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Compilation of radionuclide sorption coefficients for performance assessment

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ABSTRACT

Sorption is the main retardation factor for the transport of radionuclides from a repository of spent nuclear waste. Sorption is often quantified by distribution coefficients, K_d-values, specific for every groundwater/rock system.

A review of recent publications dealing with sorption was performed as a continuation of an earlier work by Albinsson (Albinsson, 1991). The literature from 1990 was studied intensively whereas minor effort was put into the sources of the work by Albinsson.

The report presents four possible site-specific conditions taken from three geographical areas in Sweden. It must be pointed out that none of these places have been selected as a candidate for the future repository site. They merely serve as examples of possible conditions that may be encountered.

The different sorption mechanisms applicable to the studied elements together with the K_d concept are shortly summarised.

The influence of organic substances (humic and fulvic acids) present in the groundwater on the elements sorption and mobility is also discussed.

In order to justify the selection of K_d-values selection criteria are presented together with sensitivity of K_d-values to pH, E_h and salinity.

Each element is discussed individually in respect to the elements chemistry and sorption data found.

Sorption coefficients are recommended for the radioactive elements present in the repository with the limitation of disregarding elements with no isotopes with longer half-lives than ^{60}Co (5.27 y). The reviewed elements are Cs, Sr, Ra, Ln, Ac, Th, Pa, U, Np, Pu, Am, Cm, Co, Ni, Cd, Zr, Nb, Tc, Pd, Ag, Sn, C, I, Cl, Se and Kr.

For every element, there is a recommendation of a realistic K_d-value with an uncertainty limit. The selection is based on experimental investigations or chemical analogues.

In some cases few or no K_d data were found in the scientific literature and therefore these elements sorption behaviour should be further investigated. A recommendation is therefore to perform sorption studies on elements such as Cd, Pa, Cm, Zr, Nb, Pd, Ag and Sn.

The recommended K_d-values for the different elements sorption on granitic rock, presented in this report, serve as a guidance of the sorption performance. In future, when a site for the nuclear waste repository is selected new sorption experiments for the most critical elements (in respect to their amount and half-life) should be performed. Among the critical elements are the weakly sorbing elements, such as mono- and divalent cations.

SAMMANFATTNING

Sorption är huvudmekanismen för retention i geosfären av radionuklider från ett slutförvar av använt kärnbränsle. Sorption kvantifieras ofta med distributionskoefficienter, K_d värden, som är specifika för varje grundvatten/berg system.

En genomgång av nya publikationer som handlar om sorption har genomförts och arbetet är en fortsättning av tidigare arbete av Albinsson (Albinsson, 1991). Artiklar och rapporter från 1990 och framåt har studerats intensivt medan källorna till Albinssons arbete har ägnats mindre uppmärksamhet.

Rapporten presenterar fyra möjliga platsspecifika referensvatten som är valda utifrån tre verkliga platser i Sverige. Ingen av dessa platser är aktuella för ett framtida slutförvar. De fungerar endast som exempel på förhållanden som är möjliga för ett slutförvar.

En kort summering ges i rapporten över sorptionsmekanismerna för de aktuella radionukliderna och över K_d konceptet.

Inverkan av organiskt material (humus- och fulvosyror) i grundvattnet på sorptionen och rörligheten av radionuklider diskuteras också.

Urvalsmetoden för rekommenderade K_d-värden och känsligheten för förändringar i pH, Eh och salthalt redovisas.

Varje radionuklid och dess kemi och sorptionsegenskaper diskuteras individuellt.

Sorptionskoefficienter rekommenderas för de ämnen med isotoper med längre halveringstid än ^{60}Co (5.27 y). De behandlade ämnena är Cs, Sr, Ra, Ln, Ac, Th, Pa, U, Np, Pu, Am, Cm, Co, Ni, Cd, Zr, Nb, Tc, Pd, Ag, Sn, C, I, Cl, Se och Kr.

För varje ämne rekommenderas en realistisk sorptionskoefficient tillsammans med ett osäkerhetsintervall. Valet baseras på experimentella data eller analogistudier.

I några fall återfinns få eller inga experimentella K_d-värden varför dessa bör studeras vidare. Dessa ämnen är Cd, Pa, Zr, Nb, Pd, Ag och Sn.

De rekommenderade K_d-värdena i denna rapport ska fungera som vägledning i säkerhetsanalysarbete. I framtiden när en plats för slutförvaret

är bestämd nya bör nya sorptionsförsök utföras med de mest kritiska ämnena. Bland de kritiska återfinns de svagsorberande en- och tvåvärda katjonerna.

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SUMMARY

The objective of this report is to give input sorption coefficients (K_d) for performance assessment of a future repository of spent nuclear fuel. An updated sorption database has been compiled from recent publications. The work is a continuation of an earlier compilation by Albinsson (Albinsson, 1991).

Both non-saline and saline conditions has been the reference system for the groundwater chemistry. The host rock is assumed to be granitic.

Articles and reports from 1990 and forward has thoroughly been studied in order to obtain new information based on the latest findings. The sources in Albinsson's compilation has been of minor interest and the author's judgement has been used as part of the information.

All sorption coefficients have been internally compared as well as with other databases from organisations like NAGRA, TVO, AECL and NIREX.

For each element dealt with in this report there are sections for general chemistry, sorption and recommended K_d-values. Each value is followed by an estimated uncertainty interval.

1 INTRODUCTION

The process in which a substance in solution attaches onto a solid material is often called *sorption*. The element can attach by an uptake in the solid, *absorption,* or by adhering on the surface, *adsorption*. It is sometimes difficult to distinguish these two, and therefore the term *sorption* is commonly used which includes both ways. When a radionuclide or a chemotoxic substance attaches on rock, both adsorption and absorption can be involved in the process owing to the porosity of the material.

Sorption together with matrix diffusion are the main retardation processes for dissolved elements from spent nuclear fuel. The elements will travel at much lower rates than the flowing water and, at the same time, sorption will keep the concentrations of them at low levels in the groundwater. To be able to calculate transport rates, the sorption must be quantified for all the elements of interest. These quantifications are often collected in sorption databases, specific for each repository site.

The compilation of K_d-values in this report is a continuation of a previous review made by Albinsson (Albinsson, 1991). The material on which that report was based has only extensively been reviewed and main efforts have been in recent reports and publications. When no new applicable information was found, more emphasis was put into the selection by Albinsson.

2 SORPTION

The term sorption is used to designate all processes which increase the concentration of a dissolved species at the solid-solution interface, except precipitation. The interactions between dissolved species and specific sites at the solid surface are of the same type as between different species in solution and, therefore, the same concepts are applied, i.e. chemical reactivity, electrostatic attraction/repulsion etc. The reactions at the surface are described as chemical equilibrium reactions, analogous to reactions in solution. The difference to the situation in a solution is that the surface sites are stationary so any charge they have (permanent or variable) will result in an electric field. The field will influence the ion distribution at the solid-solution interface and increase the concentration, provided the charge of the surface is of the opposite sign as the dissolved species. The same sign of charge on surface and solute will, on the other hand, cause a decrease in concentration at the surface (ion exclusion). There are a number of different models describing the solid-liquid interface and the charge potential relationships such as the *double layer model*, the *triple layer model* and the *constant capacitance model*.

The sorption reactions can be divided into three major categories: 1) ion exchange, 2) inner-sphere complexation and 3) outer-sphere complexation. Ion exchange is the process where ions, which neutralizes the permanently charged surface sites, are exchanged by other ions in the solution. Inner-sphere complexes are caused by reactions with variably charged surface sites which results in a covalent type of bond. Outer-sphere complexes are of a more electrostatic nature.

2.1 ION EXCHANGE

Permanently charged sites are found on planar surfaces of clay particles in, for exemple, bentonite. These negatively charged surface sites, $\equiv S^-$, are occupied by cations (X^+) which can be exchanged by other ion in the solution, C^+:

$$\equiv S^-X^+ + C^+ \leftrightarrow \equiv S^-C^+ + X^+$$

Typical cations, which will sorb by ion-exchange, are the non-hydrolyzed alkalies and the alkaline earths. These will have different affinities for the sites depending on the nature of the ion. For example, the equilibrium constant for Cs^+ replacing Na^+ on bentonite is 40 (Wanner, 1996).

2.2 SURFACE COMPLEXATION

Variably charged sites are found on hydrous metal oxide minerals such as silica, iron hydroxide/oxide alumina, etc. and as edge sites on clays The surface hydroxyl groups will react and the surface will be negatively or positively charged as a result.

$\equiv SOH_2^+ \leftrightarrow \equiv SOH + H^+$

$\equiv SOH \leftrightarrow \equiv SO^- + H^+$

The charged surface will affect the distribution of the species by electrostatic attraction and repulsion.

Inner-sphere complexes (more covalent type of bond) are formed with strongly hydrolyzed species such as the actinides. Outer-sphere complexes will result from the electrostatic attraction between the charged surface groups and species:

$\equiv SOH_2^+ + A^- \leftrightarrow \equiv SOH_2^+ A^-$

$\equiv SO^- + C^+ \leftrightarrow \equiv SO^-C^+$

The outer-sphere complexes will be affected by both the pH and the ionic strength of the solution. The inner-sphere complexation, on the other hand, is independent of the ionic strength but, as can be seen in the reaction below, dependent on the pH:

$\equiv SOH + C^+ \leftrightarrow \equiv SOC + H^+$

The overall distribution of the species between the solid and liquid phase will be the result of all the reactions which, in turn, are the result of the total composition of the system (pH, ionic strength, and concentrations). The pH will affect both the surface charge and the degree of hydrolysation of the dissolved speices and thus affect the complexation.

WAN 96 H. Wanner, Y. Albinsson and E. Wieland, "A thermodynamic surface model for caesium sorption on bentonite.", Fresenius J. Anal. Chem. **354** (1996) 763.

3 SORPTION TERMNOLOGY AND CONCEPTS

Different concepts and models are used to mathematically describe the distribution of a substance between a liquid phase and a solid surface. These descriptions are often based on empirical studies of such two-phase systems. The results are presented as distribution coefficients or as parameters in larger chemical-mathematical models.

3.1 THE K_d CONCEPT

The distribution of a substance between a solid surface and a liquid is often described by a distribution coefficient.

$$K_d = \frac{C_s}{C_a} \qquad \left[\mathrm{m}^3 / \mathrm{kg}\right] \qquad \text{1-1}$$

where C_s is the concentration of the substance on the surface as mole/kg and C_a is the concentration in the solute as mole/m^3.

Mass balance gives

$$m \cdot C_s + V \cdot C_a = V \cdot C_a^0 \qquad \text{1-2}$$

where m is the mass of the solid in kg, V is the volume of the solution in m^3 and C_a^0 is the original concentration of the substance in mole/m^3. The distribution coefficient, K_d, is then

$$K_d = \frac{(C_a^0 - C_a)}{C_a} \cdot \frac{\mathrm{V}}{\mathrm{m}} \quad \left[\mathrm{m}^3 / \mathrm{kg}\right] \qquad \text{1-3}$$

This coefficient is specific to the system studied. It is therefore important to define under which conditions it is applicable. The coefficient is, however, independent of the original concentration of the dissolved substance, at least within reasonable limits. For those elements which sorb by ion exchange, a saturation of the surface can occur. However, one must remember, although the radioactivity in the repository is high, the molar amounts are small and thus are also the concentrations.

The sensitivity of K_d is high to those elements that sorb by ion exchange where the ionic strength is of major importance. Saline water can be encountered in deep groundwater with a sodium concentration of several milligrams per litre (SKB 91, 1992) and is considerably different from a non-saline water. Such high sodium concentration of course affects the sorption of the alkali and to some extent the alkali earth metals, and a conservative choice must thus be made for the saline case in order to cover a possible concentration range.

For those elements which sorb by surface complexation, the pH of the water is an essential parameter. The sorption generally decreases with decreasing pH. This is true for cobalt and nickel, trivalent actinides and the lanthanides. The effect is negligible for the tetravalent actinides, where the hydrolysis is so strong that only unlikely changes of pH would affect the sorption. The pH must decrease below four in order to significantly change the sorption. This decrease is highly unlikely, even with acidification from acidic rain.

4 GROUNDWATER AT REPOSITORY SITE

4.1 GROUNDWATER COMPOSITION

The composition of groundwater in Sweden is generally determined by the infiltration of meteoric water. The oxygen in the infiltrating water is largely consumed by biological processes, first in the soil and then further along the flow path in the rock (Pedersen *et al.*, 1995). Carbon dioxide is generated, mainly in the soil, and carbonates such as calcite are dissolved by the carbonic acid. Other reactions such as weathering and ion exchange will further influence the water chemistry.

Typical deep groundwaters have a low redox potential; measurements indicate E_h in the range of -0.4 to -0.1 V (Grenthe *et al.*, 1992). With a pure meteoric origin, near neutral pH is controlled by the carbonate system, and sodium, calcium and bicarbonate are the most abundant ions.

Exceptions to this rule are frequently found, where saline water is mixed into the meteoric origin water or where the saline water is the largest or only component. Saline, chloride-dominated, groundwater is sometimes found at locations near the sea shore, or at great depths. Deep saline water is commonly found where land has been covered by the sea before the land rise. There are several possible explanations for saline groundwater, but its underlying geochemical/hydrological reason is of less interest for this report. The fact is simply that deep groundwater can be saline, and we need to analyse the consequences of that for deep disposal. This subject has been treated before. The possibility of saline groundwater was discussed in the early performance assessment study for spent fuel disposal KBS-3 (KBS-3, 1983). Saline water was also discussed in the later performance assessment study SKB 91 (SKB 91, 1992), and a saline groundwater was in fact used as reference water in the recent performance assessment study SR 95 (SR 95, 1996) where the reference water was selected from results of measurements performed at the Hard Rock Laboratory at Äspö, SE Sweden (Smellie *et al.*, 1995).

The four reference waters on which this report is based on is presented in Table 4.1. The waters were taken from four boreholes at three investigation sites. The characteristics of the waters are presented in more detail in a report by Laaksoharju *et al.* (Laaksoharju, 1997).

Table 4.1 Chemical composition of groundwater from four deep bore hole sections in Finnsjön, Gideå and Äspö. These water compositions were selected as representative for the deep groundwaters in the performance assessment study SR97.

