) as well as those in the previous assessments of Ochs and Talerico (2004) and SKB (2010), the following is pointed out:

- From a fundamental point of view, it needs to be made clear that the very strong sorption of tetravalent elements is experimentally confirmed, which is consistent with their pronounced tendency towards hydrolysis. Indeed, the mentioned best estimates are well within the range of experimentally measured K_d values for e.g. Sn(IV) and Th. Thus, they are not unusual according to the present state of the art.
- The values for the abovementioned RN in their tetravalent oxidation state are based on analogy with Th. In turn, the recommended values for Th were selected by Ochs and Talerico (2004) on the basis of high-quality and well-established experimental sorption data (Bradbury and Baeyens 2003).
- The high upper limits are simply the result of the applied uncertainty factors. As already pointed out in Ochs and Talerico (2004), it has to be admitted that it is not clearly established whether errors should be distributed around derived K_d values in a linearly or logarithmically symmetrical way. In choosing the latter option, Ochs and Talerico (2004) followed the approach of Bradbury and Baeyens (2003). In any case, when the recommended parameter space is sampled stochastically, the bounding upper/lower values will feed into safety assessment calculations as part of the entire data range.
- In the SR-PSU Data Report (in preparation) the present use of Th data as analogue for tetravalent elements is handled in a simplified way in comparison to the approach used in Ochs and Talerico (2004) and SKB (2010). Conservatively, the increased uncertainty is not considered to be log-symmetrical with respect to the selected values but is only applied to the lower limit. Thus, some of the high upper limits are avoided.

2) Modelling approach and underlying TDB

The possibility of using different modelling approaches (mainly for bentonite porewater composition) and alternative thermodynamic data for radionuclide speciation has been acknowledged in TR-04-18 as well as in the SR-Site data and process reports.

In comparison to the uncertainty in terms of groundwater, bentonite, and porewater composition that had been taken into account in the original data derivation, uncertainties in the modelling and TDB are considered as less relevant.

For example, the bentonite porewater composition is dependent on the modeling approach chosen, but also on various assumptions regarding basic boundary conditions (leachability of accessory minerals, open vs closed systems, and so on). The latter uncertainties are explored to some degree in TR-04-18. In comparison to typical porewater compositions calculated through other models (as given in various literature publications) the results indicate that the effect of such basic assumptions is clearly more important than (typically fairly minor) model differences.

Similarly, there are basic and as yet unresolved uncertainties regarding the surface speciation of RN. In particular, the influence of carbonate complexation is not clear. Based on a comparison with K_d values derived from diffusion data, it was decided in TR-04-18 to assume that carbonate complexation would not compete with sorption. It is felt that such basic assumptions have a much larger effect on calculated K_d than differences in the underlying TDB (as long as high-quality TDBs are being used).

References

- Akafia M M, Reich T J, Koretsky C M, 2011.** Assessing Cd, Co, Cu, Ni and Pb sorption on montmorillonite using surface complexation models. *Applied Geochemistry* 26, S154–S157.
- Andra, 2005.** Dossier 2005 Argile. Safety evaluation of a geological repository. Châtenay-Malabry: Agence nationale pour la gestion des déchets radioactifs (Andra).
- Baeyens B, Bradbury M H, 1997.** A mechanistic description of Ni and Zn sorption on Na-montmorillonite. Part I: Titration and sorption measurements. *Journal of Contaminant Hydrology* 27, 199–222.
- Bradbury M H, Baeyens B, 2003.** Near field sorption data bases for compacted MX-80 bentonite for performance assessment of high-level radioactive waste repository in Opalinus Clay host rock. Nagra Technical Report NTB 02-18, Nagra, Switzerland.
- Bradbury M H, Baeyens B, 2005.** Experimental measurements and modelling of sorption competition on montmorillonite. *Geochimica et Cosmochimica Acta* 69, 4187–4197.
- Bradbury M H, Baeyens B, 2006.** Modelling sorption data for the actinides Am(III), Np(V) and Pa(V) on montmorillonite. *Radiochimica Acta* 94, 619–625.
- Goldberg S, Forster H S, Godfrey C L, 1996.** Molybdenum adsorption on oxides, clay minerals, and soils. *Soil Science Society of America Journal* 60, 425–432.
- Gorgeon L, 1994.** Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux. PhD thesis. Université de Paris 06, France.
- Grambow B, Fattahi M, Montavon G, Moisan C, Giffaut E, 2006.** Sorption of Cs, Ni, Pb, Eu(III), Am(III), Cm, Ac(III), Tc(IV), Th, Zr, and U(IV) on MX 80 bentonite: an experimental approach to assess model uncertainty. *Radiochimica Acta* 94, 627–636.

