R-05-75

Assessment of uncertainty intervals for sorption coefficients

SFR-1 uppföljning av SAFE

Peter Cronstrand, SwedPower

December 2005

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co
Box 5864
SE-102 40 Stockholm Sweden
Tel 08-459 84 00
+46 8 459 84 00
Fax 08-661 57 19
+46 8 661 57 19

ISSN 1402-3091
SKB Rapport R-05-75

Assessment of uncertainty intervals for sorption coefficients

SFR-1 uppföljning av SAFE

Peter Cronstrand, SwedPower

December 2005

Abstract

Sorption coefficients, K_d, are one of the key parameters in various models that estimate the rate of transfer of radionuclides through the barriers surrounding a nuclear waste repository. This report compiles the K_d-values for the relevant substrates, cement/concrete, bentonite and sand/gravel and sand/bentonite, and evaluates the accompanying uncertainty intervals on a semi-quantitative basis.

Contents

1 Introduction

1.1 Purpose

Sorption processes are a vital part in all models which address the transfer rates of radionuclides. Due to the nature of the experimental data, which can be either extremely limited or comprehensive depending on the nuclide and the conditions, the published sorption coefficients have associated uncertainty intervals. The purpose of this report is therefore to evaluate such uncertainty intervals for the sorption coefficients originally compiled elsewhere.

1.2 Background

A manifold of processes affects the mobility of radionuclides in a waste repository. In a strictly linear model, they can be quantified by a set of migration parameters; sorption coefficients, K_d, effective diffusivity, D_e, porosity, ε and the density, ρ. Ultimately, they can be incorporated in a single parameter, the apparent diffusivity, D_a, as

$$D_a = \frac{D_e}{\varepsilon + K_d \rho} \qquad (1)$$

One of the key parameters when estimating the elements rate of transfer through the repository is therefore the K_d-value for each of the barriers (cement/concrete, bentonite, sand/gravel and sand/bentonite) surrounding the repository.

2 Methodology

Recent decades have produced an increasing pool of experimental data of which no set completely unambiguously can represent the expected conditions in a waste repository. In order to assign values of relevance and accuracy three different approaches can be distinguished;

- A qualitative approach based on “expert judgements”.
- A semi-quantitative approach based on various conversion factors.
- A fully quantitative model where the parameters in the model can be tuned to reflect the actual conditions.

In each case the necessary input can be based on

- A careful selection of a single value that exactly corresponds/match the desired conditions in the repository (“fishing”).
- A filtering process based on a comparison of the most relevant data in conjunction with qualitative discussions and analogies from which appropriate values can ultimately be derived (“filtering”).

A fully quantitative model is obviously intuitive appealing; however the methodology still necessitates a critical review of the required data due to the scarcity and occasionally poor quality of experimental data. Various complexation processes –sometimes involving co-precipitation processes– are not fully understood in detail and are thus not easily incorporated by a set of conversion factors as in a semi-quantitative model. The inherit weaknesses of a pure qualitative approach are often associated with vagueness and a subjective tendency. Clearly, the frequent use of analogies in order to compensate for the lack of relevant data may appear arbitrary, but this remains the approach on which the majority of compilations are based.

The sources of uncertainty are either related to the experimental data *per se*, *i.e.* the experimental method employed, etc or to the relevance of the data for the particular conditions. The first class of uncertainties typically involves estimations whether precipitation has affected the data. The second class of uncertainties is related to the means used to extrapolate the values to the appropriate conditions.

3 The chemical processes behind Sorption

Sorption relates to processes in which a substance in solution attaches to a solid material. Depending on whether the substance is attached by an uptake or by adhering to the surface one usually distinguishes between absorption and adsorption. Since it may be difficult microscopically to distinguish between the two types of processes and the macroscopical effect may be identical the term sorption covers both processes. Irrespective of the distinction, sorption constitutes the main retention process for dissolved elements from spent nuclear fuel. The taxonomy of sorption processes is not completely consistent, but essentially reflects three different types of chemical bonds; covalent bond, electrostatic attraction and the van der Waals bond. The resulting schemes are however somewhat obscured depending on if the focus is on the result or the process. If the emphasis is on the results the corresponding distinction separates the following type of concepts; inner-sphere complexes, outer sphere complexes and diffuse swarm complexes. If, on the other hand the focus is on the process, one usually distinguishes, chemisorption, elecrostatic adsorption (ion exchange) and physisorption. Despite the differences in chemical origin, the rates of the processes are determined by both the properties of sorbing substance and the chemistry of the substrate microscopically defined by the surface area, surface charge, density of sorbing sites and the functional groups.

3.1 Ion-exchange

Planar surfaces contain permanently negative charged sites, which normally are occupied by various types of cations. The exchange of ions is in comparison with other sorption processes rapid and reversible and a typical reaction is Cs^+ replacing Na^+. Cation-exchange is obviously dependent on the competition between all the prevalent ions to the available sorption sites and is therefore sensitive to ionic strength. In general the process is observed to be independent of the original concentration of the dissolved substance, though a saturation of the surface can occur. In comparison with other sorption processes, ion exchange is fast and reversible. Element with large ionic radius are weakly hydrated, which means that they can approach charged sites more closely and associate more strongly due to a smaller sphere of hydration than ions with small ionic radius. This phenomena elucidates the following two observed sequences with respect to sorption strength, $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and $Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

3.2 Surface complexation

Surface complexation, or chemisorption, relates to reactions with surface functional groups. Clay particles contain edge sites of hydroxyl groups, which in a reaction will be negatively or positively charged. If no water molecule resides between the functional group and the radionuclide the result is classified as inner-sphere and corresponds to a more covalent type of bond. The process is in general slow, partly irreversible and concentration-dependent. Surface complexation is typically formed with strongly hydrolized species as actinides.
If, on the other hand, at least one water molecule is between the functional group and the molecule, the complex is denoted an outer-sphere complex and occurs as a result of an electrostatic attraction between the charged surface group and the complex. In contrast to inner sphere-complexation, the process is rapid, reversible and concentration independent.

The pH will affect both the surface charge and the degree of hydrolysation of the dissolved species.