Location	**Äspö**		**Finnsjön**				**Gideå**	
Borehole	**KAS02**		**BF101**		**Kf107**		**KG104**	
Sampling section	530-535 m		439-459 m		511-516 m		404-407 m	
pH	7.7		7.0		7.9		9.3	
E_h (V)	-0.31		-		-0.25		-0.20	
Species	**mg/l**	**mmole/l**	**mg/l**	**mmole/l**	**mg/l**	**mmole/l**	**mg/l**	**mmole/l**
Na^+	2100	91	1700	74	275	12	105	4.6
K^+	8	0.2	13	0.3	2	0.05	2	0.05
Ca^{2+}	1890	47	1650	41	142	3.5	21	0.5
Mg^{2+}	42	1.7	110	4.5	17	0.7	1	0.04
Sr^{2+}	35	0.4	21	0.2	-	-	-	-
Fe^{2+}	0.24	0.004	-	-	1.8	0.03	0.05	0.0009
Mn^{2+}	0.29	0.005	0.82	0.01	0.13	0.002	0.01	0.0002
HCO_3^-	10	0.2	47	0.8	278	4.6	18	0.3
SO_4^{2-}	560	5.8	370	3.9	49	0.5	0.1	0.001
Cl^-	6410	181	5500	155	555	16	178	5.0
Br^-	40	0.5	32	0.4	-	-	-	-
I^-	-	-	0.12	0.0009	-	-	0.14	0.001
F^-	1.5	0.08	1.2	0.06	1.5	0.08	3.2	0.17
HS^-	0.15	0.005	<0.01	<0.0003	-	-	<0.01	<0.0003
NH_4^+(as N)	0.03	0.002	0.35	0.025	0.09	0.006	0.01	0.0007
NO_3^-(as N)	<0.01	<0.001	<0.005	<0.0004	<0.002	<0.001	0.009	0.0006
NO_2^-(as N)	<0.001	<0.0001	0.005	0.0004	0.01	0.0007	<0.001	<0.0001
$PO_{4,tot}$(as P)	0.005	0.0002	0.005	0.0004	0.04	0.001	0.008	0.0003
Si_{tot}	4.1	0.15	5.4	0.19	5.6	0.2	4.7	0.2
DOC_a	1		-		6		2	

a *DOC, Dissolved Organic Carbon in the groundwater*

4.3 SUMMARY AND CONCLUDING REMARKS

Natural groundwater conditions of importance to the study of sorption and the properties of the elements present in the repository are as follows:

- Both non-saline and saline groundwater may be encountered, depending on the location of the deep repository.

- The composition of groundwater from KAS02 (530-535 m) can be taken as an example of deep saline groundwater (see Table 4-1).

- The measured redox potential at 100 m and deeper is generally between -0.4 and -0.1 V. There are no traces of oxygen in deep groundwater, as demonstrated by the negative E_h values.

- The pH is normally in the range of 6.5-9.5 and is chiefly controlled by the carbonate system.

- The total concentration of carbonate ions (alkalinity) is generally below 600 mg/l. There is a tendency toward lower concentrations at greater depths, and values above 300 mg/l at 500 m are unusual.

- Sulphate concentration is highest in saline water but is not necessarily correlated to chloride concentration. The concentration at 500 m is generally below 600 mg/l.

- Sodium and calcium are the most common cations in groundwater. The concentration of both sodium and calcium is about 2000 mg/l in saline waters and usually in the range of 10-500 mg/l in non-saline waters at a depth of 500 m.

- Magnesium and potassium are generally present but their concentrations are kept relatively low by geochemical reactions. Magnesium is generally below 150 mg/l and potassium below 15 mg/l at 500 m.

- Deep groundwater contains very little nutrients such as P and N compounds. The content of dissolved gases is generally low, as are the concentrations of dissolved organic matter and colloidal particles.

5 INFLUENCE OF ORGANICS

It has been shown that synthetic organic compounds such as EDTA, NTA and DTPA can cause significant spreading of radionuclides form LLW waste sites. Even trace amounts (<1 mg/l) of these organic compounds can affect the mobility of activation products and actinides (Nordén, 1994).

Natural groundwaters contain dissolved organic carbon (DOC) which consists of many different compounds, some of which can form complexes with radionuclides. The content of organic material in water depends on where the water was collected. Surface waters can contain up to 100 mg/l (Nordén, 1994) while deep groundwater contains much less organic compounds with an approximate upper limit of 10 mg/l. Of these 10 mg/l, about 15% consists of humic substances.

Nordén *et al.* (Nordén, 1993a) studied the complex formation of Eu and Sr with fulvic acid. The authors conclude that Eu forms stronger complexes than Sr. Another study (Nordén *et al.*, 1993b) included thorium and hexavalent uranium. The conclusion of the study is that the strength of metal-fulvic complexes is $Th^{4+} > Eu^{3+} > UO_2^{2+}$.

The influence of the metal-humic complexes on the sorption properties of the metals is not obvious. Although the metal-humic complexes can be more mobile than the corresponding complex with inorganic ligands (mainly hydroxide), investigations with various concentrations of humics show that the effect is minor (Nordén, 1994). A significant effect of the sorption of Eu on alumina is observed only with 10 mg/l and higher of fulvic acid. Taking into account the observed strength of the metal-fulvic complexes and the fact that about 15% of the DOC is humic substances, one can conclude that the influence of humics is of minor importance in deep groundwaters with an organic content of less than some 10 mg/l.

6 SELECTION CRITERIA FOR K_d-VALUES

In most sorption databases for performance assessment, the K_d-values are based on experimental findings. Databases have been collected in many countries but data originate from a limited number of sources. The differences in the databases arise mainly from differences in groundwater compositions in different countries and studies and the judgement by the authors. In some cases, no K_d-values are found for the specified groundwater system. Expert judgement must then be used to justify a selection from a system which differs in chemical or geological parameters. However, there is a vast number of sources for granitic conditions as a whole. Most of these data are suitable for the database in SR97. If there are reliable data for Swedish conditions, these have of course preferentially been selected.

6.1 EXPERIMENTAL INVESTIGATIONS

It has been argued that there is a large difference between K_d-values obtained from experiments with crushed material as a solid phase and intact rock samples. In this compilation, no restriction has been made as to what sources to use as a basis for the selection. Although intact rock samples may show lower sorption, it has been asssumed that the transport of radionuclides are in water-conducting/containing cracks and fissures. The surface of these cracks and fissures is believed to be disturbed and somewhat similar to crushed rock samples.

When drilling a core in the rock and bringing it up to the surface, the core is exposed to decreased pressure and small fissures might open. Those fissures may increase the porosity of the rock sample. This effect has been ignored as it is difficult to quantify and is assumed to be of minor importance.

6.2 REFERENCE GROUNDWATERS AND LIMITATIONS

The selection of K_d-values for the **non-saline** reference groundwater system is based on a water with $7 \leq$ pH ≤ 9 , $E_h \leq$ -200 mV and a maximum salinity of 500 mg/l of chlorine.

The selection of K_d-values for the **saline** reference groundwater system is based on a groundwater with $7 \leq$ pH ≤ 9, $E_h \leq$ -200 mV and a minimum salinity of 500 mg/l of chloride to a maximum of 6500 mg/l.

Any application of this compilation outside these limitations should be performed with great care. This is especially important at lower pH conditions.

6.3 SELECTION

In those cases for which a large number of experimental studies have been performed on a particular element and the results are scattered, the most reliable data have been used. The term *reliable* is in this context either data from similar groundwater systems or reported by experimental groups that have produced data for other elements which show consistency regarding chemistry, *e.g.* tetravalent actinides.

The selection is based on the chemistry of the particular element, *e.g.* U(IV) should behave much like Th(IV) etc.

For every entry in the selection, a comparison with other elements with comparable chemistry has been made. This process is done to identify outliers that had to be studied in more detail.

The selection of values can appear to be limited from only a few experimental groups and this observation is correct. The reason has absolutely nothing to do with academic loyalties but the fact that many of these kind of investigations on Swedish conditions have been and are performed by Chalmers University of Technology and The Royal Institute of Technology. There is a large number of investigations on material and waters from the reference sites and these have preferentially been selected.

As all sorption databases, the selection in this compilation also reflects the author´s opinion, based on our background and experience.

The selection process is schematically presented in Fig. 6.1

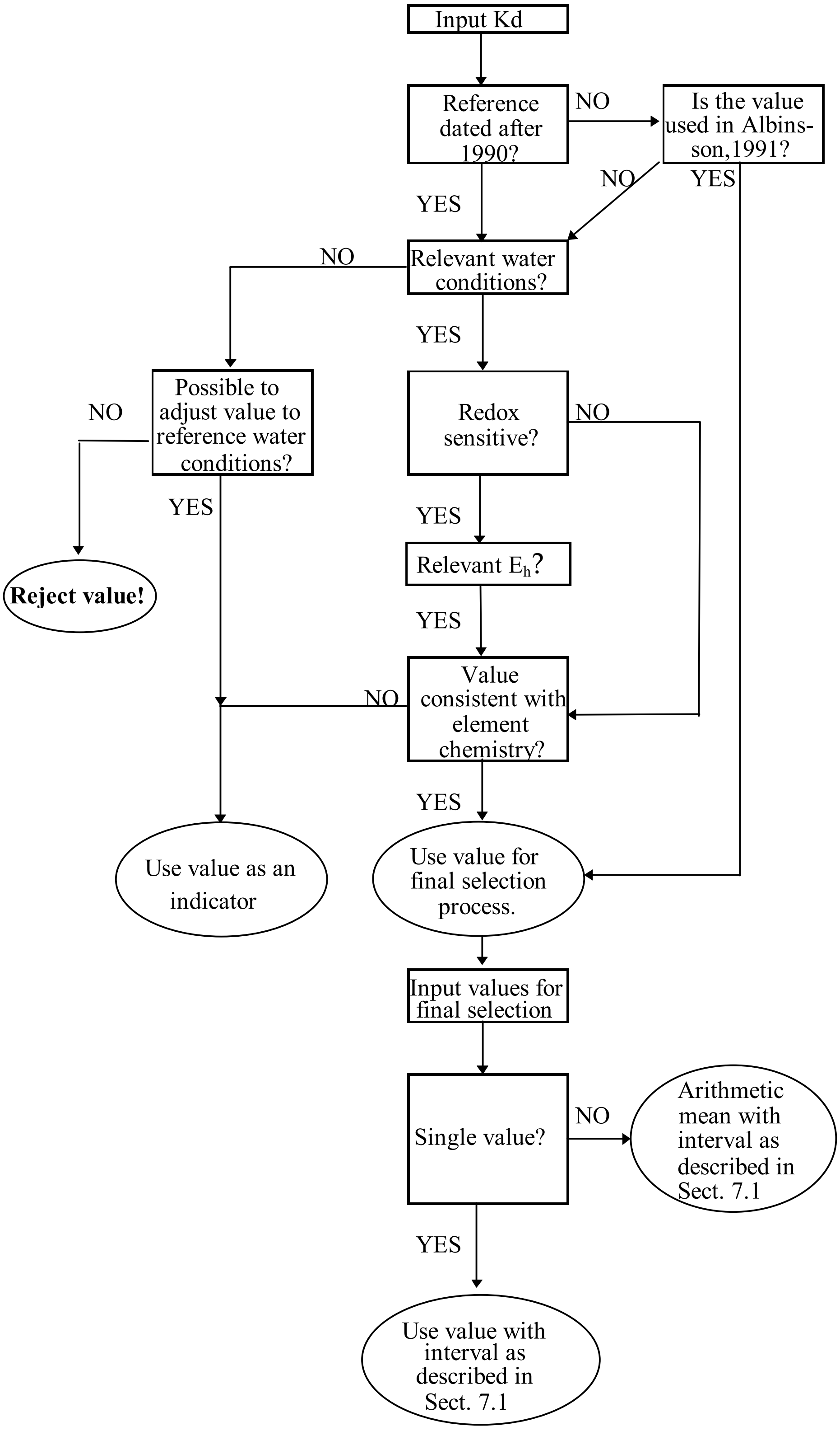

Figure 6-1 Schematic presentation of the selection process.

7 SENSITIVITY OF K_d-VALUES

7.1 GENERAL

In most reviews of K_d-values for performance assessments, a conservative approach has been used in order to cover uncertainties in groundwater chemistry and lack of reliable sorption data. Many organisations have presented both realistic and conservative values. The definition of *conservative* is seldom expressed clearly but usually includes experimental errors and possible uncertainties in groundwater composition, pH and E_h. However, the benefit of presenting two sets of values of that kind seems limited. It is difficult to defend a realistic choice instead of using a conservative value. This report gives two sets of values representative for two types of water. These waters are from two real sites and have been chosen to cover possible waters at a future repository site. The two sets of K_d-values are realistic values and do not include parameters such as ”poor chemistry” (*e.g.* SKI, 1991) or unceartanities in determinations or predictions of the groundwater composition.

Determinations of K_d-values generally have uncertainties within a factor 2 with about a 1σ confidence level. This was concluded at the ”Workshop on Sorption within Crystalline Host Rock” arranged by NAGRA, 1996. The uncertainty increases when the K_d is above 1 because of the experimental difficulties. This is not a great drawback, however, since these highly sorbing elements are practically immobile. Presumably, the most important K_d-values are those for the low sorbing elements.

Smaller uncertainties can be found in litterature but they generally origin from replicates of the same experiment and do not reflect differencies in separate experiments. The uncertainty intervals in this report are not calculated but estimated on the basis of the scattering in experimental values found in the literature. Only values representative for Swedish conditions have been included. When the number of values is low, the interval is taken as mentioned above or larger. The intervals are presented in Table 12-1.

Working with intervals associated with realistic K_d-values has the advantage of giving the modellers an opportunity to perform a sensitivity test of the transport calculations. The intervals should not be considered as being absolute but the can serve as guidance for necessary future experimental work. Again, the intervals do not cover any variances in groundwater composition.

7.2 SENSITIVITY TO pH CHANGES

The selection of K_d-values in this compilation is valid from pH 7 and above. Extremely high pH, as in the cement system (up to pH 13.5), will inevitably affect K_d-values, especially for those elements that form negatively hydroxo complexes ($Me(OH)_x^{y-}$).

Applying the K_d-values for systems with pH<7 is also doubtful. Some of the K_d-values are for elements that are assumed to be fully hydrolysed, which in some cases could be untrue with lower pH.

7.3 E_h-VARIATIONS

The redox potential, E_h, in the reference groundwaters is assumed to be less than -200 mV. This potential is probably sufficiently low to effectively keep the redox sensitive actinides in their lower oxidation states. The K_d-value for them is dependent on the oxidation state (*c.f.* section 11.3), and higher oxidation states would undoubtedly lead to a decreased sorption.

7.4 SALINITY

The salinity, expressed as concentration of chloride, is assumed to be between 1-6500 mg/l. The upper limit of the non-saline water is set to 500 mg/l. Above that limit is the saline water, with its upper limit of 6500 mg/l.

