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**Calculated distribution of radionuclides
in soils and sediments**

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ABSTRACT

The description of the accumulation of radionuclides in some biospheric compartments is in general based on a sorption distribution coefficient K_d . This value is very decisive for the concentration of long-lived radionuclides in reservoirs that are important from the dose point of view.

Sorption is due to several processes such as ion-exchange and a variety of physical and chemical interactions which are difficult to interpret with the current K_d -methodology. In addition, many of the K_d values are obtained from laboratory or geospheric conditions not comparable to conditions prevailing in the biosphere. The main objective with this work is to deepen the knowledge about the theoretical background of K_d -values. To achieve this purpose, available theoretical models for ion-exchange and surface-complexation have been adapted for simulation under biospheric conditions. The elements treated are cesium, radium, neptunium, uranium and plutonium. The results show that a triple layer surface complexation model may be used in estimating K_d -values for actinides as a function of important chemical parameters such as pH and E_H .

It is concluded that by estimating some equilibrium constants and making some careful approximations, surface complexation models can be used for performance assessment of radioactive waste repositories.

SAMMANFATTNING

Beskrivning av radionuklidens ackumulering i några biosfärskompartments är i allmänhet beroende av en sorptionfördelningskonstant, K_d . Värdet av denna är bestämmande för koncentrationen av långlivade radionuklider i reservoarer som är betydelsefulla ur dossynpunkt.

Sorption beror på ett flertal processer såsom jonutbyte och ett stort urval av kemiska och fysikaliska interaktioner vilka är svåra att översätta med den nuvarande K_d -metodik. Dessutom har många K_d -värden erhållits från laboriemiljöer eller från förhållanden i geosfären vilka ej är jämförbara med de som råder i biosfären. Målsättningen med detta arbete är att fördjupa kunskapen om den teoretiska bakgrunden till K_d -värden. För att uppnå detta syfte har tillgängliga teoretiska modeller för jonutbyte och ytkomplexering anpassats för att simulera under biosfärförhållanden. Ämnena cesium, radium, neptunium, uran och plutonium har behandlats. Resultaten visar att en tre lagers ytkomplexeringsmodell kan användas för att uppskatta K_d -värden för aktinider som en funktion av viktiga kemiska parametrar såsom pH och E_H .

En slutsats är att ytkomplexeringsmodellen kan användas för säkerhetsanalyser av deponier för radioaktivt avfall under förutsättning att några jämviktskonstanter noggrant uppskattas och nödvändiga approximationer görs mycket omsorgsfullt.

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SUMMARY AND CONCLUSIONS

This work is aimed to determine whether surface complexation models for sorption are applicable in performance assessment studies of radioactive waste repositories. A large part of the surface complexation equilibrium constants had to be estimated in order to perform the calculations. Nevertheless, the results show that the triple layer surface complexation model is suitable to estimate the dependence of K_d as a function of important chemical parameters. For all actinides studied, a combination of experimental and estimated surface complexations constants have been used. This method appears to give a correct variation of calculated K_d -values. Nevertheless, this should not be interpreted as to indicate that experimental values are unnecessary, but instead we believe that this work might contribute to increase the usefulness of surface complexation models to understand both natural systems and laboratory measurements. Results from ongoing experimental efforts (some of them in Sweden) will in the future be added to the model presented here to allow more accurate K_d -predictions.

Reasonable parameter values were used for the properties of sorbing the phase. The calculated K_d -values will however depend on, for example, the concentration of sorption sites per liter of aqueous solution, or the total cation-exchange capacity per liter. This will in turn be affected by several parameters like the specific cation-exchange capacity of the clays, or the iron oxyhydroxide percentage of the soil or sediment, or the assumed specific surface area, etc. In other words, the system modelled is over defined: equation (14) shows the interdependence of some of the parameters to consider. If some of them are quantified by, for example, chemical analysis of a given soil, the specific surface area might still be an unknown parameter which can be adjusted to fit some "in-situ" migration experiments. Our calculations show however, that refitting surface complexation equilibrium constants to specific sorption data on soil or sediment samples, will in general, create a set of surface complexation reactions that do not represent well sorption under different experimental conditions, and thus, no advantage would be gained over the K_d concept. The power of the surface complexation model is instead, that equilibrium constants obtained under well controlled laboratory conditions on well determined minerals, can easily be used to estimate sorption under a much wider variety of field conditions. When equilibrium constants are not available for the surface complexation of a given metal ion, then a chemical analogue may be used to obtain plausible K_D values that reflect the correct dependence on chemical parameters like pH, etc.