Both types of reaction are therefore dependent on the pH, but only the outer-sphere complex will also depend on the ionic strength. All the reactions must be exothermic, *i.e* Gibbs activation energy $\Delta G < 0$. Because translational freedom is reduced when adsorbed, ΔS is negative. In order to have $\Delta G < 0$, therefore ΔH, must be negative ($\Delta G = \Delta H - T\,\Delta S$). A value for the enthalpy less than – 40 kJ mol^{-1} is considered to signify chemisorption

For elements which sorb by surface complexation, the sorption will generally decrease with decreasing pH. This holds for Co, Ni, trivalent actinides and the lanthanides, but not to the same extent for the tetravalent actinides, which undergo strong hydrolysis. Only a pH below 6 will significantly affect the sorption.

3.3 Physisorption

Adsorption can also occur as a result of van der Waals forces with interaction energies lower than condensation energy, *i.e.* –44 kJ mol^{-1}. Such small energies can be absorbed as vibrations of the lattice. Enthalpies less than –25 kJ mol^{-1} is considered to signify physisorption.

4 Factors influencing sorption

The factors that influence the sorption are either related to the substrate (cement, bentonite, granite) or the groundwater chemistry. Typical factors of the first kind are the abundance of various minerals, the compactness of the bentonite, whereas the second kind includes factors as pH, redox conditions, and ionic strength. Yet a factor that influences the assessment of sorption coefficients –though not affecting the sorption *per se*– is the technique of compensating the lack of experimental data by various types of analogy considerations.

4.1 Factors related to the water chemistry

4.1.1 pH changes

pH is the most critical parameter affecting the sorption. It determines the surface complexation site, the sorbing element as well as the properties of addional participating ions as for instance carbonates. Changes in pH will affect the sorption at both ends of the pH interval, at low pH by the competition of H^+ and at high pH by a similar competition between $M(OH)^-_x$ and OH^-. Extremely high pH, as in cement (pH 13.5) will affect K_d-values, especially for those elements that form negatively charged hydroxyl complexes ($Me(OH)x^{y-}$).

A pH below 7 will also affect K_d, in particular for elements that are assumed to be fully hydrolised. For most radionuclides a lower pH corresponds to decrease of K_d. Exceptions to this are the pentavalent and hexavalent actinides that form oxo-cations U(VI), Np(V), Pu(VI,V).

Among the radionuclides whose K_d is sensitive to pH one finds elements that exists as hydrolysed cations around pH 7, in particular Am, Ce, Eu, Ho, Nb, Ni, Np, Pb, Pd, Pu, Sm, Sn, U, Zr. Since pH changes in particular affect the distribution between various complexation equilibriums present in the repository, it is impossible to assign a single numerical factor of reduction in order to address the issues related to pH.

4.1.2 Redox conditions

The impact of the redox potential is particularly emphasized in elements that switches between anionic and cationic forms and elements where change of oxidation state crucially alter the solubility. In the repository the redox potential is assumed to be less than –200 mV, which is sufficient for keeping the redox sensitive actinides in their lower oxidation state. In general, higher oxidation states correspond to a lower K_d. An exception to this rule among the radionuclides in this study is Selenium, for which a switch from II to IV leads to increasing K_d. Radionuclides that in particular are sensitive to the redox conditions are C, Np, Pd, Pu, Se, Tc and U. Because of the substantial complexity, the sensitivity of the sorption to the redox potential cannot be parameterized into a single numeric factor.

4.1.3 Ionic strength

The salinity is expressed as the concentration of chloride and especially affects elements that sorb by ion exchange, *i.e.*, alkali and alkali earth metals. The counter ions to chloride, Na and K, will compete with the other elements and reduce the K_d. In particular, the alkali and alkali earth metals (Cs, Ra, Sr) are affected by this factor.

Ions such as carbonates cannot be regarded as entirely competitive. For instance tetra– and higher valent actinides, which form hydroxyl-carbonate complexes, may by analogy form similar complexes at edge sites of clay particles and hence improve the sorption capacity. In addition to the alkali and alkali earth metals mentioned above, also Ag, Cd, Co, Ni, Np(V), Pd and U(VI) are considered to be sensitive to the salinity of the water. For most elements the reduction corresponds to a factor 5–10, but for certain elements (Sr) it exceeds 100.

4.1.4 Organic complexing agents

The degradation of cellulose within the repository may contribute with small but potent concentrations of organic acids, such as isosaccharinic acid (ISA), with a strong chelating effect, which enhances the solubility and reduces the sorption of the radionuclides. For ISA, the critical concentration has been estimated to 10^{-4} M. The quantification of this effect is in most compilations assessed as a reduction with a factor 10 for di– and trivalent elements such as Am, Cd, Cm, Co, Eu, Ho, Ni, Pd and Sm and a factor 100 for tetravalent elements and above such as Nb, Np, Pu, Sn, Tc, U and Zr.

4.1.5 Temperature

The influence of temperature is considered to be sub ordinate to other factors.

4.1.6 Summary of factors influencing the sorption

The major factors influencing the sorption with their corresponding numerical factor are displayed in Table 4-1.

Table 4-1. Factors influencing the sorption.

Factor	Numerical reduction factor	Elements
pH	Not quantifiable	Am, Ce, Nb, Ni, Np, Pa, Pb, Pd, Pu, Sm, Sn, U, Zr
Ionic strength	5 –100	Ag, Cd, Co, Cs, Ni, Np(V), Sr, Pd, Ra, U(VI)
Redox	Not quantifiable	C, Np, Pa, Pd, Pu, Se, Tc, U
Complexing organic acids	10 – 100	Am, Cm, Eu, Ho, Mo, Nb, Ni, Np, Pd, Sm, Sn, Tc, Pu, U, Zr

4.2 Factors related to the substrate

4.2.1 Type of mineral

For certain elements a correlation between sorption and the distribution of minerals has been observed. Tin exhibits sorption preferences according to the series; hematite > goethite > montmorillonite > biotite > quartz. The presence of calcite strongly affects the sorption of carbon and strontium. For trivalent actinides co-precipitation with calcite has been shown to affect the sorption. For most scenarios, the water composition is expected to be more important than the rock composition.