The elements that sorb by ion exchange, *i.e.* alkali and alkali earth metals, are the most sensitive to variations in salinity. The counter ions to chloride, mostly sodium and calcium, act as competitors, and thus an increase in their concentration will lead to reduced K_d-values. This effect can be great, giving a decrease in the K_d-value of one order of magnitude.

7.5 CONCLUSION

The compilation of K_d-values in this report is valid with the limitations mentioned in section 6. Any use outside the limitations must be done with great care and good knowledge of chemistry.

8 GEOLOGY

The reference geology for this report is crystalline granitic rock. The Äspö site is dominated by Småland granite. This granite occurs in several variations with respect to colour and grain size. A more basic type is called Äspö diorite. In the massive Småland granite, there are smaller or larger inclusions of basic rock types, such as Gabbro and Diorite. Fine-grained red granite and minor amounts of pegmatite are also common.

The Finnsjön site is dominated by granodiorite, which contains the principle minerals quartz, plagioclase, potassium feldspar, hornblende and biotite (SKB 91, 1992). Calcite is the most common fracture-filling mineral. Some fractures are filled with pure calcite, while most calcite-sealed fractures also contain other minerals such as prehnite, laumonite and chlorite.

The geological reference system as a criteria for selecting K_d-values cannot be too restrictive because of limited experimental studies on that specific system. It is clear that even within the limitation of *crystalline rock* there are large mineralogical variations between countries and sites. This is not a great problem, however, since there are almost always the same highly sorbing minerals in the rock although in different proportions. As several groups have studied the sorption onto rock with different composition, the conclusions are generally that the existence of (even at levels of some percent) highly sorbing minerals will dominate the contribution of the sorption. Such highly sorbing minerals can be micas, hematite, magnetite and clay minerals. Only a minor occurrence of these minerals will dominate over feldspars and quartz.

To conclude, experimental studies of sorption with materials from *i.e.* Finland, Switzerland, Germany, Canada and of course Sweden are of great value if the water conditions are similar to Swedish ones. The water composition is of much greater importance than the rock composition.

9 RELEVANT RADIONUCLIDES

The elements/radionuclides of the greatest importance for a nuclear waste repository safety analysis are summarised in Table 9-1. For those elements that are redox-sensitive, the possible oxidation states are indicated in the table. Carbon is the exception, where the chemical form is indicated. Only inorganic carbon is considered in this report.

Table 9-1. Radionuclides of great importance in nuclear waste deposit safety analysis. ε is designed for either electron capture (EC), positron decay ($\beta^{+)}$ or a combination of these two. Data collected from Browne (Browne *et al.*, 1986).

Radionuclide	Redox sensitive	Valency/possible oxidation states in groundwater	$t_{1/2}$ (y)	Decay mode
^{14}C		HCO_3^-	5730	β^-
^{36}Cl		Cl^-	$3.01 \cdot 10^5$	β^-
^{60}Co		Co^{2+}	5.271	β^-
^{59}Ni		Ni^{2+}	$7.5 \cdot 10^4$	ε
^{63}Ni		Ni^{2+}	100.1	β^-
^{79}Se	Yes	Se(-II, IV,VI)	$6.5 \cdot 10^4$	β^-
^{85}Kr		inert gas	10.72	β^-
^{90}Sr		Sr^{2+}	28.5	β^-
^{93}Zr		Zr^{4+}	$1.53 \cdot 10^6$	β^-
^{94}Nb		Nb(V)	$2.03 \cdot 10^4$	β^-
^{99}Tc	Yes	Tc(IV,VII)	$2.13 \cdot 10^5$	β^-
^{107}Pd		Pd^{2+}	$6.5 \cdot 10^6$	β^-
^{108}mAg		Ag^+	127	ε, IT
^{113m}Cd		Cd^{2+}	$9.3 \cdot 10^{15}$	β^-
^{126}Sn		Sn^{4+}	$1 \cdot 10^5$	β^-
^{129}I	Yes	I^-	$1.57 \cdot 10^7$	β^-
^{135}Cs		Cs^+	$3.0 \cdot 10^6$	β^-
^{137}Cs		Cs^+	30.0	β^-
^{151}Sm		Sm^{3+}	90	β^-
^{154}Eu		Eu^{3+}	8.8	β^-
^{166m}Ho		Ho^{3+}	1200	β^-

Table continues on next page

Table 9-1. Cont.

Radionuclide	Redox sensitive	Valency/possible oxidation states in groundwater	$t_{1/2}$ (y)	Decay mode
^{226}Ra		Ra^{2+}	1600	α
^{227}Ac		Ac^{3+}	21.77	β^-, α
^{229}Th		Th^{4+}	7340	α
^{230}Th		Th^{4+}	$7.54\cdot10^{4}$	α
^{232}Th		Th^{4+}	$1.405\cdot10^{10}$	α
^{231}Pa	Yes	Pa(IV,V)	$3.276\cdot10^{4}$	α
^{233}U	Yes	U(IV,V,VI)	$1.592\cdot10^{5}$	α, SF
^{234}U	Yes	U(IV,V,VI)	$2.454\cdot10^{5}$	α
^{235}U	Yes	U(IV,V,VI)	$7.037\cdot10^{11}$	α, SF
^{236}U	Yes	U(IV,V,VI)	$2.342\cdot10^{7}$	α, SF
^{238}U	Yes	U(IV,V,VI)	$4.468\cdot10^{9}$	α, SF
^{237}Np	Yes	Np(IV,V)	$2.140\cdot10^{6}$	α, SF
^{238}Pu	Yes	Pu(III,IV,V)	87.74	α, SF
^{239}Pu	Yes	Pu(III,IV,V)	$2.411\cdot10^{4}$	α, SF
^{240}Pu	Yes	Pu(III,IV,V)	6563	α, SF
^{242}Pu	Yes	Pu(III,IV,V)	$3.763\cdot10^{5}$	α, SF
^{241}Am		Am^{3+}	432.7	α, SF
^{242m}Am		Am^{3+}	141	IT, α
^{243}Am		Am^{3+}	7380	α, SF
^{242}Cm		Cm^{3+}	0.446	α, SF
^{243}Cm		Cm^{3+}	28.5	α, ε
^{244}Cm		Cm^{3+}	18.11	α, SF
^{245}Cm		Cm^{3+}	8500	α, SF
^{246}Cm		Cm^{3+}	4730	α, SF

10 SORPTION DATABASES

Over the years several organisations have established databases for sorption. These have served as inputs for the transport modelling of the release of radionuclides from a repository.

The databases should always reflect the expected specific groundwater conditions for each country and comparisons between them thus sometimes show large differences. For example, the database for the Canadian program, CNFWM, is very influenced by the expected more oxidising conditions, whereas Swedish conditions are expected to have much more reducing conditions. The Swiss program by NAGRA has similarities but generally includes more organic material in the water.

It is therefore difficult to draw any conclusions from a comparison. Furthermore, it is always the transport rates of the radionuclides that should be compared since these also include the transport models and not only the sorption. The transport rates reflect the whole treatment of sorption, diffusion, matrix diffusion and advective flow.

Data from sorption databases are for the readers interest included as an appendix after the references

11 CHEMISTRY AND SORPTION OF THE INVESTIGATED ELEMENTS

11.1 ALKALI AND ALKALINE EARTH METALS

Cs is among the alkali metals an element with isotopes with long half-lives. The sorption of Cs on granite has been investigated by several authors. In the report by Vieno *et al.* (Vieno, 1992) it is pointed out that sorption of Cs and U measured *in situ* is significantly higher owing to sorption on fraction fillings containing iron hydroxides.

11.1.1 Cesium (Cs)

General

Cesium is one of the most abundant fission products in spent nuclear fuel (Choppin *et al.*, 1995). The relatively long half-lives of ^{135}Cs and ^{137}Cs, $3.0 \cdot 10^6$ and 30.17 years, respectively, make it an element of interest. ^{135}Cs has a fission yield of 6.54% and is a pure β^- emitter (E_β = 0.2 MeV). The isotope ^{137}Cs (cumulative chain fission yield is 6.18%), which is often mentioned in connection with the nuclear deposition after the Chernobyl accident, is a β^- emitter (E_β = 0.5 MeV). Approximately 85% of the β decays goes to a metastable Ba (^{137m}Ba, $t_{1/2}$ = 2.6 min). At cooling times, 10-1000 years, the activities of ^{90}Sr and ^{137}Cs (with daughters) dominate in the repository (Choppin *et al.*, 1995).

Chemistry

Cesium is a univalent ion and is non-complexed in the environment found in natural groundwaters. The element sorbs on granite by cation exchange. The binding of Cs to the granite is significantly stronger than, for example, Li and Na.

The sorption of Cs on granite is influenced by pH, Cs-concentration, CEC (cation exchange capacity) of the minerals and the ionic strength of the groundwater.

The variation in Cs sorption with varied pH (range 6-9) depends on the chemical change of the mineral and rock surfaces, since Cs is non-complexed in this pH interval. As was concluded by Albinsson (Albinsson, 1991), the mineral´s pH-dependence is small, thus giving a maximum deviation of the Cs-sorption of about 3 to 6. The higher sorption is obtained at the higher pH.

Because of the low concentrations of Cs in the groundwater outside the repository, the Cs sorption is independent of the cesium concentration. The K_d-values for Cs follows the CEC of the rocks and minerals. The Cs sorbs by cation exchange, and the sorption is strongly influenced by the ionic strength of the groundwater.

Sorption

Ittner *et al.* (Ittner, 1990) concluded that cesium (in synthetic granitic groundwater) migrates into the rock (Finnsjö, Stripa and Studsvik granite) in high-capacity mineral veins (biotite, chlorite, hornblende etc.) as well as in fissures and fractures sealed with high-capacity minerals. The relatively strong sorption of cesium on high-capacity minerals and most weathering products (with high CEC values) implies significant removal of cesium from the groundwater.

Aggeryd *et al.* (Aggeryd, 1991) found a sorption of cesium dissolved in artificial groundwater (Allard water, non-saline, pH=8.2) on whole Klipperåsen granite of 0.39 m^3/kg. The difference in K_d-values was the result of different compositions of the materials and different surface areas of the minerals. It has been shown in fracture mineral studies that cesium preferentially sorbs on clay minerals such as muscovite, biotite and hornblende.

In situ K_d-values for cesium were found to be in the range of 10-290 m^3/kg. The discrepancy between *in situ* K_d-values and K_d-values from batch experiments is possibly caused by the different minerals involved in whole rock samples, as compared with fracture fillings, and the different reaction times.

Similar results were observed by Landström *et al.* (Landström, 1995) as they investigated fracture fillings and "gouge" (loose material in fractures) found at a depth of 500 m at the Klipperåsen granite. The sequential leaching technique used showed a irreversible sorption of cesium on the gouge.

Byegård *et al.* (Byegård, 1995) investigated the crushed Finnsjön granite in different size fractions and found a K_d-value in the range of 0.01-0.06 m^3/kg. The lowest values are valid for a grain size of 1-0.5 mm and the highest for particles with a diameter of 0.25-0.09 mm. The authors also concluded that only 10 % of the sorbed Cs could be desorbed with 2 M ammonium acetate.

Vieno *et al.* (Vieno, 1992) pointed out that sorption of Cs and U measured *in situ* is significantly higher because sorption on fraction fillings containing iron hydroxides.

Sätmark *et al.* (Sätmark, 1992) measured a K_d-value of 0.05 m^3/kg on silica colloids in an SGG (synthetic granitic groundwater, pH=8.2) groundwater. The investigation showed that the sorption of Cs on the silica colloids was independent of the surface area after a contact time of 73 days. Experiments carried out with colloids made of Finnsjön granite and SGG groundwater exhibited a K_d-value of 5-15 m^3/kg. The sorption of Cs was independent of the surface area (SGG groundwater) and only slightly dependent on the pH in the range of 6 to 9 (I=0.01 M, $NaClO_4$).

Cui *et al.* (Cui, 1996d) investigated sorption of Cs on Stripa granite in SGG groundwater and found a K_d-value of 0.02 m^3/kg. They concluded that the desorption of Cs was partly (50%) irreversible and that the sorption was pH-independent. One significant finding was that the K_d-value increased by a factor of 10 when magnetic fractions of the fracture-filling material was used. This indicates that clay in the granitic rock plays a significant role, despite the fact that, the clays weight percentage was low (3%).

Landström *et al.* (Landström, 1995) investigated the distribution of stable elements and natural radionuclides in natural fracture systems (at Äspö, saline ground water). The authors pointed out that clay minerals have high sorption capacity and are important in the retention of Cs. They concluded that the Cs sorption is characterised by two processes: one rapid surface adsorption, followed by a slower inter-layer sorption. It is true, as pointed out by Aggeryd *et al.* (Aggeryd, 1991) as well, small amounts of clay minerals in fractures and fracture zones can also significantly influence radionuclide migration. Landström *et al.* (Landström, 1995) related the Cs concentration in the groundwater taken from the same place as the investigated gouge material and found an *in situ* K_d-value of 0.22-1 m^3/kg.

This K_d-value for cesium is similar to that found by Andersson (Andersson, 1983) when they investigated Cs sorption on crushed rock and rock-forming minerals. Landström *et al.* (Landström, 1995) also concluded that the sorption of Cs on Fe-oxyhydroxide and calcite was insignificant.

Byegård *et al.* (Byegård, 1995) made desorption studies of Cs from Finnsjön granite in saline groundwater under reducing conditions. The time used for the sorption experiments was short (8 days), which was indicated by the relative low K_d-value of 0.06 m^3/kg found after desorption with 1 M ammonium acetate.

11.1.2 Strontium (Sr)

General
Strontium exists in high level radioactive waste as a fission product. The isotope of strontium with the longest half-life is ^{90}Sr ($t_{1/2}$ = 28.5 years, pure β^- emitter, E_β=0.5 MeV). The release of Sr from the nuclear fuel is expected to be slow compared to cesium (Ramebäck *et al.*, 1994), which gives a low concentration of Sr in groundwater-conducting fissures. As mentioned above, the activity of ^{90}Sr and ^{137}Cs dominates the nuclear fuel during the cooling time period of 10-1000 years. The sorption behaviour of Sr is in this perspective important, in the case of a nuclear fuel canister failure.

Chemistry
Under the conditions presently expected in a nuclear waste repository, Sr exists as Sr^{2+}. Strontium forms hydroxide and carbonate complexes at a pH above 9 and/or in the presence of larger amounts of carbonate. Formations of such complexes favour the sorption of Sr. Strontium sorbs on granite by cation exchange, and the sorption is mainly controlled by CEC and pH.