Care must be taken when surface complexation equilibrium constants are extracted from some experimental study. It has been found during this work that it is necessary to check, with some preliminary calculations, that it is possible to reproduce both the experimental fractions of metal sorbed, and the measured dissolved metal concentrations reported in the literature.

Differences in the aqueous data base, and in the properties of the solid phase might require a readjustment of the $\log_{10}K^{\text{int}}$ values in order to reproduce the experiments reported in the literature. Furthermore, these preliminary calculations indicate whether the reported sorption reactions refer to inner- and outer-sphere complexes.

If some environmental conditions are known, such as the concentration of calcium, the K_d -value for radium could be estimated more precisely with the method described here. However, sorption of cesium consists of such complicated processes that further analysis needs to be done to judge the applicability of ion-exchange models for performance assessment.

One phenomenon which is not taken into account in our calculations, is the formation of solid solutions, which might be of importance, specially for the system $\text{Ra}^{2+}/\text{Ca}^{2+}/\text{CO}_3^{2-}$. Some approximate calculations may be done as proposed by Langmuir and Riese [48], if the Ra-contents of the calcium carbonate in a soil or sediment is known. However, most soils and sediments in the Swedish biosphere scenarios are very poor in carbonates, and therefore, the formation of solid solution was not included in this work.

1 BACKGROUND

The behaviour of long-lived radionuclides which may migrate from repositories of high-level radioactive waste constitutes an important aspect for the judgement of the safety aspects and the design of such facilities. There are two major aspects in the behaviour of the nuclides: their movement in the geosphere and in the biosphere respectively. In the geosphere it is important to show that the mobility of the radionuclides is so low that most of the eventually released radionuclides from the near field area will not reach the biosphere in amounts that can cause any substantial exposure to man. On the contrary, accumulation in the biosphere caused by low mobility may increase the potential exposure to man. This exposure may be through inhalation caused by dust resuspension, or simply by consumption of soil, specially for children. However, a high accumulation would also cause low bioavailability of the nuclides decreasing their importance in the exposure pathways of the food-chain.

This accumulation in certain reservoirs of the biosphere, is in general described with a distribution coefficient, K_d , which is a measure of the sorption of an element under given assumptions. However this sorption may be due to several processes, like ion-exchange, and diverse physical and chemical interactions which are impossible to consider explicitly with the current K_D methodology. Another disadvantage is that many K_d -values used in biosphere models are obtained from the geosphere. Usually the conditions in the geosphere are not comparable with those prevailing in the biosphere. Other disadvantages with the distribution factors are:

- lack of theoretical background
- K_D -values relevant to a specific problem are often missing. Therefore, extrapolated values must be used, which present some difficulties due to the lack of theory
- there is no quantitative relation between species in solution and K_d -values
- it is difficult to separate between precipitation and adsorption processes

It has also been shown in many assessments studies for repositories of long-lived radioactive nuclides that most of the uncertainty related to the calculations are due to the transport parameters [1, 2]. These transport parameters are in general based upon the use of K_d factors when describing the accumulation of the nuclides in soil and sediments. In addition, the accumulation process (i.e., the K_d parameter) has been identified as a dominating contributor to the uncertainty in calculated results for several scenarios handled within the international BIOMOVs study [3,4]. One

reason for this, is the large uncertainties used for the K_d -values, which are due to the lack of theoretical knowledge needed to select more realistic K_d -ranges for specific conditions.

The overall purpose with this work is to deepen the knowledge on factors influencing the accumulation of long-lived radionuclides in soils and sediments. This will lead to increased accuracy and lower uncertainty in the choice of K_d -values, which are used to represent different conditions in the biosphere. This is particularly necessary in the uncertainty analyses of radiological safety studies. However, the results will also be applicable when modelling the transport of radionuclides in the geosphere. To achieve this purpose, available theoretical surfacecomplexation models were used to simulate the conditions in the biosphere. In addition the project aims at identifying the process giving the largest contribution to the uncertainty in the sorption model.

The work in this report addresses these problems with the overall purpose to obtain manageable theoretical relations, which either can be used instead of, or as help for the selection of appropriate K_d -values.

2 NUCLIDES

The following radionuclides were selected to be studied within this work: Cs-135, Ra-226, U-234, Np-237 and Pu-239. They were chosen because they have been found to be of radiological importance in previous safety analyses for spent fuel [5]. This is valid especially for Ra-226 and Np-237. Pu-239 is included because of its potential hazard. In addition the choice of nuclides is based upon the available information about their chemical behaviour.