4.2.2 Compactness of the bentonite

The degree of compaction of bentonite affects the mobility of radionuclides, but it has been shown to be difficult to separate the potential changes of K_d from variations in porosity. Ion exchange capacity follows the scheme: $Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+}$, *i.e.* in general Ca will more easily replace Na than vice versa. The ion exchange capacity originates from charge deficit in the lattice and exposure of structural elements. It is a universal series, but of course controlled by ion concentration. The dependence on concentration also is influenced by the type and valence of the ion. Decreasing amount of calcium increases the difficulty of releasing the remaining calcium, in contrast to sodium which tends to become easier to release. Magnesium and potassium seem less affected by such saturation effects, possibly due to size and charge conditions. This scheme of selectivity can also be related to the compactness of the bentonite. Compact clay seems to prefer monovalent cations, whereas loose clay has a stronger tendency to accept divalent cations.

4.2.3 Degradation/alteration of bentonite due to prolonged contact with the concrete

The quantification of this effect is in compilations estimated as a factor of occasionally as high as 100, but this includes also changes in pH.

4.3 Factors related to the use of analogies

The occasionally scarce amount of experimental data motivates the use of analogies in order to address the sorption for certain elements. The primary idea behind these analogy assessments has exclusively been a common oxidation state, while other important chemical concepts as ionic radius or the principle of hard/soft acid/base (HSAB) in general has been neglected. Whereas the ionic radii of an element determines the hydration and ultimately the ability to approach a sorption site, the HSAB principle provides clues regarding the most likely ligands when forming complexes. The classification of hard and soft acids and bases is essentially an empiric conclusion, but coincides with many other chemical properties such as charge densities, ionic radii, electron affinities and solubility and can also partly be motivated on a molecular orbitals (MO) basis. Hard Lewis acids are characterized by a high positive charge in combination with small ionic radius and low electron affinity. The species do not in general contain electron pairs in their valence shell and the lowest unoccupied molecular orbital (LUMO) are often high in energy. The soft Lewis acids, in contrast, have large ionic radii in combination with a lower charge and are —compared to the hard acids– easy to oxidise and polarise. The valence shells contain electron pairs and the LUMOs are lower in energy. Intermediate species borrow properties from both classes. The essence of the principle is that hard acids prefer forming complexes with hard bases and soft acids with soft bases. A selection of relevant ions in this classification scheme is shown in Table 4-2.

Table 4-2. Selected hard, soft and intermediate metal centres and ligands.

	Ligand (Lewis bases)	Metal centres (Lewis acids)
Hard class (a)	F^-, Cl^-, OH^-, CO_3^-, NO_3^-, SO_4^-	Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{4+}, Sn^{4+}, Fe^{3+}, Co^{3+}, Pu^{4+}, Zr^{4+}, Mo^{3+}
Soft class (b)	I^-, CN^-	Ag^+, Cd^{2+}, Pd^{2+}
Intermediate	Br^-, NO_2^-, SO_3^-	Co^{2+}, Ni^{2+}, Sn^{2+}, Fe^{2+}

Out of 26 elements, approximately 10 elements are mainly assessed through analogy considerations (see Table 4-3). Frequently employed elements when assigning K_d-values are Th, Am, Eu, Np and Ni. Undoubtedly, the most employed object of comparison is Th, which has served as a gauge for the actinides as well as Tc, Zr and Sn in a limited pH interval. Although most likely sharing oxidation state, the substantial differences in ionic radii may raise objections to this approach. While Th has ionic radius of 1.02 Å, it is far lower for Sn(IV) and Zr(IV), 0.71 and 0.79, respectively. Therefore Sn and Zr will be more strongly hydrated than Th, which may reduce the applicability of this comparison. The same situation will occur for the pair Ni(II) and Cd(II) where the difference in ionic radii is 0.26 Å (0.69 Å compared to 0.97 Å). While Cd and Pd are typical soft acids, Ni is considered to be an intermediate species with only vague preferences regarding bonding. Yet a similar and possibly not entirely adequate analogy concerns the elements Cs and Ag, especially since the major sorption process here is ion exchange. The difference in ionic radii is 0.46 Å (1.67 Å and 1.26 Å) which should imply a considerably stronger hydration of Ag and hence a lower sorption. Moreover, while Cs usually is considered a hard acid in the HSAB classification, Ag is a soft acid with completely different preferences regarding complexation. For the actinides and lanthanides there are only minor mutual differences in ionic radii and the analogies appear more valid.

Table 4-3. Questionable analogies marked with a star (*).

Base	Oxidation state	Elements
Th	IV	Np(IV), Pu(IV), U(IV), Zr(IV)*, Tc(IV)*, Sn(IV)* (in narrow pH interval only)
Am	III	Pu(III)
Eu	III	Ce, Ho, Sm
Np	V	Pu(V)
Ni	II	Co(II), Cd(II)*, Pd(II)*
Cs	I	Ag(I)*

In conclusion, the concepts of ionic radii and hard/soft acid/bases may not be sufficient to explain certain observed features, but definitely emphasize the limited scope of some of the employed analogies.

5 Data and uncertainties for the sorbing elements

5.1 Quantifying uncertainties

Following the approach of Ochs et al. /9/, one can assign uncertainty factors for each of the factors influencing the sorption. The observation that errors are distributed symmetrically on a log-scale motivates the introduction of up– and downshifting multiplicative uncertainty factors, σ_u and σ_d. The upper and lower limits are thus evaluated as

$$\widehat{K}_d = K_d \sigma_u \tag{2}$$

$$\breve{K}_d = \frac{K_d}{\sigma_d} \tag{3}$$

which on a log scale correspond to addition and subtraction of log σ. Assuming a symmetrical uncertainty interval implies that $\sigma_u = \sigma_d = \sigma$ and the relations above can be written as

$$\log \widetilde{K}_d = \log K_d \pm \log \sigma \tag{4}$$

The factors suggested by Ochs et al. /9/ are either related to uncertainties of the experimental data *per se*, *i.e.*,

- Uncertainty of source data, σ_d

or to uncertainties introduced when scaling to data to application conditions, *i.e.*

- Cationic exchange capacity conversion (CEC), σ_c.
- pH conversion, σ_p.
- Speciation, σ_s.
- Analogy considerations, σ_a. A good analogue corresponds to a factor 2.5, whereas a more questionable corresponds to a factor 4.
- Batch conversion, σ_b. This factor includes uncertainties related to extrapolations regarding the substrate, *e.g.* compactness of the bentonite, aging of the concrete etc.