Landström *et al.* (Landström, 1995) investigated the distribution of stable elements and natural radionuclides in natural fracture systems (at Äspö). The authors pointed out that Sr was mainly associated with the part of the fracture filling material that easily ion exchanges Sr (21%) and with the carbonate phase (78%). The carbonate phase consisted of calcite. The relatively stable Ca/Sr ratio indicate a co-precipitation of these elements. However, the authors also concluded that the Sr concentrations in the Äspö groundwater seemed to be controlled by ion exchange on clay minerals. Large variations in Sr and Ca/Sr ratios in calcite (Sr values higher by a factor of 10 in fresh calcite precipitates compared with older fracture calcites) were attributed to high precipitation rates for fresh carbonates and/or the release of Sr during recrystallisation of the older fracture calcites.

Sorption
Sorption of Sr on silica colloids in synthetic granitic groundwater (non-saline) performed by Sätmark *et al.* (Sätmark, 1992) showed a K_d-value of 0.05 m^3/kg. On the other hand, a much higher K_d-value (3.5 m^3/kg) was found when Sr was sorbed on Finnsjön granite.

Cui *et al.* (Cui, 1995) investigated the sorption of Sr on Stripa mine fracture filling material in non-saline SGG water (pH 8.2, oxic conditions) and found a completely reversible sorption with a K_d-value of 0.007 m^3/kg.

The sorption of Sr on granite by batch sorption and column experiments was investigated by Hatipoglu *et al.* (Hatipoglu, 1994). The results of the batch experiment gave a K_d of 0.1 m^3/kg. The K_d-value obtained from the column experiment was only 0.01 m^3/kg and the difference was attributed to the short contact time between the Sr ions and the granite in the column experiment compared to the batch experiment.

Byegård *et al.* (Byegård, 1995) investigated crushed Finnsjön granite of different size fractions and found a K_d in the range of 0.00004-0.00008 m^3/kg. The lowest values are valid for the grain size of 1-0.5 mm and the highest for particles with a diameter of 0.25-0.09 mm. The authors concluded that approximately 90 % of the sorbed Sr was mobilised with 2 M ammonium acetate after 2 days of desorption.

Measurements on Äspö granite indicate a K_d of 0.0001 m^3/kg in saline conditions (Albinsson *et. al.*, 1997).

11.1.3 Radium (Ra)

General
Very few data have been reported for the sorption of Ra on granitic rock. There is only one long-lived radium isotope (^{226}Ra, $t_{1/2}$=1600 y, α-emitter). ^{226}Radium is a daughter of the very long-lived ^{238}U.

Chemistry
Radium belongs to the group of alkaline earth metals in the periodic table. The species expected under the environmental conditions in a nuclear waste deposit is as non-complexed Ra^{2+}. The chemistry is similar to that of Ba^{2+} and Sr^{2+}. Since the sorption of Ra on granite is an ion exchange reaction, it is sensitive to pH changes because of the changes in the surface charge. Bruno *et al.* (Bruno, 1995) suggest that under anoxic conditions Ra will exist as Ra^{2+} in deep groundwaters.

Sorption
Kipatsi (Kipatsi, 1983) investigated the sorption of Ra on Finnsjön granite and determined a K_d-value of 0.25 and 0.5 m^3/kg for high and low ionic strengths, respectively. The corresponding values for the analogue Sr were determined to be 0.01 and 0.016 m^3/kg, respectively. This indicates a substantially stronger sorption for the larger radium ion compared to strontium. A possible explanation can be the difference in the solubility products of $RaSO_4$ (log K_s=-10.37) and $SrSO_4$ (log K_s=-6.50).

Griffault *et al.* (Griffault, 1994) who studied the disequilibrium of U in Canadian granite, concluded that ^{226}Ra was actively deposited on fracture in-fillings. Ra was preferentially retained by illite/smectite clays.

11.2 LANTHANIDES

11.2.1 Lanthanides (Ln)

General

The lanthanide series consist of 15 elements (La-Lu). The lanthanides with long half-lives are ^{144}Nd($t_{1/2}$=2.1·10^{15} y), ^{147}Sm($t_{1/2}$=1.06·10^{11} y), ^{151}Sm($t_{1/2}$=93 y), ^{152}Eu($t_{1/2}$=13.33 y), ^{166}Ho($t_{1/2}$=1200 y) and ^{176}Lu($t_{1/2}$=3.6·10^{10} y). Isotopes with a half-life of more than 10^{10} y can be considered stable, as these isotopes give a negligible radiological dose to man. The low cumulative fission yield and the small amounts present in nuclear reactor material make these isotopes rare in nuclear waste. Of interest for nuclear waste assessment are therefore only Sm, Eu and Ho.

Chemistry

The lanthanides are used as analogues for the trivalent actinides, and measured K_d´s for lanthanides on mineral surfaces can thus be of interest. Within the lanthanide series, the dominant valency state is +3. The lanthanides are strongly hydrolysed at pH levels above 6 (Baes *et al.*, 1976). The strong hydrolysis makes the lanthanides fully hydrolysed at pH 8-9, and they therefore exhibit a strong sorption on mineral surfaces. The hydrolysed lanthanides have a small solubility product. It is therefore impossible to obtain high concentrations in water solutions of the lanthanides as a result of precipitation.

A rise in the pH of the surrounding groundwater in a repository, *e.g.* by the use of concrete, will therefore reduce the mobility of these elements.

Sorption

Several experimental groups have studied the sorption of lanthanides. The most frequently used elements are Europium (Eu) and Promethium (Pm). Although Pm is an element of no interest for performance assessment the element is suitable for K_d investigations since ^{147}Pm has an appropriate half-life and can be detected at very low concentrations. The results of these investigations clearly point to the fact that the lanthanides exhibit a very strong sorption, although possibly less than the actinides. Owing to the weaker hydrolysis of the Ln’s, they are more sensitive to changes in pH. Vannerberg (Vannerberg, 1994) studied the sorption behaviour of Pm onto quartz, silica, goethite and hematite and derived K_d-values of at least 3 m^3/kg in the applicable pH range of 7-9. The author also concluded that the sorption was rather insensitive to changes in ionic strength because of the non-specific forces involved in the sorption. Nordén *et. al.* (Nordén, 1994) used Eu as a tracer during the studies of the influence of organics. In systems with minor amounts of fulvic acid (<10 mg/l) the K_d reached a value of >3 m^3/kg with quartz and alumina as solid phases.

Allard *et al.* (Allard, 1977 and 1979) and Kipatsi (Kipatsi, 1983) investigated the sorption of cerium (Ce), neodymium (Nd) and europium (Eu) on Finnsjön granite in Allard water and after 6 months found K_d-values of 8-32 m^3/kg.

Erdal *et al.* (Erdal, 1979) measured K_d for Ce and Eu and gave representative values of around 0.24 and 0.55 m^3/kg, respectively. Desorption of Ce and Eu from the material gave significantly higher K_d values of around 1.4 and 1.5 m^3/kg, respectively.

Neodymium sorption on orthose and orthoclase (minerals present in granite) was investigated by Mecherri *et al.* (Mecherri, 1990, 1992), who found K_d-values in the range of 0.7 to 1 m^3/kg.

Aggeryd *et al.* (Aggeryd, 1991) measured K_d-values for terbium (Tb) and ytterbium (Yb) on Klipperås granite in deionised water to be 0.41 and 0.47 m^3/kg, respectively. The study also included determination of Tb and Yb sorption on gneiss from the Studsvik test site. In deionised water, K_d-values of 4.4 and 4.2 m^3/kg, respectively, were found.

11.3 ACTINIDES

General
The actinide elements represented in the inventory of spent nuclear fuel are Ac, Th, Np, Pu, Am and Cm, *c.f.* Table 9-1. Of these elements, Am and Cm have a stable trivalent oxidation state in the water conditions expected in the repository. Thorium also has a stable state but is tetravalent. Uranium, neptunium and plutonium have a much more complicated chemistry with several oxidation states and some states may even coexist in appreciable amounts. This is especially pronounced for plutonium, where the states III, IV, V and VI may coexist (Allard *et. al.*, 1983a). It is therefore essential to describe the groundwater conditions thoroughly *e.g.* regarding redox potentials. However, since the actinides sorb by covalent bonds (innersphere complexes) and are hydrolysed at low pH (when in their lower oxidation state), they are insensitive to moderate changes in ionic strength. In other words, the local groundwater conditions, such as salinity at a site for the repository, is of moderate interest. In addition, the influence of organics such as humic and fulvic acids at low concentrations is suppressed by the strong hydrolysis of these elements (Nordén *et. al.*, 1993b).

Sorption studies of these elements is somewhat complicated. Firstly, the elements readily form colloids (true colloids) for which it must be decided whether they belong to the solid phase or the solute. Secondly, the solubility is low, typically less than 10^{-10} mole/l for the tetravalent actinides. Thirdly, the availability of short-lived isotopes is limited, and thus several experimental studies have used saturated or nearly saturated systems, which must be considered when selecting recommended values for sorption (Carbol *et. al.*, 1995).

11.3.1 Actinium (Ac)

Chemistry and sorption
The chemistry of actinium is somewhat similar to that of its homologue lanthanum (Cotton, 1972). Actinium has only one stable oxidation state (III), and the ionic radii of Ac and La are similar. Am is also a candidate for analogue chemistry. The amount of sorption data for actinium is very limited. To assess a K_d-value, analogue chemistry is necessary.

11.3.2 Thorium (Th)

Chemistry
Thorium is a product from the decay series of long-lived actinides. As mentioned previously, the tetravalent state is the prevalent one in any

groundwater. Although the hydrolysis may be weaker than for U(IV), Np(IV) and Pu(IV), it is still sufficiently strong to suppress any other complexing reactions in groundwater and the complex $Th(OH)_{4,aq}$ is anticipated.

Sorption
Engkvist (Engkvist, 1993) presented data for sorption of Th onto quartz in the pH interval of 2-12; at pH 7-9 the K_d reaches a maximum of 1-10 m^3/kg (although the author incorrectly converted ml/g to m^3/kg, thus presenting the K_d three orders of magnitude too low). Since quartz is a low sorbing mineral, it can be anticipated that the sorption will be considerably higher in mixtures such as granite.

11.3.3 Protactinium (Pa)

Chemistry
The most stable oxidation state of Pa is Pa(V) (Stenhouse, 1995). The chemistry of Pa is not well investigated, possibly because of the experimental difficulties involved.

Sorption
Allard *et. al.* (Allard, 1979) studied the sorption of Pa onto quartz and aluminium oxide and observed a very strong sorption above pH 6 with values between 1 and 10 m^3/kg.

11.3.4 Uranium (U)

Chemistry
Hexavalent uranium is dominant under mildly reducing or oxidising conditions. In an aerated system and presumably in oxidising deep granitic groundwaters, the dominating species are $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ (Wanner, 1992). The tetravalent state dominates in highly reducing conditions, the dominating species being $U(OH)_4$.

Sorption
Since experimental data for the sorption of uranium in reducing conditions are sparse, thorium must be used as an analogue. As for Th, the hydrolysed tetravalent uranium is strongly sorbed onto rock surfaces. Ticknor (Ticknor, 1994) studied the sorption of uranium onto different minerals in waters with different ionic strengths. The results indicate strong sorption onto goethite, hematite and kaolinite with K_d-values of >1 m^3/kg. This strong sorption was especially pronounced in waters that were purged with nitrogen prior to use.

Although several investigations indicate that the reduced $U(OH)_{4,aq}$ does not dominate in sligthly reducing conditions (E_h <-100mV) Ahonen *et al.* (Ahonen, 1994) measured the uranium redox speciation in uranium-rich groundwaters at the Palmutto uranium deposit in Finland. The investigation clearly points out that only $U(OH)_{4,aq}$ dominates in waters with E_h <-150 mV and pH<9. These waters contained only small amounts (1.3 g/l TDS) of dissolved solids.

Until it can be shown that reduced form of uranium will dominate in the near and far field from the repository, sorption of hexavalent uranium has to be included in these kind of compilations.

Ticknor (Ticknor, 1994) performed experiments on granitic material with areated synthetic groundwater. The waters were comparable the the saline and non saline referencewaters in this report. The results indicate a K_d of 0.012±0.0016 m^3/kg for saline water conditions and a K_d of 0.094±0.022 m^3/kg.

The same author (Ticknor, 1991) studied the sorption of uranium onto fracture infilling minerals. The waters in this investigation had differences to the reference waters in respect to salinity where the saline waters was less saline and the low salinity had higher salt content than the reference waters. The results of the investigation showed a variety of K_d's depending of the sustrate. Goethite, Kaolinite and Muscovite sorbed uranium strongly with numbers as 1-1.8 m^3/kg. Other infilling minerals like Calcite, Epidote and Illite do not sorb any stronger than the granite mass.

11.3.5 Neptunium (Np)

General and chemistry

In a repository for spent nuclear waste, the only isotope of Np of significance is ^{237}Np with a half-life of 2 million years. Neptunium exists in a variety of oxidation states from III to VII. In natural groundwaters, the oxidation states of importance are III, IV, V. The tetravalent oxidation state shows a similar chemistry to that of Th^{4+}, with the uncharged $Th(OH)_{4,aq}$ as the dominating species in groundwaters with limited concentrations of carbonate.

Sorption

The oxidised Np(V) exists primarily as $NpO_2(OH)_{aq}$ or $NpO_2(CO_3)^-$ (Albinsson, 1991). It has been shown that pentavalent Np sorbs significantly onto rock or clay minerals, but the K_d-values are scattered, probably depending on the how the experiments were performed and what minerals were used (Ticknor, 1992), (Albinsson, 1991).

In the reference waters presented in this report, tetravalent Np is presumed to be dominant. This assumption is supported by observations by Hakanen *et. al.* (Hakanen, 1995). These authors conclude that "spiking" solutions with Np(V) were reduced completely to Np(IV) in contact with rock at an E_h of <-200 mV. In this case, the sorption was so strong that the concentration in solution approached the detection limit, thus indicating similarities with the other tetravalent actinides.

Untill it has been clearified that the assumption of neptunium being in its reduced form, sorption values for the oxidised form is included. Ticknor (Ticknor, 1993) studied the sorption of Np onto granitic material in two types of waters. The first had similarities to the saline reference water and the other with the non-saline water. The experiments were perormed in aerated conditions and the results showed weak sorption onto granite in both waters with values typically less than 0.001 m^3/kg.

Vannerberg (Vannerberg, 1994) studied the sorption of Np(V) onto hematite and goethite at various pH and ionic strength. The author concluded that the sorption was only slightly dependent on the ionic strength but of course much dependent on pH. At pH above 7 K_d reached the value of 1 m^3/kg for hematite and 100 m^3/kg for goethite.