For comparison and evaluation, the K_d -values previously used in an assessment [6] of conversion factors between unit releases of radionuclides to the biosphere and resulting doses to man, are shown in Tables 1 for soil. The ranges were obtained from estimations of the varying literature values.

Table 1. Distribution coefficients (K_d , m³/kg) for soil/water, from Bergström and Nordlinder [6].

Element	Best estimate	Range
Cs	1.0	0.1 - 10
Ra	0.5	0.05 - 5
U	0.1	0.01 - 1
Np	0.1	0.01 - 1
Pu	50.0	1 - 100

Comments to the values in Table 1:

Cs Best estimate taken from Coughtrey et al, 1985 [7]. In this reference, even a lower minimum value than that listed in Table 1 is given. The best value we have used is a factor of ten higher than what it is recommended for the base case in the Swiss safety assessments for a HLW repository scenario [8]. However the conservative value they used was twice our best estimate value. In a specific study concerning the variability of doses from Cs-137 and Ra-226 released to a lake ecosystem, a best estimate of 0.5 was used with ranges from 0.02 to 30 [9]. However, many studies have pointed out that the fish pathway is mostly dominant for Cs-nuclides due to the high uptake of Cs into fish-flesh. Because of that, decreasing the ranges for accumulation into the soil, would not affect the doses obtained from releases of cesium into lake ecosystems.

Bergström et al [10] and Andersson et al [11], concluded that most sorption occurs by ion-exchange and the presence of cations decreases the sorption.

- In a Cs-sorption study on a well defined illite, a K_d higher than $5 \text{ m}^3/\text{kg}$ was found at $\text{pH}=7$ [12].
- For Cs-sorption on illite, an irreversible fixation of a large part of the Cs occurs. Similar effects are observed for K^+ , Rb^+ and NH_4^+ . If large quantities of these ions are present, they would inhibit the sorption of cesium [10].

Investigations in Finland on K_d -values for some nordic clays showed low values for sandy clay ($0.006 \text{ m}^3/\text{kg}$), but for muddy and heavy clay, the values were much higher, 0.2 and $0.7 \text{ m}^3/\text{kg}$, respectively [13].

Ra The values in Table 1 are taken from Bergström et al [10]. Actual measurements of distribution coefficients are very rare. Sheppard [14] gives in a literature survey, values in the range 0.1 to $0.5 \text{ m}^3/\text{kg}$. As radium is chemically similar to strontium, data for strontium may be used to increase the base of knowledge for radium. Sorption studies of Sr-90 on illite gave distribution coefficients in the range $0.004\text{-}1.0 \text{ m}^3/\text{kg}$ [12].

The following summary concerning the migration of Ra in soil is taken from the conclusions in Evans and Eriksson [15]:

Most of the Ra is strongly sorbed in soil. High Ca^{2+} concentrations causes Ra to be more permanently fixed to the soil, thus reducing the amount of exchangeable Ra and decreasing the amount available for plant uptake. Rusanova, 1962 indicated that the most rapid desorption of Ra took place at $\text{pH}=3$ and that as the pH increased, desorption decreased. The migration of Ra in soils appears to depend on the Ca^{2+} concentrations only in an indirect manner.

The same study [15] reported values for "concentration factors" from 25 samples. The geometric mean was $0.68 \text{ (m}^3/\text{kg)}$, with a 95 % confidence interval of $0.29\text{-}1.61$.

U Values taken from Grogan [8]. Evans and Eriksson [15] report "concentration factors" water/soil from 25 samples to a geometric mean of 0.39 and 0.47 for U-234 and U-238, respectively.

Np The distribution factor for the pentavalent ion of Np-237 has shown to be a factor of ten lower than the corresponding value for uranium [16]. Compared to other actinides, neptunium has been found to be relatively mobile in soil, as well as bioavailable. However, under reducing conditions, a K_d - value of $5 \text{ m}^3/\text{kg}$ is recommended, while under oxidizing conditions, values usually fall in the range

0.001-0.1 m³/kg [12]. It has also been shown that sorption on goethite is very significant, even under oxidizing conditions [17]. The best estimate given in Table 1 is extracted from this information, and it should be noted that the range used covers the values used in the Swiss safety assessments [8].

Pu Several reviewers [18] have obtained K_D -values in the range of 0.3 to 5 m³/kg. For granite rocks, K_d -values are always above 1 m³/kg. Billon [19] presents K_d -values for clay/water in the range of 10-100 m³/kg. High K_d -values in the range of 10 to 100 m³/kg were also used when modelling the transport of Pu-239 through a river sediment, which was one scenario within the BIOMOVs study [20].