A summary of these quantifications of uncertainties is displayed in Table 5-1.

Table 5-1. A quantification of the uncertainty factors.

Factor	σ	Comments
Source data	1.6	
CEC conversion	1.4	
pH conversion	2.5	
Speciation	1.4	
Analogy consideration	2.4/4.0	Relevant/questionable
Conversion of batch data	2.0	

A worst-case scenario hence corresponds to a factor 60 ($\sigma_s \times \sigma_c \times \sigma_p \times \sigma_s \times \sigma_a \times \sigma_b$), for a less questionable analogue the factor is reduced to approximately 40 at maximum. For elements where no analogies were employed the uncertainty is further reduced to approximately 15 and if the element moreover is insensitive to ionic strength the factor can be assumed to be even lower, approximately 10. In spite of the high degree of structure of this scheme, there are ambiguous cases where contradictory data motivates even more generous uncertainty intervals. This could also be motivated for elements with uncertain oxidation state, scarcity of relevant data in conjunction with refutable analogues. There are also situations where the experimental data are such that the uncertainty interval may be asymmetric even on a log-scale.

The assessment of uncertainties for the K_d-values in this report has partly employed the scheme described above, but also included additional qualitative judgements based on the inconsistencies within the previous assessments.

5.2 Alkali, alkali earth elements and Silver

Cesium (Cs). Cesium is a univalent ion and sorbs by cation exchange, mainly on ballast. According to this fact –and as verified by several studies– sorption increases with decreasing ionic strength, but exhibit only weak pH dependence. Both cement and bentonite are dynamic substrates and the sorption is likely to depend on the state of the cement and the bentonite. For cement and high ionic strength and pH >12.5 the value 0.001 m^3/kg is suggested (Wiborgh et al. /10/), whereas for cement depleted of highly soluble alkali hydroxides and a low ionic strength and pH > 11 the value 0.1 m^3/kg has been suggested (Allard et al. /2/). The sorption on bentonite has shown to be dependent on the chemical changes in the material inferred from the contact with concrete. A K_d-value 0.2 m^3/kg have been proposed for fresh bentonite and 0.005 m^3/kg for bentonite affected by components from the concrete (Wiborgh et al. /10/). Considering this effect as well as a total uncertainty factor evaluated from the scheme in Section 5.1, a span of 0.0005-0.05 m^3/kg is selected (Andersson /3/). The sorption on granite appears to be sensitive to the type of minerals and only indirectly to the pH dependence through the chemical change of the mineral and rock surfaces /6/. A pessimistic value of 0.01 m^3/kg for sorption on granite is here selected, which is slightly lower than the value suggested by Carbol et al. /6/.

Silver (Ag). Silver is present in groundwater as Ag(+I) and is considered to exhibit sorption properties in parity with Cs. All values proposed are only derived using Cs as an analogue where one expects cation exchange as the dominating process and sensitiveness to ionic strength. However the substantial difference in ionic radii indicates that the sorption should be lower than for Cs, but in particular that the uncertainty interval should be wider. Silver forms insoluble compounds with several anions, but not with carbonates, and hydrolysis of Ag will typically lead to either AgOH or $Ag(OH)_2^-$. A pessimistic approach suggests K_d-values in accordance with Cs, 0.001 m^3/kg in cement (Skagius et al. /7/), 0 m^3/kg in bentonite (Andersson /3/) and values between 0.01–0.05 m^3/kg for granite (Carbol et al. /6/) but with substantial uncertainty intervals.

Strontium (Sr). Strontium will be one of the species dominating the activity the initial 1,000 years and additional care may therefore be taken when assigning the corresponding sorption coefficients. Under the expected conditions, strontium will be divalent and form preferably hydroxide and carbonate complexes at pH above 9. Strontium will sorb by cation exchange and is therefore sensitive to the ionic strength and also to some extent on pH. The sorption is correlated with the concentration of the competitive ion Ca^{2+}. Although Ca^{2+} is more weakly sorbing than Sr^{2+} a larger concentration may effectively reduce the sorption of Sr. Similar to Cs, the sorption will depend on the condition of cement and bentonite. For cement a K_d-value of 0.02 m^3/kg is suggested for pH > 11 and low ionic strength whereas 0.002 m^3/kg (Allard et al. /2/) is suggested for pH > 12.5 and high ionic strength. Most estimates are in the interval 0.001–0.005 m^3/kg (Skagius et al. /7/, Bradbury et al. /4/, Bradbury et al. /5/). The assessments for bentonite vary between 0.001–0.1 m^3/kg (Wiborgh et al. /10/, Yu et al. /12/, Andersson /3/) depending on the effects of the concrete. A reduction of a factor 10 is assumed for bentonite influenced by concrete, i.e. 0.0001–0.01 m^3/kg. Large amount of carbonate favour carbonate complexes and the presence of calcite may explain the seemingly large variation in proposed values for granite, 0.0001–0.1 m^3/kg (Carbol et al. /6/). Because of the important role of strontium in the initial activity, the suggested values are indeed pessimistic, cement, bentonite and granite 0.001, 0.001, 0.0001 m^3/kg.

Radium (Ra). Radium is expected to exist uncomplexed as Ra^{2+}, with chemistry similar to Sr. The major sorption process is ion exchange and radium is assumed to compete with Ca^{2+} for sorption sites. The K_d-values are slightly higher than for Sr, possibly due to differences in solubility products, but also due to a weaker hydration as inferred by the larger ionic radii. Data are, however, scarce and the proposed values for cement vary between 0.05 m^3/kg (Skagius et al. /7/) and 0.5 m^3/kg (Yu et al. /12/), where an intermediate value is selected. In bentonite 0.005 m^3/kg is suggested (close to the value suggested by Vieno et al. /11/) and 0.01 m^3/kg in granite (Carbol et al. /6/).