11.3.6 Plutonium (Pu)

Chemistry
Plutonium chemistry is very complicated, and experimental work with the element involves several serious difficulties. Nevertheless, plutonium should be regarded as one of the elements of main interest in the performance assessment. Plutonium has a large radiological impact due to its long half-life and decay mode.

The solubility of plutonium is low, with a typical value of less than 10^{-10} M and with $PuO_{2(s)}$ as the limiting phase. Under reducing conditions, the species in solution are $PuCO_3^+$, Pu^{3+} and $PuOH^{2+}$ (Allard, 1984). Under oxidising conditions, the soluble species is presumably $Pu(OH)_{4,aq}$ (Albinsson, 1991).

Sorption
Plutonium is prone to form colloids and, if the metal concentration is not kept sufficiently low, experiments will result in erroneous K_d-values, either too high or too low depending on the separation technique.

Ticknor (Ticknor, 1993) investigated the sorption of plutonium onto different minerals and onto granite in three waters. The first and the third have similarities with the saline and the non-saline reference water respectively. The investigation showed a strong dependance on ionic strength which is surprising since plutonium sorbs by inner sphere complexes and ought to be only slightly dependent och the total amount of dissolved solids.

Ticknor presents in the investigation K_d-values of 0.008-0.38 m^3/kg with the higher value for low ionic strength.

In another investigation by the same author (Ticknor, 1992) the opposite relationship is observed but for fracture infilling minerals. The sorption is increasing with increasing ionic strength, ranging from 1-5 m^3/kg for hematite, kaolinite and illite.

11.3.7 Americium (Am)

Chemistry
Americium is a trivalent actinide in groundwater conditions. Its speciation is more complicated than Th in terms of possible complexes. Although the hydrolysis is strong, carbonate complexes or a mixture of hydroxo-carbonate species are possible. The solubility is limited to about 10^{-8} M in the reference conditions and, similar to the tetravalent actinides, Am is prone to colloid formation. Again, great care must be taken when performing sorption experiments. Exceeding the solubility limit will inevitable cause erroneous K_d-values.

Sorption
Generally, the sorption is as high as for the tetravalent actinides, with K_d-values of 1-10 m^3/kg. The strength of the sorption is not very dependent on the solid phase (mineral) which indicates that the sorption is non-specific (Albinsson, 1991).

Most experimental work has been with ^{241}Am with a half-life of 430 y. This fairly long half-life results in difficulties in measuring high K_d-values without exceeding the solubility limit (Carbol *et al.*, 1995).

It must be taken into account that some experiments with values in the lower region are based on sorption onto quartz, which is generally a ”low sorbing” mineral, and that the extent of sorption is considered to be much higher on fracture infilling minerals. This is especially pronounced for the trivalent actinides, which can form coprecipitates with calcite ($CaCO_3$). For these reasons, a K_d-value of 5 m^3/kg could be realistic in both saline and non-saline conditions.

11.4 TRANSITION ELEMENTS

11.4.1 Cobalt (Co)

General
Cobalt is present in nuclear waste as an activation product, as the element is present in the metallic construction material in the nuclear reactor. The only isotope of cobalt that has a substantially long half-life is ^{60}Co ($t_{1/2}$=5.272 y, β^- decay, E_β=0.3 MeV).

Chemistry
The main species of cobalt is expected to be Co^{2+}. Cobalt forms complexes with chlorides at high chloride concentrations, preferably $CoCl_2$. In the presence of ammonia, Co^{3+} can be stabilised as complexing agent. Cobalt(+II) undergoes hydrolysis, which becomes important at pH >7.5. A precipitation of $Co(OH)_{2,s}$ will form at higher pH (above 8.5). Due to the amphoteric character of Co(II) hydroxide, the precipitate will dissolve in an alkaline solution, yielding $Co(OH)_4^{2-}$ ions.

Sorption
Andersson *et al.* (Andersson, 1993) concluded that hydrolysis has a strong influence on the sorption of Co on granite. Maximum sorption is observed at a certain pH, at which easily sorbed hydrolysis products are formed. The decrease in sorption at higher pH is ascribed to the formation of negatively charged hydrolysis products, which are poorly sorbed at the negatively charged mineral surfaces. The K_d-values found for cobalt sorption on granite at low and medium ionic strength and pH 7-9 were 0.024-0.49 m^3/kg.

Parameters such as radionuclide concentration, CEC and temperature were found to be of minor importance owing to the sorption by non-specific forces.

Allard *et al.* (Allard, 1983b) proposed that cobalt and nickel are expected to have similar chemical behaviour.

11.4.2 Nickel (Ni)

General

Nickel present in the metallic parts of the fuel elements is activated during nuclear power operation. The two long-lived isotopes of nickel are ^{63}Ni, with a half-life of 100 y and a low energy β^- decay of 0.07 MeV, and ^{59}Ni, with a half-life of $7.5 \cdot 10^4$ y and a β^+ decay.

Chemistry

Nickel is predominantly divalent in aqueous solution and is highly soluble in water at $pH < 6.7$. The analogy with Co is observable. The two elements are found in the same geological formations on the earth. The relatively small difference in ionic radius and charge gives them a similar chemical behaviour. The hydrolysis constants are almost identical for these elements. The sorption is mainly dependent on hydrolysis of Ni, and consequently on pH. The sorption of Ni on granite is only slightly dependent on the cation exchange capacity (CEC).

Sorption

Sorption of Ni on granite was investigated by Ticknor (Ticknor, 1994) in the pH range of 7.4 to 8.8 and a total concentration of Ni of 10^{-8} M. The sorption of Ni increased with pH. On the other hand, the effect of increased concentrations of Ca and Mg affected the sorption only slightly. It is an open question whether Ni can precipitate as Ni_2SiO_4 or even as $NiSiO_3$. The K_d was measured to be in the range of 0.062 to 0.66 m^3/kg for pH 8.7 and low concentrations of HCO_3^- in the solution (HCO_3^- <1 mg/l).

11.4.3 Cadmium (Cd)

General

Cadmium is a highly toxic element and is therefore of interest not only with respect to its radiotoxicity but also as a stable element in a nuclear deposit. The element exists in the nuclear waste because of its usage as a good neutron absorber in control rods.

Chemistry

The valence state of cadmium in aquatic waters is as Cd^{2+}. The existence of sulphides in the water will probably precipitate cadmium as CdS. Cadmium has a tendency to form complexes with halogens, especially iodine, bromine and chloride. At high concentrations of halogens, a negatively charged species, such as $CdCl_3^-$ and $CdCl_4^{2-}$, may be formed.

Calculations of the first complex formation of Cd with hydroxide, sulphate and chloride for both non-saline and saline groundwaters (pH range of 7-9) show that the chloride complex will form. The presence of carbonate, CO_3^{2-}, in the groundwater may also affect the speciation of Cd, especially at higher pH.

11.4.4 Zirconium (Zr)

General

Zirconium has only one long-lived isotope on the neutron-rich side, ^{93}Zr. The isotope decays through emission of a low energy (0.06 MeV) β^- particle. ^{93}Zr has a half-life of $1.5\cdot10^6$ years. The high cumulative fission yield of the A=93 isobar gives a relatively high amount of this isotope in nuclear waste. Zirconium is also used as encapsulation for nuclear fuel due to its low neutron absorption cross-section and anti-corrosive properties. However, a minor part of the zircalloy is neutron-activated, which adds to the amount of ^{93}Zr in the nuclear waste. The relatively high presence of this radioisotope in the fuel makes it an important radionuclide in the assessment performance.

Chemistry

Zirconium exists preferably in the +4 valence state in aqueous solutions. The natural presence of zirconium shows that the element behaves in a way similar to uranium, niobium and thorium (Choppin *et al.*, 1995).

The hydrolysis constants indicate a strong hydrolysis and formation of polymeric species at pH levels above 2 (Baes *et al.*, 1976). The element exhibits a weaker hydrolysis than the actinides. As is typical for tetravalent actinides, the solubility is low, presumably less than 10^{-10} M (Stenhouse, 1995).

Sorption

As mentioned above, zirconium in the tetravalent state has properties similar to those of tetravalent actinides, although experimental studies indicate that the sorption is somewhat weaker (Allard *et al.*, 1979).

Bruno *et al.* (Bruno, 1995) writes that Zr has been predicted to exist as $Zr(OH)_5^-$ in seawater. On the other hand, in the TRACEX database, the most probable species of Zr under reducing conditions is $Zr(OH)_4$. The solubility controlling solid in the database is ZrO_2(am).

The existence of negatively charged $Zr(OH)_5^-$ could indicate a decreasing sorption with increasing pH. This assumption is contradicted by the observations of Pilkington *et. al.* (Pilkington, 1990). These authors studied the sorption of zirconium in the cement system with waters with very high pH (>10). Under these extraordinary water conditions, zirconium still sorbs strongly, with a K_d-value of about 1 m^3/kg.

Due to the fact that zirconium readily forms true colloids (Baes *et al.*, 1976) or sorbs on particles (Bruno *et al.*, 1995) and considering the experimental difficulties associated with that, the uncertainty interval is larger than -50%-+100%. The similarities with tetravalent actinides indicate that the sorption is practically insensitive to variations in the groundwater salinity.

11.4.5 Niobium (Nb)

General
The only long-lived isotope of niobium is ^{94}Nb. The niobium nucleus decays with a half-life of $2 \cdot 10^4$ years. The emitted β^- particle has an energy of 0.5 MeV. Since ^{93}Nb is a shielded isotope, the main process for formation of ^{94}Nb in the nuclear reactor is by neutron activation of ^{93}Nb (Liljenzin, 1996). The stable niobium exists in the reactor as part of the construction material to an extent of several percent. As a consequence of the long half-life of ^{93}Zr, only a minimal part of ^{93}Nb is formed which would yield ^{94}Nb through neutron capture. Choppin (Choppin *et al.*, 1995) confirms that the amount of ^{94}Nb in the nuclear waste is small.

Chemistry
Niobium is a VB element, and these elements show oxidation states from -1 to +5. The relevant oxidation state for niobium is +5, as the stability of the lower oxidation states decreases when going down the group (Cotton, 1972). Niobium exists preferably with a valence of +5 in natural groundwaters. Equilibrium diagrams (Baes *et al.*, 1976) of potential versus pH for an aqueous system of Nb show that niobium exists preferably as $Nb(OH)_6^-$ in the pH range of 7.5-9 and E_h=-0.3 V. Niobium forms, in moderately concentrated solutions, polynuclear oxyl ions, $H_x(Nb_6O_{19})^{8-x}$.

Bruno *et al.* (Bruno, 1995) concludes that coherent with the chemical behaviour of similiar elements, such as titanium, zirconium, hafnium, tantalum and yttrium, niobium is not mobile in natural groundwaters. The TRACEX database included in their report suggests that niobium exists as $Nb(OH)_5$ under reducing conditions. The solubility-controlling solid phase is suggested to be $Nb_2O_{5(s)}$.

The speciations refered to above indicate that the most probable species is $Nb(OH)_{5,aq}$ and/or $Nb(OH)_{6,\ aq}^-$.

Speciation calculations may show that negatively charged species dominate in alkaline solutions, but the effect on the sorption is minor, as demonstrated

by Pilkington *et. al.* (Pilkington, 1990). These authors found that the sorption in those solutions was about 1 m^3/kg.
The sorption experiment indicates a strong sorption which suggests that niobium exists as $Nb(OH)_{5,aq}$. In this report we assume that $Nb(OH)_{5,\ aq}$ is the dominating species in the groundwater.

Sorption
Robertson *et al.* (Robertson, 1983) studied transport of niobium in soils and sediments. The groundwater had a pH of 8-9. The results showed that niobium did not appear to be mobile. Niobium release was partitioned as follows: 58% particulate, 34% cationic and 8 % anionic. The cationic form of niobium was adsorbed by the soil, while the anionic form of niobium was mobile.

11.4.6 *Technetium* (Tc)

General
All isotopes of technetium are radioactive. The only long-lived Tc-isotope in the nuclear waste will be ^{99}Tc, with a half-life of $2.13 \cdot 10^5$ years. ^{99}Tc is a fission product with a cumulative fission yield of 6.13 %. The isotope decays by β^- emission with a maximal energy of 0.3 MeV.

In nature, the element is continuously produced by spontaneous decay of ^{235}U. Natural transport of Tc is limited to studies of uranium-rich rock deposits.

Chemistry
The most stable oxidation states for Tc are +VII and +IV. In water solutions under oxidising conditions, TcO_4^- is formed. The pertechnetate ion, TcO_4^-, has a tetraedic formation and is weakly oxidising. Technetium does not form poly-anions. Under reducing conditions, technetium exists as Tc(IV). Tc exhibits a chemical behaviour similar to that of molybdenum and tungsten.

In groundwater conditions present in a deep nuclear waste repository, only Tc(VII) and Tc(IV) are stable oxidation states of technetium. In oxic groundwaters, highly soluble Tc(VII) is present as the TcO_4^- anion with very slight sorptive interaction with geological material.

Sorption
Batch sorption experiments performed by Cui *et al.* (Cui, 1996b) in an oxidising atmosphere indicated a K_d-value of 0.00076 m^3/kg. The reduction of TcO_4^- in granitic groundwaters is controlled by the redox equilibrium of

Fe^{2+}/Fe^{3+}. The iron-containing minerals are, for example, magnetite and Fe-chlorite. Although these minerals exists in only a minor fraction, they control the reduction of Tc.

Cui *et al.* (Cui, 1996a) concluded that the reduction of TcO_4^- to $TcO_2{\cdot}nH_2O_{(s)}$ is a three-electron process on the surfaces of a Fe(II) containing precipitate or mineral. The investigation showed that magnetite is at least 1.5 orders of magnitude more efficient as a reductant than either Stripa granite or fracture filling materials. The authors also concluded that the TcO_4^- reduction is influenced by ionic strength and the pH of the solution.

Nevertheless, once technetium is precipitated as $TcO_2{\cdot}nH_2O_{(s)}$ [$=Tc(OH)_{4(s)}$], exposure to air-saturated solution does not seem to dissolve the precipitate. A probable mechanism is that Fe^{2+} is oxidised, and not until all Fe^{2+} is consumed will $TcO_2{\cdot}nH_2O_{(s)}$ be dissolved. Addition of H_2O_2 dissolves the technetium precipitate rather rapidly.

Eriksen *et al.* (Eriksen, 1993) investigated the solubility of technetium, as $TcO_2{\cdot}nH_2O_{(s)}$, under reducing conditions ($E_h<0$ mV). The dissolution of $TcO_2{\cdot}nH_2O_{(s)}$, in a carbonate-free solution was found to be independent of pH in the range $6<pH<9.5$. The dissolved species was identified as $TcO(OH)_{2(aq)}$. In solutions with pH 7-9, the concentration of dissolved Tc(IV) was found to be 10^{-9} to 10^{-8} M.