3 METHODOLOGY

Sorption K_d values for each radionuclide studied are obtained from chemical equilibrium calculations which give both aqueous concentrations and adsorbed quantities for a given solid/water ratio. The dissolved and adsorbed quantities are calculated with a combination of chemical equilibrium models: complexation both within the aqueous solution and on the surface of an iron oxide, as well as equilibrium ion exchange (for Cs and Ra).

Following the work of Bond et al. [21], [22], and [23], we assume that sorption of U, Np and Pu in soils and sediments is mainly determined by their contents in iron oxyhydroxides, which in this work is assumed to be 5 % in goethite. This, in essence, agrees with other modelling work on UO_2^{2+} sorption [24] and [25], on Zn^{2+} sorption [26], on Ni^{2+} sorption [27], etc.

The average chemical composition of the water used in this modelling calculations is given in Table 2. The values correspond to average values for Swedish surface waters.

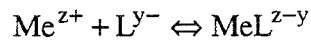
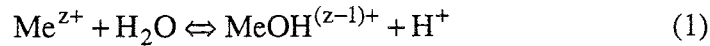
Table 2. Chemical composition of the aqueous solutions used in the numerical calculations.

Elements	Units	Average	Ranges
Na	mg/l	5	1 - 16
	mol/l	$2 \cdot 10^{-4}$	$(0.4 - 7) \cdot 10^{-4}$
K	mg/l	2	0.4 - 4.0
	mol/l	$5 \cdot 10^{-5}$	$(1 - 10) \cdot 10^{-5}$
Ca	mg/l	60	2 - 120
	mol/l	$1.5 \cdot 10^{-3}$	$(0.05 - 3) \cdot 10^{-3}$
Mg	mg/l	2.4	2 - 7
	mol/l	$1 \cdot 10^{-4}$	$(0.8 - 3) \cdot 10^{-4}$
HCO_3	mg/l	30	0 - 120
	mol/l	$5 \cdot 10^{-4}$	$(0 - 2) \cdot 10^{-3}$
pH (soil)	-		4 - 5
pH (sediment)	-		6 - 7

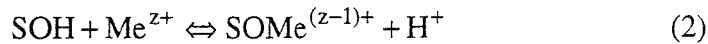
3.1 THE CHEMICAL MODEL

The chemical model is based in: a) chemical equilibrium reactions and b) mass- and charge- balance equations (for given total aqueous concentrations, and particle sorption site densities). The equations used are described in many literature studies [28-43], but will be summarised here.

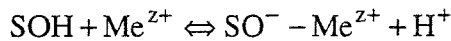
Interactions between solid particles and an aqueous solution include phenomena like sorption, precipitation and dissolution. The sorption model used here is a surface complexation model, i.e., an equilibrium model based partly on homogeneous aqueous equilibrium reactions, which using hydrolysis and complex formation (with a ligand "L") can be written as follows:



and also based on particle/solute equilibria of type:



for inner-sphere surface complexes, and



for outer-sphere surface complexes. SOH represents a particle surface site.

Particle surfaces in contact with aqueous solutions are in general electrically charged. This is due to acid-base reactions of type:



For a given aqueous system, "master" or "basis" species are selected for each chemical component (for example, Ca^{2+} for calcium, CO_3^{2-} for carbon, UO_2^{2+} for uranium, etc). For all the other species, only one equilibrium reaction is considered: that of formation from the "basis" species. All equilibrium reactions are then described by their stoichiometry and free energy change. For the formation of species "j" from all the "basis" species "k", an equilibrium reaction is written as:

$$j + \sum_{j,k} v_{j,k} k = 0$$

The stoichiometric coefficients, $v_{j,k}$, are positive on the right-hand side of the reaction, and negative on the left-hand side. In general, if all species i in a reaction are not classified into one complex and "basis" species, a reaction is written as:

$$\sum v_i i = 0$$

The standard equilibrium constant, K_r° related to the standard Gibbs free energy change:

$$\Delta G_r^\circ = -R T \ln(10) \log_{10} K_r^\circ$$

$$\log_{10} K_r^\circ = \sum v_i \log_{10} \{i\} \quad (4)$$

where R is the gas constant (8.31451 J / K mol), T the absolute temperature, and $\{i\}$ indicates the activity for species "i" (where "i" is both the complex of interest, "j", and the "basis" component species, "k"). The value of K_r° is temperature and pressure dependent. However, in this work all calculations are performed for 25°C and 1 bar (≈ 1 atm).