5.3 Divalent transition element

Nickel (Ni). Nickel is predominantly divalent and forms inner sphere complexes. According to the HSAB classification, Ni is a typical intermediate species with no clear preferences regarding complexation. The sorption depends on the hydrolysis and increases with pH. However, there are also indications that Ni will be present as free divalent ion, and not substantially hydrolysed until pH exceeds 10. There are also uncertainties concerning the type of sorption; ion exchange (proposed for bentonite by for instance Yu et al. /12/) or surface complexation (for granite). These uncertainties are also manifested in the fact that Ni is considered to be sensitive to both ionic strength and pH. Sorption experiments at high pH have been claimed to be easily influenced by precipitation, possible with $NiSiSO_4$, $NiSiO_3$ or $Ni(OH)_2$ as the insoluble compound. For cement, K_d has been determined to 0.04 m^3/kg in an experiment when care was taken to avoid precipitation (Skagius et al. /7/). Other investigations propose 0.5–1 m^3/kg (Wiborgh et al. /10/, Allard et al. /2/). Similar to ion exchanging elements, the sorption on bentonite is considered to be affected by the chemical changes attributed to the contact with concrete. For fresh bentonite a K_d-value of 0.2 m^3/kg has been suggested, but at least 10 times lower for bentonite influenced by cement, 0.01 m^3/kg (Wiborgh et al. /10/). Although only a weak dependence on the concentrations of Ca^{2+} and Mg^{2+} concentrations have been reported, a reduction from 0.1 m^3/kg to 0.02 m^3/kg for saline groundwater and granite is suggested by Carbol et al. /6/.

Cobalt (Co). Cobalt can be considered as an analogue to Ni in many aspects. It shares the same position in the HSAB classification table and similar to Ni hydrolysis has an influence on the sorption. Although less prevalent than for Ni, precipitation may occur as $Co(OH)_2$ (s), but due to its amphoteric nature dissolves in alkaline solution to form $Co(OH)_4^{2-}$. Likewise to Ni, Co has been reported to be sensitive to the ionic strength. Measurements on crushed cement have been performed and give values between 0.2–0.4 m^3/kg (Wiborgh et al. /10/), but the same value as for Ni is selected. Also for bentonite and granite the same values as for Ni are selected, 0.01 m^3/kg and 0.01 m^3/kg respectively.

Palladium (Pd). Few experiments have been found for Palladium. Some reports assume it to behave similar to Ni and Co and form complexes with most soft ligands, as NH_3 while others point out Ni and Pb as credible analogues. In comparison with these analogues, Pd is considered to be a softer metal centre and less likely to bind to the available ligands under the present conditions. The available oxidation states are Pd(II) and Pd(IV), where the former is considered to be most prevalent under reducing conditions. The predominant species in aqueous solution is $Pd(OH)_2$. The range of proposed values for cement is 0.04–0.5 m^3/kg (Skagius et al. /7/, Wiborgh et al. /10/), where an intermediate value is selected. In bentonite the corresponding interval is 0–0.1 m^3/kg (Andersson /3/, Vieno et al. /11/, Yu et al. /12/), where most suggestions are on the order of 0.001 m^3/kg. Though no data was found for granite, the suggested values are predictable lower than for Ni and in the interval 0.001–0.01 m^3/kg (Carbol et al. /6/).

Cadmium (Cd). Cadmium is divalent and bears some similarities with Ni, but has considerably larger ionic radii and unlike Ni is considered to be a soft metal centre. This should imply a weaker hydration, less inclined to form complexes with hard Lewis bases as carbonates. However, the net sorption effect may be counterbalanced by an improved ability to ion exchange. In weakly alkaline solutions $Cd(OH)_2(s)$ precipitates, dissolving only at high pH and forms $Cd(OH)_4^{2-}$. Apart from this dependence on pH, it is also believed to be sensitive to ionic strength. The proposed similarities with Ni and Co have been advocated to suggest values on the order of 0.04 m^3/kg in cement (Skagius et al. /7/), 0.02 m^3/kg in bentonite (Wiborgh et al. /10/) and 0.01 m^3/kg for granite (Carbol et al. /6/). However, since essential data are missing in conjunction with the devised inconsistencies with the analogies with Ni, it appears advisable to lower these values and expand the uncertainty intervals.

5.4 Trivalent elements

Americium (Am). Americium is trivalent both under oxidizing and reducing conditions and likely to form carbonate complexes. The sorption appears to increase with pH up to 10–11 and is critical only if pH is below 6. Since Am is prone to colloid forming, care is needed to avoid errors related to precipitation in experiments. Most experiments suggest values in the interval 1–5 m^3/kg for cement (Wiborgh et al. /10/, Allard et al. /2/). Estimations for bentonite fall in the interval 0.3–3 m^3/kg (Wiborgh et al. /10/, Andersson /3/), whereas for granite values between 1 and 10 m^3/kg have been reported (Carbol et al. /6/). Moreover, it cannot be excluded that a complex such as $AmCO_3^+$ may participate in ion exchange.

Curium (Cm). All assessments for curium employ americium as an exact analogue.

Samarium (Sm), Europium (Eu), Holmium (Ho). The members of the lanthanide series are trivalent and are all hard metal centres. Most experiments are performed on Eu, which also frequently serves as an analogue to the trivalent actinides, such as Am. The hydrolysis is somewhat weaker than for the actinides, which explains a slightly increased sensitivity to pH changes. They are, however, still fully hydrolysed at pH > 8–9 and the corresponding products have small solubility product, which is why precipitation may influence the measurements, but naturally also reduce the mobility. Non-specific forces appear to be involved in the sorption process and consequently, the sorption is relatively insensitive to ionic strength.

Based on experiments which originally yielded K_d-values substantially above 5 m^3/kg, Skagius et al. /7/ selects a value of 5 m^3/kg for cement. The major parts of estimate for bentonite are in the range 0.2–1 m^3/kg (Andersson /3/), whereas for granite values greater than 5 m^3/kg have been reported (Carbol et al. /6/).

5.5 Tetravalent elements

Plutonium (Pu). Plutonium has a complicated chemistry with a variety of oxidation states (III-VI) and all suggested values are based on analogies; Am as an analogy to Pu(III), Th as Pu(IV), Np(V) as Pu(V), and, finally, Pu(VI) is considered to behave as U(VI). Except for the less probable Pu(V), all oxidation states are predicted to have large K_d-values, but with an apparent dependence on pH. Pu has low solubility for the most likely formations and the accompanying tendency to form colloid may influence experiments. A set of general oxidation state independent assessments for cement constitutes the range 1–10 m^3/kg (Wiborgh et al. /10/, Allard et al. /2/, Skagius et al. /7/), which neglects the low sorbing species P(V). For bentonite the similar interval is 0.3–3 m^3/kg ((Wiborgh et al. /10/, Vieno et al. /11/, Andersson /3/) and for granite 0.5–5 (Carbol et al. /6/).