- Ikeda T, Amaya T, 1998.** Model development of chemical evolution in repository Vol.II Acquisition of nuclide migration data in near-field. Technical Report PNC ZJ 1281 98-003, Power Reactor and Nuclear Development Corporation, Japan.
- Khan S A, Rehman R, Khan M A, 1995.** Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite. *Waste Management* 15, 271–282.
- Missana T, Alonso U, García-Gutiérrez M, 2009.** Experimental study and modelling of selenite sorption onto illite and smectite clays. *Journal of Colloid and Interface Science* 334, 132–138.
- Montavon G, Guo Z, Lützenkirchen J, Alhajji E, Kedziorek M A M, Bourg A C M, Grambow B, 2009.** Interaction of selenite with MX-80 bentonite: effect of minor phases, pH, selenite loading, solution composition and compaction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 332, 71–77.
- Motta M M, Miranda C F, 1989.** Molybdate adsorption on kaolinite, montmorillonite, and illite: constant capacitance modeling. *Soil Science Society of America Journal* 53, 380–385.
- NEA, 2005.** Management of uncertainty in safety cases and the role of risk: workshop proceedings, Stockholm, Sweden, 2–4 February 2004. Paris: Nuclear Energy Agency, Organisation for Economic Co-operation and Development.
- NEA, 2012.** Thermodynamic sorption modelling in support of radioactive waste disposal safety cases. NEA Sorption Project Phase III. Paris: Nuclear Energy Agency, Organisation for Economic Co-operation and Development.
- Ochs M, Talerico C, 2004.** SR-Can. Data and uncertainty assessment. Migration parameters for the bentonite buffer in the KBS-3 concept. SKB TR-04-18, Svensk Kärnbränslehantering AB.
- Oda C, Ikeda T, Shibata M, 1999.** Experimental studies for sorption behavior of tin on bentonite and rocks, and diffusion behavior of tin in compacted bentonite. JNC TN8400 99-073, Japan Nuclear Cycle Development Institute.
- Pabalan R T, Turner D R, 1997.** Uranium(6+) sorption on montmorillonite: experimental and surface complexation modelling study. *Aquatic Geochemistry* 2, 203–226.
- Rabung T, Pierret M C, Bauer A, Geckeis H, Bradbury M H, Baeyens B, 2005.** Sorption of Eu(III)/Cm(III) on Ca-montmorillonite and Na-illite. Part 1: Batch sorption and time-resolved laser fluorescence spectroscopy experiments. *Geochimica et Cosmochimica Acta* 69, 5393–5402.
- Shibutani T, Yui M, Yoshikawa H, 1994.** Sorption mechanism of Pu, Am and Se on sodium-bentonite. In Barkatt A, Van Konynenburg R A (eds). Scientific basis for nuclear waste management XVII: symposium held in Boston, Massachusetts, USA, 29 November – 3 December. Pittsburgh, PA: Materials Research Society. (Materials Research Society Symposium Proceedings 333), 725–730.
- Tachi Y, Shibutani T, Nishikawa Y, Shinozaki T, 1999.** Sorption behavior of selenium on bentonite and granodiorite under reducing conditions. JNC TN8410 94-395, Japan Nuclear Cycle Development Institute.
- SKB, 2010.** Data report for the safety assessment SR-Site. SKB TR-10-52, Svensk Kärnbränslehantering AB.
- Tertre E, Berger G, Castet S, Loubet M, Giffaut E, 2005.** Experimental sorption of Ni²⁺, Cs⁺ and Ln³⁺ onto a montmorillonite up to 150°C. *Geochimica et Cosmochimica Acta* 69, 4937–4948.
- Ulrich H J, Degueldre C, 1993.** The sorption of ²¹⁰Pb, ²¹⁰Bi and ²¹⁰Po on montmorillonite: a study with emphasis on reversibility aspects and on the radioactive decay of adsorbed nuclides. *Radiochimica Acta* 62, 81–90.

Yu J-W, Neretnieks I, 1997. Diffusion and sorption properties of radionuclides in compacted bentonite. SKB TR 97-12, Svensk Kärnbränslehantering AB.

Zhou W, Kozak M, Xu S, Stenhouse M, 2009. Review and Assessment of SFR 1 Long-term Safety Analyses, Report MSCI-2818-3 Rev 3.1, SSM dnr 2008/3239.