At pH>10, Tc may form $TcO(OH)_3^-$, which increases the solubility of technetium and decreases sorption of technetium on geological material. Experiments under reducing conditions with carbonated groundwater showed that the formation of mixed hydroxy-carbonate complexes is important for the solubility of $TcO_2{\cdot}nH_2O_{(s)}$.

The authors concluded that, in hydrocarbonate groundwaters under reducing conditions, the solubility is pH-dependent. In the pH interval of 5-7.5, the solubility of Tc(IV) is constant ($<10^{-8}$ M) and the dominating species is $TcO(OH)_{2(aq)}$.

At pH 8 to 11, the solubility increases and the dominating anionic complex is $TcO(OH)_3CO_3^-$.

Allard *et al.* (Allard, 1979b) reported a K_d-value for technetium in an artificial saline groundwater under reducing conditions to be 0.05 m^3/kg. Under aerated conditions, the K_d-value was determined to be <0.001 m^3/kg.

Andersson *et al.* (Andersson, 1983b) concludes that the time dependence of the sorption seems to be related to the kinetics of the E_h-controlling system. The K_d-values reported for aerated systems in saline groundwaters indicate that technetium in contact with Fe(II)-bearing minerals exhibits a weak sorption, typically in the range of 0-0.001 m^3/kg.

Sätmark *et al.* (Sätmark, 1992) studied the sorption of TcO_4^- on Finnsjön granite, under aerated conditions in saline synthetic granitic groundwater, at pH 4 and 10.5. They concluded that no sorption occurred at any of the studied pH levels.

Byegård *et al.* (Byegård, 1991) performed a tracer experiment in a highly conductive fracture zone at the Finnsjön study site using a dipole geometry. They injected $^{99m}TcO_4^-$ into the reducing groundwater and concluded that the Tc(VII) was reduced to Tc(IV) and none of the injected activity was recovered. There is always a question of losses of $^{99m}TcO_4^-$ activity in metallic junctions, but the amount of activity injected was large enough to compensate for this sorption. Byegård *et al.* (Byegård, 1992) performed new batch-wise sorption studies in the laboratory and showed that the sorption of technetium in contact with Fe(II) containing mineral is rapid. They found that the reduction is independent of Tc-concentration in the range of $5 \cdot 10^{-9}$ to $6 \cdot 10^{-6}$ M. The authors also observed that the sorption/reduction is strongly dependent on the surface-to-volume ratio.

11.4.7 Palladium (Pd)

General

Palladium is present in the nuclear waste as a fission product represented by its only long-lived isotope, ^{107}Pd ($t_{1/2} = 6.5 \cdot 10^6$ years). The cumulative fission yield is 0.15 %. The isotope decays through emission of a soft β^- particle with a maximal energy of 0.03 MeV.

Chemistry

Palladium belongs to the platinum metals group (Ru, Rh, Pd, Os, Ir and Pt). The element is sufficiently noble that, in contact with water, the metal is stable with respect to the evolution of hydrogen throughout the pH range 1-14 (Baes *et al.*, 1976). In water, palladium exists in a +2 oxidation state. Pd forms complexes with most ligands, especially with soft ligands (such as NH_3). In non-saline solution (concentration of Cl^- <500 mg/l) and pH 7-9, the dominating aqueous species will be $Pd(OH)_{2(aq)}$. In saline groundwater conditions (concentration of Cl^- <6500 mg/l), an uncertainty exists whether a minor part of Pd may form chloride complexes such as $PdCl_4^{2-}$.

Bruno *et al.* (Bruno, 1995) suggest that chloride complexation of Pd is restricted to highly acidic and oxidising environments. The authors use $Pd(OH)_2$ in the TRACEX database as the most probable species under anoxic conditions in deep groundwaters. The solubility-controlling phase is PdO. The authors also point out the possibility for Pd to form complexes with "soft" ligands such as sulphide and thiosulphites.

Under reducing conditions in the presence of hydrogen peroxide and hydrogen, palladium complexes can form metallic palladium (Albinsson, 1991). Metallic palladium tends to be incorporated in metal-containing minerals such as olivin and iron-containing minerals. Owing to the relative affinity of palladium to sulphide and oxygen, one can expect palladium to form solid solutions with these elements.

Sorption
No new data were found for Pd sorption on granitic rock under reducing conditions. As a consequence of the large discrepancy between the existing experimental sorption data for Pd, we strongly recommend performing new sorption experiments for palladium sorption on granitic rock in saline and non-saline groundwater under reducing conditions.

11.4.8 Silver (Ag)

General
Stable silver is neutron-activated in the reactor (activation product). The only long-lived Ag-isotope is ^{108}Ag, which decays by electron capture with a half-life of 127 years.

Chemistry
In natural groundwaters, silver exists as Ag(+I). Natural silver exists as Ag_2S or in mixtures with Cu_2S. Large amounts of silver also exist as Ag_2SbS_3 and to a lesser extent as AgCl. Silver is hydratised in groundwater as Ag^+. The hydrolysis of silver leads to only two species, AgOH and $Ag(OH)_2^-$ (Baes *et al.*, 1976). As mentioned above, silver forms rather insoluble compounds with many anions but not with F^-, NO_3^-, CO_3^{2-}, ClO_3^- or ClO_4^-.

Sorption
No data were found for silver´s sorption on granitic rock. Sorption experiments of Ag^+ sorption on sand (mainly quartz) indicate a stronger sorption than Cs^+ (Carbol, 1993). The K_d-value, obtained at pH~6 and low ionic strength (I=0.001 M), was 0.9 m^3/kg. The main sorption mechanism for Ag^+ will be by ion exchange into minerals such as vermicullite, smectite and illite.

Sorption of Ag^+ is dependent on the ionic strength as are all mono- and divalent ions. On the other hand, the dependence on pH (in the pH range of 7-9) can be neglected.

11.5 OTHERS

11.5.1 Tin (Sn)

General
There are only a few data available on the sorption of tin on granite and rock minerals. The reason tin is considered a nuclear waste hazard is because of its only long-lived isotope, ^{126}Sn, with a half-life of about 10^5 years. The cumulative fission yield is about 0.05%. The isotope decays by a β^- decay with an energy of 0.3 MeV to the daughter nuclide ^{126}Sb. ^{126}Sb in turn decays within days to the stable isotope ^{126}Te.

Chemistry
The aqueous chemistry is not well known. Under oxidising conditions, the tetravalent state is expected. The divalent state (Sn^{2+}) is most probable under reducing conditions in the pH range 7-9. The divalent state is much more soluble than the tetravalent state (Albinsson 1991).

Bruno *et al.* (Bruno, 1995) rewieved the solubility-controlling minerals for different elements in geochemical environments relevant for repository conditions. They found that, for Sn, the most probable solubility-controlling phase under reducing conditions will be SnO_2(am), being in equlibrium with $Sn(OH)_4$(aq). The speciation was valid even for high saline groundwaters.

Ticknor *et al.* (Ticknor, 1996) made a geochemical modelling for saline ([Cl^-] >500 mg/l) and non-saline groundwater under oxidising conditions and concluded that the main aqueous Sn species was $Sn(OH)_4$, which accounted for more than 97% of all dissolved Sn at pH values of 7 and 8. In the higher pH range, $Sn(OH)_5^-$ accounted for 22% of the Sn in solution at a pH of 9. The modelling indicated that crystalline SnO_2 and possibly amorphous SnO_2 could precipitate.

Sorption
The batch sorption experiment of Sn on granite indicated a K_d-value of 4 m^3/kg. It could also be concluded that the sorption of Sn was in the order hematite>goethite>montmorillonite>biotite≈K-feldspar>quartz. Finally, the investigation showed that an increased dissolved organic carbon concentration decreased the sorption of Sn.

The presence of large amount chlorides (in saline groundwaters) may alter the aqueous speciation, thus giving the anionic species $SnCl_3^-$ and $SnCl_5^-$, which dramatically alter the sorption behaviour.

11.5.2 Carbon (C)

General and chemistry
The only long-lived radionuclide of carbon is the β^- emitting ^{14}C ($t_{1/2}$=5730 y, E_β=0.2 MeV). ^{14}C released from the nuclear waste in the repository will equilibrate with the inorganic CO_2-HCO_3^--CO_3^{2-} system in the groundwater.

Sorption
The sorption mechanism for carbon is probably an isotope exchange reaction with carbonate, present as the mineral calcite in the rock fractures. Allard *et al.* (Allard, 1981 and 1983) reported a K_d-value of 0 m^3/kg for the sorption of HCO_3^- on Stripa granite, even after 6 months contact time. Sorption of $H^{14}CO_3^-$ on calcite was, on the other hand, substantial and showed increased sorption with increasing time. After a time of 6 months a K_d-value of 0.083 m^3/kg has obtained.

Calcite is a generally occurring fracture filling mineral in Swedish granite rock (Landström *et al.*, 1995). The relatively high concentration of Ca in the Swedish groundwater favours precipitation of calcite on the fracture walls.

11.5.3 Iodine (I)

General
Iodine is present in nuclear waste as a fission product. Several iodine isotopes exist, most of them with short half-lives (days), except ^{129}I. ^{129}I has a half-life of $1.57 \cdot 10^7$ y, decaying by β^- emission with an energy of 0.2 MeV. The cumulative fission yield is about 0.8%.

Chemistry
In deep groundwater, iodine will be present as the iodide ion (I^-) and possibly as the iodate ion (IO_3^-). As most minerals are negatively charged at the conditions prevailing in a nuclear safety deposit, the sorption of iodide is hindered owing to the electrostatic forces. The sorption of iodide increases with decreasing pH, as expected for an anion exchange process. The presence of humic substances (HA and FA) in the groundwater allows a certain amount of iodide being bound by the organic material, as this material is known to adsorb iodide.

Sorption
Kipatsi (Kipatsi, 1983) presented a K_d-value of 0.0006 m^3/kg at moderate ionic strength. Allard *et al.* (Allard, 1980) investigated iodine sorption on

chemisorbing minerals (*e.g.* cinnabar HgS, galena PbS *et cetera*), hydroxides (such as ferric hydroxide $Fe(OH)_3$, aluminium hydroxide $Al(OH)_3$ *et cetera*) and silicate minerals (quartz SiO_2, olivine $(Mg, Fe)_2SiO_4$ *et cetera*). The results indicated a significant sorption on chemisorbing minerals (K_d-value 0.1 m^3/kg), small sorption on the large surface area hydroxide minerals (K_d-value 0.01 m^3/kg) and small sorption on silicate minerals (K_d-values 0.01-0.001 m^3/kg). Quartz exhibited a K_d-value of 0.001 m^3/kg.

Andersson *et al.* (Andersson, 1983b) concluded that sorption of iodide is possible on granitic rock containing such metals as Hg, Ag, Bi, Cu, Pb *et cetera,* due to the low solubility of these metal iodides. Their investigation showed that no sorption of iodide could be detected on Stripa granite, while a low but significant K_d-value (0.004 m^3/kg) was observed for Studsvik granite.

Byegård *et al.* (Byegård, 1991) concluded from tracer experiments in deep rock formations that I^- is transported unretarded, comparable to Br^-, which indicates negligible sorption on granitic rock.

11.5.4 Chlorine (Cl)

General and chemistry

The only long-lived isotope of chlorine is the β^--emitting ^{36}Cl ($t_{1/2}=3\cdot10^5$ y, $E_\beta=0.7$ MeV). The only species expected in the deep groundwater is Cl^-.

Sorption

The chloride ion is one of the most conservative (i.e. non-sorbing or unreactive) ions in the geosphere. Several tracer experiments have shown that chloride can be used as a conservative tracer and, due to ion exclusion in the matrix, the chloride ion can even be more mobile than tritium-labelled water (Vieno *et al.*, 1992; Hölttä *et al.*, 1992). The relatively high concentration of chloride in the deep groundwater disfavours sorption of chloride on granite.

11.5.5 Selenium (Se)

General

The fission product ^{79}Se has a cumulative fission yield of 0.04% and a half-life of approximately $6.5\cdot10^4$ years. It decays with a β^- energy of 0.2 MeV (Albinsson, 1991).

Chemistry

In the environment, Se is found in the di-, tetra- and hexavalent state in aqueous solutions. Under oxidising conditions, selenium is present in natural groundwater as the anions $Se0_2^{2-}$ and SeO_4^{2-}. Bruno *et al.* (Bruno, 1995) suggested that Se will exist as HSe^- or as Se^{2-} in deep groundwaters (saline and non-saline) under reducing conditions. As the solubility-controlling solid phase, FeSe is proposed. Incorporation into FeS minerals is also a possible sorption mechanism. This is possible owing to the similiar ionic radius for sulphur (S^{2-} 1.84 Å) and selenium (Se^{2-} 1.91 Å).

Vourinen *et al.* (Vourinen, 1992) also suggest Se being present as the HSe^- species in reducing groundwaters. In any case, as anion species, Se will exhibit little sorption, and low K_d-values are expected.

Sorption

Ticknor *et al.* (Ticknor, 1996) obtained a K_d-value of 0.004 m^3/kg as they investigated the sorption of Se on granite under oxidising conditions (E_h=150 mV, saline and non-saline groundwater). Geochemical modelling indicated $HSeO_3^-$ as the dominating species around pH 7, while SeO_3^{2-} dominated in the pH range of 8-9. Oversaturation of elemental Se was not found in the experiment, even if the geochemical modelling indicated so. It was concluded that precipitation of crystalline Se at low temperature conditions is unlikely due to kinetic reasons.

It could also be concluded that the sorption of Se was in the order hematite> goethite>biotite>montmorillonite>granite. The investigation also showed that increased dissolved organic carbon concentration did not appear to influence the sorption of Se.

The two sets of experiments indicate that Se under slightly reducing conditions has a K_d of approximately 0.04 m^3/kg.

11.5.7 Krypton (Kr)

General and chemistry

There are no known measurements of krypton sorption on minerals reported. Krypton belongs to the class of noble gases in the periodic table. This class is characterised by elements unwilling to react with other elements. The amount of krypton in the atmosphere is approximately 0.00011 vol-%. The element is of meteoritic origin. Krypton is a monoatomic gas with a boiling point of -152.9 °C. Approximately 11 vol-% of krypton is dissolved in water at a temperature of 0 °C and a pressure of 0.1 MPa. The only krypton isotope with an appreciable half-life (10.78 y) is ^{85}Kr. It has mainly a β^- decay with an energy of 0.7-0.8 MeV.