Uranium (U). Most actinides are presumed to be in their tetravalent state under reducing conditions, but for uranium a hexavalent state may appear under more oxidizing conditions, for which one expects the formation of anionic low sorbing carbonate complexes at higher pH (possibly above pH > 8). A reduction to the strongly hydrolysed tetravalent state increases the sorption by several magnitudes of order and the corresponding dominating species is $U(OH)_4$. Uranium sorbs by covalent bonds (inner-sphere complexes) and is therefore rather insensitive to ionic strength, but easily affected by pH and redox conditions. All suggestions for the K_d-value in cement derived from experiments fall in the range 1–10 m^3/kg (Wiborgh et al. /10/, Allard et al. /2/). For bentonite the estimates are lower, 0.01–1 m^3/kg (Andersson /3/), whereas for granite most reports point out values between 1 and 5 m^3/kg (Carbol et al. /6/). However, until the presence of hexavalent U completely can be excluded, additional care is required.

Neptunium (Np). Neptunium can exhibit a large variety of oxidation states, but is expected to be reduced from the pentavalent form to the tetravalent form when $E_H < -200mV$ and is thus considered to have a substantial sorption. Likewise to the other actinides, the underlying sorption process is more dependent on pH than on the ionic strength. The recommended value for K_d is 5 m^3/kg (Skagius et al. /7/), which is in accordance with the other actinides, whereas for bentonite and granite the K_d-value 0.1 m^3/kg and 1 m^3/kg is suggested (Andersson /3/, Carbol et al. /6/). Similar to Uranium, the existence of another low sorbing oxidation state (+V) motivates further investigations as well as additional care when assigning K_d-values.

Technetium (Tc). Although several oxidation states exist, the tetravalent form appears to be the most stable under reducing conditions and similar to the tetravalent actinides the hydrolysis is expected to be strong. The reduction from (VII) to (IV) may be controlled by the redox equilibrium of Fe^{2+} and Fe^{3+}. The less likely oxidation state considering the expected conditions, Tc(VII), exist as TcO_4^- ion for which K_d is assumed to be zero.

Technetium has shown to exhibit significant pH dependence due to the formation of various anions. In the interval pH 8–11 the solubility increases and sorption decreases possibly due to the formation of carbonate complexes such as $Tc(OH)(CO_3)_2^-$. For sorption in cement, the assessments of K_d have been 0.1–2 m^3/kg (Wiborgh et al. /10/, Allard et al. /2/). Predictions for bentonite are in the interval 0.005–0.1 m^3/kg (Wiborg et al. /10/, Vieno et al. /11/) and for granite 0.3–3 m^3/kg (Carbol et al. /6/).

Zirconium (Zr). Zirconium share several characteristics with Technetium; tetravalency, resistance to ionic strength and strong hydrolysis, but exhibit weaker sorption than the tetravalent actinides. The differences from Tc are expressed as a reduced sensitivity to redox conditions and also a slightly lower sorption.

In accordance with Technetium, the existence of the anionic complex, $Zr(OH)_5^-$, indicates a decreasing sorption with increasing pH, though not as dramatic as for technetium. Recommended sorption values are quite independent of the actual substrate; for cement 0.5–5 m^3/kg (Skagius et al. /7/, Bradbury et al. /4/, Bradbury et al. /5/), for bentonite in the range 0.05–2 m^3et al.kg (Veno et al. /11/, Anderssom /3/) and granite 0.5–3 m^3/kg (Carbol et al. /6/).

Tin (Sn). The aqueous chemistry of Tin is not well known; in reducing conditions both the divalent state and the tetravalent state are probable. The divalent form is far more soluble than the tetravalent (Albinsson /1/). Tin forms strong hydroxyl complexes and unrealistic sorption coefficients have been obtained in experiments, which have encountered problems with solubility and the formation of colloids. The presence of Cl may lead to various anionic species, such as $SnCl_3^-$, with severe consequences for the sorption. Due to the variety of complexes, Sn is thought particularly sensitive to pH. Due to the tendency to form colloids the suggestions show a wide span of values; in concrete 0.5–1 m^3/kg (Skagius et al. /7/, Bradbury et al. /4/, Bradbury et al. /5/), in bentonite, 0.001 m^3/kg to 3 m^3/kg (sic) (Andersson /3/, Yu et al. /12/). For bentonite Th has been proposed as an analogue in a narrow pH interval which according to the discussion in Section 5.1 should imply large uncertainty intervals. Values as high as 4 m^3/kg have been measured in granite (Carbol et al. /6/), but due to the lack of recent experiments, more realistic estimates are on the order of 0–0.01 m^3/kg (Skagius et al. /7/). The selected values for cement, bentonite and granite are 0.5, 0.01 and 0 m^3/kg.

5.6 Pentavalent elements

Niobium (Nb). Niobium can exhibit oxidation states between –I and +V, where the latter is the most likely in natural groundwaters and yields complexes such as $Nb(OH)_5$ or $Nb(OH)_6^-$. The negatively charged ion may be more probable in alkaline solution, but the observed low mobility seems to indicate a large fraction of $Nb(OH)_5$. Sensitivity to both pH and ionic strength has been reported. The strong hydrolysis should cause strong sorption, although there is a large span in experimental data (0.2–120 m^3/kg for cement). More modest suggestions fall in the range 0.5–1 m^3/kg (Wiborgh et al. /10/, Skagius et al. /7/). The suggestions for bentonite are lower, but equally scattered, 0–1 m^3/kg (Andersson /3/, Vieno et al. /11/), which again may reflect the presence of oversaturation and precipitation.

Assuming that $Nb(OH)_5$ is the dominant species, Carbol et al. /7/ suggests a K_d-value 0.1 m^3/kg for granite.