Krypton reacts chemically with strongly electron negative elements such as fluorine and oxygen. The aqueous specie of Kr will be as uncharged krypton gas. The adsorption on granitic rock is most certainly negligible. The natural retention of krypton is by dissolution in water.

12 RECOMMENDED K_d-VALUES

12.1 ALKALI AND ALKALINE EARTH METALS

12.1.1 Cesium (Cs)

More recent K_d determinations (Landström, 1995), (Aggeryd, 1991), (Sätmark, 1992) indicate somewhat increased K_d-values for cesium sorption on granite. We recommend a K_d-value of 0.5 m^3/kg with an uncertainty range of 0.1-1 in non-saline waters and 0.05 m^3/kg with an uncertainty range of 0.01-0.1 in saline waters. This moderate decrease in sorption in saline waters is based on the selectivity of sorption sites for Cs where Na is not a strong competitor.

12.1.2 Strontium (Sr)

The K_d determinations made in the past years indicate a somewhat decreased K_d-value for strontium sorption on granite (Cui, 1995). In non-saline conditions, we recommend a K_d-value of 0.01 m^3/kg with an uncertainty rage of 0.005-0.05. In saline conditions the value is further reduced due to recent investigations (Byegård, 1995), (Albinsson, 1997) to 0.0002 m^3/kg with an uncertainty range of 0.0001-0.001 for saline groundwaters.

12.1.2 Radium (Ra)

On the basis of the observation of K_d-values presented in the literature, a recommended realistic value for non-saline is 0.1 m^3/kg; in saline groundwater conditions we assess 0.02 m^3/kg. The lower value for the saline groundwater conditions is due to the competition between Ra and Ca for the sorption sites. The uncertainty range is set to 0.05-0.5 for the non-saline and 0.01-0.1 for saline groundwater. An comparison with Sr is of no value since the chemistry is signifficantly different and the sorption is expected to increase as the element is further down the group in the periodic table (Albinsson, 1997).

12.2 LANTHANIDES

K_d determinations made over the past years does not give a clear picture of the sorption of the lanthanides on granite as the values are scattered. Values in the higher region could be biased by supersaturaded solutions in respect to the metal studied. We therefore recommend a K_d-value of 2 m^3/kg for both non-saline and saline conditions. Taking into account the experimental difficulties working with elements with a very limited solubility, we assign an uncertainty of 1-5 m^3/kg. These values are applicable for all the lanthanides in saline and non-saline water.

12.3 ACTINIDES

12.3.1 Actinium (Ac)

As no investigations were found of the sorption of actinium, we recommend a K_d-value of 3 m^3/kg for both saline and non-saline conditions with an uncertainty interval of 1-5 m^3/kg similar to Am (*c.f.* sect. 11.3.1).

12.3.2 Thorium (Th)

Although the values are scattered in the interval of 0.25-5 m^3/kg, we recommend for Swedish conditions the value of 5 m^3/kg as realistic (*c.f.* sect. 11.3.2). Due to the experimental difficulties with sorption studies with Th, the possible errors can be large. We therefore recommend an uncertainty interval of 1-10 m^3/kg. This applies both for non-saline and saline conditions.

12.3.3 Protactinium (Pa)

No recent investigations were found in the review. As a total, the number of experimental investigations is very limited, we recommend a K_d-value of 1 m^3/kg as representative for both non-saline and saline conditions, with an uncertainty interval of 0.5-5 m^3/kg. The upper limit of this interval is possibly too low, as Allard *et. al.* (Allard, 1979) reported values up to 10 m^3/kg. However, this limitation is of no practical importance, as K_d-values in that range merely indicate total immobility.

12.3.4 Uranium (U)

Taking into account the probable speciation of uranium (*c.f.* sect. 11.3.4) and its similarities with thorium, for tetravalent uranium we recommend a K_d-value of 5 m^3/kg in both non-saline and saline conditions, with an uncertainty interval of 1-10 m^3/kg.

In order to cover the possibility of oxidised uranium we recommend a K_d-value of 0.01 m^3/kg for non-saline conditions and 0.005 m^3/kg for saline with uncertainty intervals of 0.005-0.02 and 0.001-0.01 m^3/kg respectively. This selection is in accordance with (Albinsson, 1991)

12.3.5 Neptunium (Np)

As no new experiments contradict the selection by Albinsson (Albinsson, 1991), for tetravalent neptunium, we recommend the same value for both non-saline and saline conditions (5 m^3/kg), with an uncertainty interval of 1-10 m^3/kg.

For the oxidised pentavalent form the sorption is low. Although Vannerberg (Vannerberg, 1994) present high values, *c.f.* sect. 11.3.5, the values by Ticknor (Ticknor, 1993) give support to be careful in the selection. The selection by Albinsson (Albinsson, 1991) seems justified and we recommend therefore for non-saline conditions a K_d-value of 0.01 m^3/kg and for saline conditions a K_d-value of 0.005 m^3/kg with uncertainty intervals of 0.005-0.05 m^3/kg and 0.001-0.01 m^3/kg respectively.

12.3.6 Plutonium (Pu)

Since plutonium is a key element in performance assessment and because the experimentally obtained K_d-values are scattered (0.1-10 m^3/kg), a conservative choice of K_d is in the lower region. This is contradicted by diffusion experiments in clay, which result in a retardation not unlike the other tetravalent actinides or trivalent americium. As a K_d-value of 5 m^3/kg has been assessed for those elements with an uncertainty interval of 1-10 m^3/kg and nothing supports a different choice for plutonium, identical K_d-values is recommended.

12.3.7 Americium (Am)

Considering the experimental difficulties in determining high K_d-values and the similarities in chemistry to europium, for which a K_d-value of 3 m^3/kg has been assessed, we recommend 3 m^3/kg as a realistic value with an uncertainty interval of 1-10 m^3/kg for both saline and non-saline conditions.

12.3.8 Curium (Am)

There is not a great deal of information on the sorption of Cm in the literature. The chemistry similar to that of Am supports a similar K_d-value of 3 m^3/kg, with the same uncertainty interval of 1-10 m^3/kg for both saline and non-saline conditions.

12.4 TRANSITION ELEMENTS

12.4.1 Cobalt (Co)

A recommendation is to select a K_d-value similar to that found for Ni, which is 0.1 m^3/kg with an uncertainty range of 0.05-0.5 for non-saline conditions and 0.02 m^3/kg with an uncertainty range of 0.01-0.1 for saline conditions. A comparison with Sr is not applicable since Sr is a hard acid and thus forms outer sphere complexes which are sensitive to increases in ionic strength. Co is a soft acid and forms inner sphere complexes which are less sensitive to such changes (Albinsson, 1997).

12.4.2 Nickel (Ni)

The K_d-value of 0.1 m^3/kg is recommended for non-saline and 0.02 m^3/kg for saline groundwater. The uncertainty range is 0.05 to 0.5 for non-saline and 0.01 to 0.1 for saline groundwater. In case of a comparison with Sr, *c.f.*sect. 12.4.2. Ni is also an soft acid which forms inner sphere complexes.

12.4.3 Cadmium (Cd)

The similarity between the two elements Cd and Ni indicate that the K_d-value selected for Ni is also valid for sorption of Cd on granite. In this case, a recommendation is to use a K_d-value of 0.02 m^3/kg for saline and 0.1 m^3/kg for non-saline groundwater. The uncertainty range is 0.01-0.1 for non-saline and 0.05-0.5 for saline groundwater. In case of a comparison with Sr, *c.f.*sect. 12.4.2. Cd is also an soft acid which forms inner sphere complexes.

12.4.4 Zirconium (Zr)

The similarity between zirconium and niobium is significant, as was discussed earlier, and is also expressed in the similar choice of K_d-values. The K_d-values for zirconium sorption on rock seem to point towards a value of 1-2 m^3/kg.

Taking into consideration the formation of polymeric species and the low solubility of $ZrO_{2,s}$ and $Zr(OH)_{4,(s)}$, we recommend a realistic K_d-value of 1 m^3/kg (Pilkington, 1990) with an uncertainty of 0.5-3 m^3/kg for zirconium sorption on crystalline rock. This is applicable to both non-saline and saline conditions.

12.4.5 Niobium (Nb)

The lack of applicable experimental investigations supports the uncertainty interval being large, and we therefore recommend a K_d-value of 1 m^3/kg to be used in non-saline as well as saline conditions. With that value, an uncertainty interval of 0.5-3 m^3/kg is appropriate.

12.4.6 Technetium (Tc)

The reduced form of technetium is tetravalent. Similar to other tetravalent elements the sorption is anticipated to be strong. Results of investigations are scattered. This is possibly due to difficulties obtaining sufficiently low redox potenital to reduce pertechnetate ($Tc(VII)O_4^-$) to Tc(IV). On the basis of the investigation by Byegård (Byegård, 1991), *c.f.* sect. 11.4.6, we recommend a K_d-value of 1 m^3/kg with an uncertainty range of 0.3-3 m^3/kg for sorption of technetium under reducing conditions in both saline and non-saline groundwaters.

In aerated groundwater systems, the sorption of TcO_4^- is negligible, and we set the K_d-value to 0 m^3/kg.

12.4.7 Palladium (Pd)

No investigations of the sorption of Pd was found in the review. Anticipating that the sorption behaviour is similar to Co and Ni and that the chloride concentration in the groundwater is less than 6500 mg/l, we recommend a K_d-value of 0.01 m^3/kg as a realistic value with an uncertainty of 0.001-0.05 m^3/kg. In non-saline groundwaters, a K_d-value for Pd of 0.1 m^3/kg with an uncertainty of 0.01-0.5 m^3/kg should be used.

12.4.8 Silver (Ag)

Due to the lack of reported data on silver sorption on granitic rock, we suggest the same K_d-value as proposed for cesium. The recommended K_d-value for silver in non-saline and saline groundwater is 0.5 and 0.05 m^3/kg, respectively. The uncertainty interval for silver is identical to that for cesium.

12.5 OTHERS

12.5.1 Tin (Sn)

As a consequence of the lack of new data for the sorption of Sn on granite, we recommend the same K_d-value, 0.001 m^3/kg (for saline and non-saline groundwaters), as was recommended by Albinsson (Albinsson, 1991).

12.5.2 Carbon (C)

Until this point there has been no newly reported investigation on carbonate sorption on granite that changes the recommended K_d-value given by Albinsson (Albinsson, 1991), which was 0.001 m^3/kg. However, we assign an uncertainty range of 0.0005-0.005 m^3/kg.

12.5.3 Iodine (I)

Taking the K_d-values measured for iodide into consideration, the value of 0 m^3/kg is recommended.

12.5.4 Chlorine (Cl)

The recommended K_d-value is 0 m^3/kg.

12.5.5 Selenium (Se)

It is concluded that a K_d-value of 0.001 m^3/kg is reasonable in both non-saline and saline groundwaters. The uncertainty interval for non-saline and saline groundwater is chosen to be 0.0005-0.005 m^3/kg.

12.5.6 Krypton (Kr)

Since radon (Rn) belongs to the same group in the periodic table, the similarity with Rn is obvious. Radon is formed by radioactive decay in the rock matrix. The most long-lived Rn-isotope has a half-life of 3.8 days. Since Rn can be measured above thick soil layers (>50 m thick) this can be used as an indication of a rapid transport of Rn through geological media, *i.e.* a small retention of Rn in the geological material. Nothing indicates that the small retention is also valid for krypton. The K_d-value chosen for Kr is 0 m^3/kg.

12.6 SUMMARY

The recommended K_d-values for the elements investigated are given in Table 12-1. The selection criteria are given in section 6 and the sensitivity analysis in section 7.

Table 12-1. Recommended K_d-values for element sorption on granitic rock. The non-saline and the saline groundwaters are represented by the type of water found at the Gideå and Äspö study site, respectively. The restrictions for the non-saline water are: $pH \geq 7$, $[Cl^-] < 500$ mg/l and $E_h < -200$ mV . The restrictions for the saline water are: $pH \geq 7$, 500 mg/l $< [Cl^-] < 6500$ mg/l and $E_h < -200$ mV.

Element	Chemical form/redox state	Non-saline K_d (m^3/kg)	Uncertainty interval	Saline K_d (m^3/kg)	Uncertainty interval
C	HCO_3^-	0.001	(0.0005-0.002)	0.001	(0.0005-0.002)
Cl	Cl^-	0	-	0	-
Co	Co(II)	0.1	(0.05-0.5)	0.02	(0.01-0.1)
Ni	Ni(II)	0.1	(0.05-0.5)	0.02	(0.01-0.1)
Se	Se(-II, IV,VI)	0.001	(0.0005-0.005)	0.001	(0.0005-0.005)
Kr	inert gas	0	-	0	-
Sr	Sr(II)	0.01	(0.005-0.05)	0.0002	(0.0001-0.001)
Zr	Zr(IV)	1	(0.5-3)	1	(0.5-3)
Nb	Nb(V)	1	(0.5-3)	1	(0.5-3)
Tc	Tc(IV)	1	(0.3-3)	1	(0.3-3)
Tc	Tc(VII)	0		0	
Pd	Pd(II)	0.1	(0.01-0.5)	0.01	(0.001-0.05)
Ag	Ag(I)	0.5	(0.1-1)	0.05	(0.01-0.1)
Cd	Cd(II)	0.1	(0.05-0.5)	0.02	(0.01-0.1)
Sn	Sn(IV)	0.001	(0-0.01)	0.001	(0-0.01)
I	I-	0	-	0	-
Cs	Cs(I)	0.5	(0.1-1)	0.05	(0.01-0.1)
Sm	Sm(III)	2	(1-5)	2	(1-5)
Eu	Eu(III)	2	(1-5)	2	(1-5)
Ho	Ho(III)	2	(1-5)	2	(1-5)
Ra	Ra(II)	0.1	(0.05-0.5)	0.02	(0.01-0.1)
Ac	Ac(III)	3	(1-5)	3	(1-5)
Th	Th(IV)	5	(1-10)	5	(1-10)
Pa	Pa(IV,V)	1	(0.5-5)	1	(0.5-5)
U	U(IV)	5	(1-10)	5	(1-10)
U	U(VI)	0.01	(0.005-0.02)	0.005	(0.001-0.01)
Np	Np(IV)	5	(1-10)	5	(1-10)
Np	Np(V)	0.01	(0.005-0.05)	0.005	(0.001-0.01)
Pu	Pu(III,IV)	5	(1-10)	5	(1-10)
Am	Am(III)	3	(1-5)	3	(1-5)
Cm	Cm(III)	3	(1-5)	3	(1-5)

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APPENDIX

In this appendix it is possible to compare the selection of realistic K_d-values for performance assessment with selections in other databases and reviews.