5.7 Hexavalent elements

Molybodenum (Mo). Molybodenum is expected to be present as the anionic species (MoO_4^{2-}) at reducing conditions and having a correspondingly low sorption, which may decrease with increasing pH, presumably due to the formation of $CaMoO_4$ complexes. For cement the value 0.006 m^3/kg is selected in accordance with Skagius et al. /6/ even though other estimates have assumed the existence of two different oxidation states and propose 0.001 m^3/kg for Mo(VI) and 0.2 m^3/kg for Mo(III). In bentonite and granite most estimates (Andersson /3/, Skagius et al. /6/) are far lower and therefore 0 m^3/kg is selected.

Selenium (Se). Despite considerable chemical differences, most estimates treat Se and Mo as analogues with a low sorption and forming primarily anionic species. Of the three possible oxidation states, Se(–II), Se(IV) and Se(VI) only the tetravalent is considered to exhibit any significant sorption. Se is possibly a divalent anion under reducing conditions (however tetra and hexavalent states are available and hence redox conditions are of importance). The complexes HSe^-, SeO_3^{2-} and SeO_4^{2-} are pointed out as the most important complexes and $CaSeO_3$ as a possible result of precipitation. Unlike other elements, higher oxidation states do not lead to decreasing K_d. For cement the same value as for Mo is selected.

A realistic value for bentonite proposed by Andersson /3/ is 0.003 m^3/kg, a more pessimistic is 0 m^3/kg. The sorption on granite has shown to be slightly stronger, but the results may have been influenced by precipitation and the value suggested by Carbol et al. /6/ 0.04 m^3/kg, is reduced to 0.001 m^3/kg.

5.8 Halides

Chlorine (Cl). Although Chlorine as chloride, Cl^-, is an extremely unreactive ion, other processes than pure sorption may be responsible for an observed retention in cement and the values suggested vary between 0.006–0.02 m^3/kg (Bradbury et al. /4/, Skagius et al. /7/). These processes may be disfavoured by the intrusion of additional competing Cl ions from saline water. As an anionic process one can also expect an increasing sorption with decreasing pH. All available assessments in other materials, as bentonite and granite, select the K_d-value 0 m^3/kg (Andersson et al. /3/, Vieno et al. /11/).

Iodine (I). Iodine, as I^-, has a complicated aqueous chemistry and sorption may increase if iodine is allowed to form metal iodides with soft metals such as Hg, Pb, Cu, Ag, Bi etc. Similar to chloride, sorption may also increase with decreasing pH. For cement the range of proposed values is 0.003–0.03 m^3/kg (Allard et al. /2/). In bentonite, all available assessments select the value 0 m^3/kg (Wiborgh et al. /10/). Despite the wide span of suggested values for K_d for granite -possibly depending on the type of chemisorbing minerals- the value 0 m^3/kg is selected.

5.9 Other

Carbon (C). Carbon (IV) can exist in either inorganic or organic carbon, but since no reliable sources have reported any sorption at all for organic carbon, the remaining discussion is confined to inorganic carbon. The underlying mechanisms behind the observed retention of carbon are more related to precipitation than sorption. Therefore it is rather resistant to ionic strength, pH, quite sensitive to altered redox conditions, but most strongly correlated to the chemical condition of the substrate. In cement, an effective sorption coefficient of as high as 4.5 m^3/kg /Safe 2001 /8/) can be evaluated from the amount of carbonate available in the cement and the solubility of calcium carbonate in pore water. This value is expected to increase with decreasing pH. A more modest proposed value is 0.2 m^3/kg by Skagius et al. /7/.

A prerequisite for a high K_d-value in bentonite is the presence of calcite. In the absence of calcite the sorption is severely reduced. In general the most recommended value is 0 m^3/kg (Allard et al. /2/, Yu et al. /3/, Ochs et al. /9/). It is also assumed to be zero (0 m^3/kg) in granite, if not calcite is present (0.083 m^3/kg) (Carbol et al. /6/). Since Ca is rather common in Swedish groundwater the most pessimistic value might not be entirely relevant, 0.001 m^3/kg as given by Albinsson /1/.

Tritium (H). No sorption is expected on any substrate since tritium primarily will exist as water (Skagius et al. /7/).

6 Summary of results

The sorption coefficients and the corresponding uncertainty intervals for the radionuclides are summarised in Tables 6-1 to 6-4.

Table 6-1. Sorption coefficients for concrete and cement, m^3/kg.

		Min	Max	Recommended
M(I)	^{3}H	0	0	0
	^{135}Cs	0.0001	0.01	0.001
	^{108}Ag	0.00002	0.05	0.001
M(II)	^{59}Ni	0.008	0.2	0.04
	^{60}Co	0.004	0.4	0.04
	^{113}Cd	0.002	0.8	0.04
	^{107}Pd	0.004	0.4	0.04
	^{90}Sr	0.0005	0.05	0.001
	^{226}Ra	0.005	0.5	0.05
	^{126}Sn	0.025	10	0.5
M(III)	^{241}Am	0.2	5	1
	^{242}Cm	0.2	5	1
	^{151}Sm	1	25	5
	^{154}Eu	1	25	5
	^{166}Ho	1	25	5
M(III,IV)	^{242}Pu	1	25	5
M(IV)	^{233}U	1	25	5
	^{237}Np	1	25	5
	^{93}Zr	0.05	5	0.5
	^{99}Tc	0.05	5	0.5
	^{14}C	0.01	4	0.2
M(V)	^{94}Nb	0.1	2.5	0.5
M(VI)	^{93}Mo	0.0001	0.4	0.006
M(–I)	^{36}Cl	0.0006	0.06	0.006
	^{129}I	0.0003	0.03	0.003
M(–II,IV,VI)	^{79}Se	0.0001	0.4	0.006

Table 6-2. Sorption coefficients for bentonite, m^3/kg.

		Min	Max	Recommended
M(I)	^{3}H	0	0	0
	^{135}Cs	0.0005	0.05	0.005
	^{108}Ag	0	0.005	0
M(II)	^{59}Ni	0.004	0.1	0.02
	^{60}Co	0.002	0.2	0.02
	^{113}Cd	0.001	0.4	0.02
	^{107}Pd	0	0.1	0
	^{90}Sr	0.0002	0.005	0.001
	^{226}Ra	0.0005	0.05	0.005
	^{126}Sn	0.0005	0.2	0.01
M(III)	^{241}Am	0.2	5	1
	^{242}Cm	0.2	5	1
	^{151}Sm	0.04	1	0.2
	^{154}Eu	0.04	1	0.2
	^{166}Ho	0.04	1	0.2
M(III,IV)	^{242}Pu	0.2	5	1
M(IV)	^{233}U	0.002	0.05	0.01
	^{237}Np	0.02	0.5	0.1
	^{93}Zr	0.002	1	0.05
	^{99}Tc	0.001	0.1	0.01
	^{14}C	0	0	0
M(V)	^{94}Nb	0	0.2	0
M(VI)	^{93}Mo	0	0.003	0
M(–I)	^{36}Cl	0	0	0
	^{129}I	0	0	0
M(–II,IV,VI)	^{79}Se	0	0.003	0

Table 6-3. Sorption coefficients for sand and gravel, m^3/kg.

		Min	Max	Recommended
M(I)	^{3}H	0	0	0
	^{135}Cs	0.001	0.12	0.01
	^{108}Ag	0.0002	0.5	0.01
M(II)	^{59}Ni	0.002	0.05	0.01
	^{60}Co	0.001	0.1	0.01
	^{113}Cd	0.0005	0.2	0.01
	^{107}Pd	0.0001	0.01	0.001
	^{90}Sr	0.00002	0.0005	0.0001
	^{226}Ra	0.001	0.1	0.01
	^{126}Sn	0	0.01	0
M(III)	^{241}Am	0.2	5	1
	^{242}Cm	0.2	5	1
	^{151}Sm	0.2	5	1
	^{154}Eu	0.2	5	1
	^{166}Ho	0.2	5	1
M(III,IV)	^{242}Pu	0.2	5	1
M(IV)	^{233}U	0.2	5	1
	^{237}Np	0.2	5	1
	^{93}Zr	0.05	5	0.5
	^{99}Tc	0.03	3	0.3
	^{14}C	0.00002	0.01	0.0005
M(V)	^{94}Nb	0.1	2.5	0.5
M(VI)	^{93}Mo	0	0	0
M(–I)	^{36}Cl	0	0	0
	^{129}I	0	0	0
M(–II,IV,VI)	^{79}Se	0.00001	0.03	0.0005

Table 6-4. Sorption coefficients for sand and bentonite, m^3/kg.

		Min	Max	Recommended
M(I)	^{3}H	0	0	0
	^{135}Cs	0.0008	0.1	0.01
	^{108}Ag	0.0002	0.5	0.009
M(II)	^{59}Ni	0.002	0.05	0.01
	^{60}Co	0.001	0.1	0.01
	^{113}Cd	0.0005	0.2	0.01
	^{107}Pd	0.0001	0.02	0.0009
	^{90}Sr	0.00004	0.001	0.0002
	^{226}Ra	0.002	0.05	0.01
	^{126}Sn	0.00005	0.03	0.001
M(III)	^{241}Am	0.2	5	1
	^{242}Cm	0.2	5	1
	^{151}Sm	0.2	5	0.9
	^{154}Eu	0.2	5	0.9
	^{166}Ho	0.2	5	0.9
M(III,IV)	^{242}Pu	0.2	5	1
M(IV)	^{233}U	0.2	5	0.9
	^{237}Np	0.2	5	0.9
	^{93}Zr	0.02	9	0.5
	^{99}Tc	0.01	5	0.3
	^{14}C	0.00002	0.009	0.0005
M(V)	^{94}Nb	0.1	2	0.5
M(VI)	^{93}Mo	0	0.0004	0
M(–I)	^{36}Cl	0	0	0
	^{129}I	0	0.0001	0
M(–II,IV,VI)	^{79}Se	0.000009	0.03	0.0005

7 Conclusions

The uncertainty intervals for the sorption coefficients of the radionuclides in a nuclear waste repository have been evaluated through the scheme devised in Section 5.1 in conjunction with the qualitative discussion in Section 5.2–5.10. As expected, the intervals, displayed in Tables 6-1 to 6–4 are in accordance with the observed experimental span of variation. Particular large intervals are seen for elements where the available assessments exclusively have been made by questionable analogy considerations.

8 References

/1/ **Albinsson Y, 1991.** “Sorption of radionuclides in granitic rock”, SKB Arbetsrapport AR 91-07, Svensk Kärnbränslehantering AB, Stockholm.

/2/ **Allard B, Höglund L O, Skagius K, 1991.** “Adsorption of radionuclides in concrete”, SKB Progress Report SFR 91-02, Svensk Kärnbränslehantering AB.

/3/ **Andersson J, 1999.** “SR 97. Data and uncertainties. Compilation of data and data uncertainties for radionuclide transport calculations”, SKB TR-99-09, Svensk Kärnbränslehantering AB.

/4/ **Bradbury M H, Sarrot F-A, 1994.** “Sorption database for the cementitious Near-Field of a L/ILW Repository for performance assessment”, Nagra Rechnical Report 93-08, Wettingen, Switzerland.

/5/ **Bradbury M H, Van Loon L R, 1998.** “Cementitious Near-Field database for performance assessment of a L/ILW repository in Parlfris Marl Host Rock” (CEM94: Update I, June 1997), PSI Bericht Nr. 98-01, Paul Scherrer Institut, Villigen, Switzerland.

/6/ **Carbol P, Engkvist I, 1997.** “Compilation of radionuclide sorption coefficients for performance assessment”, SKB R-97-13; Svensk Kärnbränslehantering AB.

/7/ **Skagius K, Pettersson, Wiborgh M, Albinsson Y, Holgersson S, 1999.** “Compilation of data for the analysis of radionuclide migration from SFL 3–5”, SKB R-99-13, Svensk Kärnbränslehantering AB.

/8/ **Project SAFE, 2001.** “Compilation of data for radionuclide transport analysis”, SKB R-01-14, Svensk Kärnbränslehantering AB.

/9/ **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.

/10/ **Wiborgh M, Lindgren M, 1987.** “Database for the radionuclide transport calculations for SFR.” SKB Progress Report SFR 87-09, Svensk Kärnbränslehantering AB.

/11/ **Vieno T, Nordman H, 1999.** “Safety assessment of spent fuel disposal in Hästholmen, Kivetty, Olkiluoto and Romuvaara – TILA-99.” Posiva Report 99-07, Posiva OY, Helsinki.

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