Cesium

Albinsson (Albinsson, 1991) recommended a realistic K_d-value (pH approximately 8) for cesium of 1 m^3/kg (although 0.25 is mentioned as a conservative value in the summary table of recommended values). In saline groundwaters (I=0.1-0.5 M), he suggested a decrease of a factor of five.

A summarised database for K_d-values applied by different organisations for Cs sorption on granitic rock was made by McKinley *et al.* (McKinley, 1991) and is presented in Table A-1.

Table A-1. Summary of K_d-values (m^3/kg) sampled from various databases for granite/crystalline rock (McKinley *et al.*, 1991).

Element	NRC realistic	NAGRA realistic	SKI reducing best estimate	AECL	TVO reducing
Cs	0.1	0.25	0.05	0.1	0.06

These K_d-values presented by McKinley *et al.* (McKinley, 1991) are somewhat lower than the ones presented by Stenhouse *et al.* (Stenhouse, 1994). From the latter presentation we conclude that the K_d-values from NAGRA are set to 0.5 m^3/kg and from TVO to be 0.4 m^3/kg.

Stronium

A summary of the strontium sorption on granitic rock was made by McKinley *et al.* (McKinley, 1991) and is presented in Table A-2.4

Table A-2. Summary of K_d-values (m^3/kg) sampled from various databases for granite/crystalline rock (McKinley *et al.*, 1991).

Element	NRC realistic	NAGRA realistic	SKI reducing best estimate	AEC L	TVO reducing
Sr	0.02	not given	0.004	0.01	0.001

The K_d-values presented by McKinley *et al.* (McKinley, 1991) are on the same level as found in the most recent experiments.

Albinsson (Albinsson, 1991) recommends a realistic K_d-value (pH around 8) at low and medium ionic strengths for strontium sorption on granite of 0.03 m^3/kg. In saline groundwaters (I=0.1-0.5 M), he gives a recommendation of 0.01 m^3/kg.

Radium

McKinley *et al.* (McKinley, 1991) summarise in their granite crystalline rock database the K_d-values presented by NRC, NAGRA, PAGIS (Performance Assessment of Geological Isolation Systems for radioactive waste), GOLDER (Golder Associates) and SKI. The following realistic K_d-values were given for radium by NRC, NAGRA, GOLDER and SKI: 0.05, 1.0, 0.08 and 0.1 m^3/kg, respectively.

Vieno *et al.* (Vieno, 1992) give a conservative K_d-value of 0.05 m^3/kg for the sorption of Ra on rock.

Albinsson (Albinsson, 1991) recommends a realistic K_d-value of 0.5 m^3/kg for a low ionic strength water and gives a value of 0.1 m^3/kg for a saline water.

The similarity in chemistry with Sr is limited *c.f.* the different solubility products. In other words, Ra and Sr should not be compared with respect to their K_d-values.

Lanthanides

A summary of the lanthanide elements′ sorption on granitic rock was made by McKinley *et al.* (McKinley, 1991) and is presented in Table A-3.

Table A-3. Summary of K_d-values sampled from various databases for granite/crystalline rock (McKinley *et al.*, 1991b).

Lanthanide elements	KBS-2 best estimate	NAGRA realistic	AECL	SKI reducing best estimate
Ce	12.6		1	
Eu	7.8		1	
La				5
Nd	4.2		1	
Sm		2.5		

Albinsson (Albinsson, 1991) recommends a K_d-value for lanthanides of 3 m^3/kg.

Thorium

Sorption data for Th are scarce possibly because of the difficulties obtaining appropriate radioisotopes. The study by McKinley *et al.* (McKinley, 1984) recommended a conservative value of 1 m^3/kg. Andersson *et al.* (Andersson, 1983a) and Allard *et al.* (Allard, 1991) recommended a realistic value of 5 m^3/kg. The corresponding conservative value in Allard *et al.* (Allard, 1983) was 3 m^3/kg. Hakanen *et al.* (Hakanen, 1992) recommends 0.5 and 0.2 m^3/kg as realistic and conservative values, respectively.

Protactinium

Albinsson (Albinsson, 1991) recommends a realistic K_d-value of 2 m^3/kg. Stenhouse (Stenhouse, 1995) makes the comparison with Zr/Nb and, with the lack of reliable data, recommends a K_d-value of 1 m^3/kg. Hakanen *et al.* (Hakanen, 1992) are more conservative and select a value of 0.1 m^3/kg.

Uranium

Andersson (Andersson, 1983a) recommends a K_d-value of 5 m^3/kg.

Neptunium

Albinsson (Albinsson, 1991) recommends a realistic K_d-value of 5 m^3/kg in groundwaters at a pH of 8 in both high and low ionic strength.

Plutonium

The K_d-values in several reviews range between 0.3 and 5 m^3/kg (Vandergraaf, 1982), (Andersson, 1983a), (McKinley *et al.*, 1984), (SKI 90) and (Hakanen *et al.*, 1992). The lower values can be attributed to higher oxidation states with plutonyl complexes dominating. In the reference waters in this report, only the lower oxidation states are expected to be significant and thus only a K_d-value in the higher region is considered

Americium

Albinsson (Albinsson, 1991) recommends a realistic value of 1 m^3/kg in favourable conditions.

Andersson (Andersson, 1983a) and McKinley (McKinley *et al.*, 1984) both recommend 5 m^3/kg as the best estimate.

Hakanen (Hakanen *et al.*, 1992) present a realistic K_d-value of 0.5 m^3/kg for granitic conditions and all groundwaters.

Vandergraaf *et al.* (Vandergraaf, 1982), on the other hand, recommend a high value of 8 m^3/kg in their review.

Nickel
Albinsson (Albinsson, 1991) recommends a K_d-value of 0.02 m^3/kg for high ionic strength and 0.1 m^3/kg for low ionic strength and pH around 8.

Allard *et al.* (Allard, 1983b) makes reference to an investigation made by Meyer *et al.* (Meyer, 1979), who found that the K_d-value decreased with increasing ionic strength.

Stenhouse *et al.* (Stenhouse, 1994) reported choice of realistic K_d-values for a crystalline rock-water system made by NAGRA, TVO and CNFWM, which were 0.5, 0.2 and 0.03 m^3/kg, respectively.

Cadmium
The literature contains very little information on Cd sorption on granite. However, Caron (Caron, 1995) recommended a K_d-value for Cd sorption on sand of 0.08 m^3/kg.

Zirconium
Albinsson (Albinsson, 1991) recommends a K_d-value of 2 m^3/kg as a reasonable value. Table A-4 gives the selected K_d-values for zirconium and the organisation according to McKinley *et al.* (McKinley, 1992).

Table A-4. K_d-values (given as m^3/kg) summarised by McKinley *et al.* (McKinley, 1992).

Element	KBS-3, reducing, conservative	NRC realistic	NAGRA realistic	SKI reducing best estimate	AECL	TVO reducing conditions
Zr	4	0.5	5	4	1	1

Stenhouse *et al.* (Stenhouse, 1994) summarise realistic K_d-values for zirconium given by NAGRA, SKB and TVO as being 1, 2 and 2 m^3/kg, respectively.

Niobium

The anionic form of niobium was considered by Hakanen *et al.* (Hakanen, 1992) as a conservative K_d-value in the Finnish study summarised by Vieno *et al.* (Vieno, 1992). The realistic K_d-value recommended by Hakanen *et al.* (Hakanen, 1992) was 1 m^3/kg.

Until batch sorption experiments are performed, the conservative K_d-value given by Vieno *et al.* (Vieno, 1992) seems reasonable with respect to the sorption of negatively charged species on granite.

Caron (Caron, 1995) recommends a K_d-value of 0.75 m^3/kg for niobium sorption on sand.

Kulmala *et al.* (Kulmala, 1993) report K_d-values of 0.7-5 m^3/kg in saline conditions and 0.7-2.5 m^3/kg in non-saline conditions.

McKinley *et al.* (McKinley, 1992) gives the following K_d-values for the respective organisations, see Table A-5.

Table A-5. K_d-values (given as m^3/kg) summarised by McKinley *et al.* (McKinley, 1992).

Element	KBS-3, reducing, conservative	SKI reducing best estimate	AECL	TVO reducing conditions
Nb	4	4	0.21	1

Stenhouse *et al.* (Stenhouse, 1994) summarised realistic K_d-values given by NAGRA, SKB and TVO as being 1, 2 and 2 m^3/kg, respectively. Since no batch experiments have been reported during the past years on niobium sorption on crystalline rock, the uncertainty remains. The decrease in recommended K_d-values made by several organisations (NAGRA, SKI, TVO) over the past years indicate uncertainty regarding the early experiments performed. We strongly recommend a new experimental study of niobium sorption on granitic rock to verify the set of K_d-values. Meanwhile, Stenhouse *et al.* (Stenhouse, 1995) recommends a realistic K_d-value of 1 m^3/kg for niobium sorption on crystalline rock.

Technetium

Albinsson (Albinsson, 1991) recommends a K_d-value of 2 m^3/kg for naturally reducing conditions and 0.0002 m^3/kg for oxidising conditions. He also concludes that the sorption is very little dependent on pH and salinity.

In the Finnish safety analysis of spent nuclear fuel summarised by Vieno *et al.* (Vieno, 1992), the recommended K_d-value for technetium in non-saline and under reducing conditions is 0.05 m^3/kg.

Table A-6 gives the selected realistic K_d-values for technetium for different organisations according to McKinley *et al.* (McKinley, 1992).

Table A-6. Realistic K_d-values (given as m^3/kg) summarised by McKinley *et al.* (McKinley, 1992).

Element	NRC realistic	NAGRA realistic	PAGIS	SKI reducing best estimate	AECL	TVO reducing conditions
Tc	0.0004	0.25	0	0.005	0.026	0.05

In his comparison, Stenhouse *et al.* (Stenhouse, 1994) presented the realistic K_d-values for technetium on granitic rock under reducing conditions: NAGRA 0.5 m^3/kg and CNFWM 0.2 m^3/kg. The relatively low K_d-value adopted by CNFWM is dependent of less reducing conditions in Canadian bedrock.

Palladium

Sorption data for palladium on granitic rock are sparse. Albinsson (Albinsson, 1991) reports K_d-values for the sorption of palladium on granitic rock in the range of 0.01-0.05 m^3/kg. Due to the few data available, Albinsson (Albinsson, 1991) recommends a conservative K_d-value of 0.001 m^3/kg for both saline and non-saline groundwater in the pH range of 6-9.

In a review by Vieno *et al.* (Vieno, 1992), the authors fixed the K_d-value for palladium in granitic rock under reducing conditions and saline groundwater to 0.001 m^3/kg, as they expect palladium to migrate as an anion.

Stenhouse *et al.* (Stenhouse, 1994) concludes that there is a large difference between K_d-values found for Pd and that this is a consequence of the scarcity of the experimental sorption data. The authors deduce that, in the NAGRA review, $Pd(OH)_2$ is considered to be the dominant aqueous species of this element. The sorption of this species on granitic rock under reducing conditions is expected to be strong, thus giving a K_d-value of >0.5 m^3/kg. Nevertheless, the authors conclude that the final NAGRA K_d-values selected for Pd were based on analogy to Ni. The sorption of Ni increases significantly with pH in the range of 7-8.

Tin

Albinsson (Albinsson, 1991) recommends a K_d-value of 0.001 m^3/kg in saline and non-saline groundwater. Stenhouse *et al.* (Stenhouse, 1994) give the following K_d-values for Sn sorption on crystalline rock-water systems (non-saline groundwaters): NAGRA, TVO and CNFWM to be 0.5, 0.2 and 0.2, respectively. An appropriate selection of the K_d-value for this element is based on whether Sn exists as Sn(II) or Sn(IV) and whether the hydroxo complex, $Sn(OH)_3^-$ or $Sn(OH)_4$, dominates over the chloride complexes $SnCl_3^-$ and $SnCl_5^-$.

Carbon

Albinsson (Albinsson, 1991) recommended a K_d-value of 0.001 m^3/kg owing to the presence of calcite in the granite. Stenhouse *et al.* (Stenhouse, 1994) presented a comparison where NAGRA and TVO recommended a realistic K_d-value of 0.001 m^3/kg. CNFWM, on the other hand, sets a realistic K_d-value equal to 0 m^3/kg. This would indicate considering the transport of carbon as anionic carbonate (HCO_3^-) exposed to anion exclusion. It should be noted, however, that no reports are given on the incorporation of ^{14}C in organic material (such as FA, HA and low molecular organic acids) and the fate of the organic material in the deep groundwater system.

Iodine

The literature survey made by Andersson *et al.* (Andersson, 1983a) indicated that the experiments performed by different researchers give a K_d-value of iodide on granitic rock in the range of 0-0.001 m^3/kg.
McKinley *et al.* (McKinley, 1991a) summarise in their crystalline rock database the K_d-values presented by NRC, NAGRA, PAGIS (Performance Assessment of Geological Isolation Systems for radioactive waste), GOLDER (Golder Associates) and SKI. For iodide, the following realistic K_d-values were given by NRC, NAGRA, GOLDER and SKI: 0, 0.001, 0 and 0 m^3/kg, respectively.

Stenhouse *et al.* (Stenhouse, 1994) presented the choice of realistic K_d-values for iodide sorption on crystalline rock-water system made by NAGRA, TVO and CNFWM, which were 0.001, 0.0008 and 0 m^3/kg, respectively. Albinsson (Albinsson, 1991) recommends a K_d-value of 0 m^3/kg.

Chlorine

Stenhouse *et al.* (Stenhouse, 1994) presented a realistic K_d-value of 0 m^3/kg, proposed by NAGRA, and 0.0001 m^3/kg, proposed by TVO.

Selenium

Albinsson (Albinsson, 1991) suggested a K_d-value of 0.001 m^3/kg for Se sorption on granite.

McKinley *et al.* (McKinley, 1991a) summarised in an review of crystalline databases (KBS-3, NRC, NAGRA, AECL and SKI) an average K_d-value for Se sorption on granite to be 0.005 m^3/kg.

The Finnish safety analysis summarised by Vieno *et al.* (Vieno, 1992) is based on the lowest K_d-value recommended for Se sorption on rock. The K_d-value was set to 0.0005 m^3/kg. A comparison of the sorption databases used in recent performance assessments (for example the Swiss radionuclide database summarised by McKinley *et al.* (McKinley, 1991a) involving crystalline host rock was made by Stenhouse *et al.* (Stenhouse, 1994). The realistic K_d-values given for NAGRA and CNFWM are 0.01 and 0.04 m^3/kg, respectively.