When the equilibrium constant is known, the activity of a complex "j" is calculated from the activities of all "basis" species k and from Eqn. (4):

$$\log_{10} \{j\} = \log_{10} K_r^\circ - \sum v_{j,k} \log_{10} \{k\} \quad (5)$$

For aqueous ions, it is not possible to assume that activities are equal to concentrations. This is mainly due to coulombic ion-ion interactions. For homogeneous aqueous reactions, the relationship between "apparent" (or concentration) equilibrium constants and standard equilibrium constants is specified by the activity coefficients, γ_i , and Eqn. (4) becomes:

$$\begin{aligned} \log_{10} K_r^\circ &= \sum \log_{10} \{i\} = \sum v_i (\log_{10} [i] + \log_{10} \gamma_i) \\ &= \log_{10} K_r^{\text{app}} + \sum v_i \log_{10} \gamma_i \end{aligned} \quad (6)$$

where $[i]$ indicates the concentration of species "i" (mol/l) and the concentration equivalent to Eqn. (5) is:

$$\log_{10} [j] = \log_{10} K_r^{\text{app}} - \sum v_{i,k} \log_{10} [k] \quad (7)$$

In this work, γ_i for aqueous ions are estimated with Davies equation (which is an extension of the Debye-Hückel limiting law):

$$\log_{10}\gamma_i = -z_i^2 A_\gamma \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \quad (8)$$

where z_i is the ionic charge, the Debye-Hückel constant A_γ has the value of 0.509 at 25°C, and I is the ionic strength (mol/l):

$$I = \frac{1}{2} \sum z_i^2 m_i \quad (9)$$

therefore, for aqueous ions:

$$\log_{10}\{i\} = \log_{10}[i] - z_i^2 A_\gamma \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \quad (10)$$

For neutral aqueous molecules, the approximation is made in this work that $\gamma_i=1$, and therefore $\{i\}=[i]$.

For each component "k" in the aqueous system of interest, the model used here also includes either the known activity of a species (for example, $\text{pH} = -\log_{10}\{\text{H}^+\}$), or a mass-balance constrain (the total concentration):

$$[k]_{\text{TOT}} = [k] + \sum v_{j,k} [j] \quad (11)$$

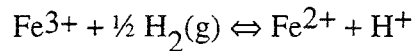
where $v_{j,k}$ is the stoichiometric coefficient for component "k" and complex "j" (in the reaction of formation of complex j from the components). For example, the mass-balance equation for uranium would be:

$$[\text{U}]_{\text{TOT}} = [\text{UO}_2^{2+}] + 2 [(\text{UO}_2)_2(\text{OH})_2^{2+}] + [\text{U}(\text{OH})_4(\text{aq})] + [\text{SO-UO}_2\text{OH}^+] \dots$$

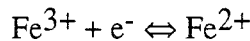
Redox reactions are treated in conjunction with the half cell defined by the standard hydrogen electrode, which has by definition a zero potential:



Due to this convention, all redox reactions are written in terms of the hypothetical species "e⁻", for example, the reduction of Fe³⁺ by hydrogen gas:



is instead written as:



The redox potential of an aqueous solution at redox equilibrium is related to the activity of the hypothetical species e^- :

$$\begin{aligned} E_H &= - (R T \ln(10) / F) \log_{10}\{e^-\} \\ &= -0.05916 \log_{10}\{e^-\} \quad (\text{at } 25^\circ\text{C}) \end{aligned}$$

where F is the constant of Faraday (96485.3 C/mol). The value of E_H can (at least in principle) be measured experimentally, or calculated from mass-balance constrains, for example, from a given partial pressure of $H_2(g)$ or $O_2(g)$, from the solubility equilibrium of some solid phase, etc.

For surface complexation reactions (i.e., reactions 2 and 3), the equilibrium constant is defined similarly to the homogeneous equivalent, c.f. Eqns. (4) & (6). However, the activity of a surface species is not related to its concentration in the same way as Eqn. (10) for aqueous ions. For surface complexation reactions, the measured "apparent" equilibrium constant, K_T^{app} , based on bulk concentrations (c.f. Eqn. 7),

$$\log_{10}K_T^{\text{app}} = \sum v_i \log_{10}[i] \quad (12)$$

is found to vary with pH, aqueous electrolyte composition, etc, indicating large variations of the activity coefficients for the adsorbed species.

As the activity coefficients for aqueous ions are related to the ion-ion interactions, the activity coefficients of surface species are largely due to the coulombic interaction between the charged surface and the electrolytic solution.

The differences between the various mathematical formulations for surface complexation reactions, depend on how the free energy of adsorption is resolved into two components: electrostatic and chemical, i.e., on how the activity coefficients for surface species are estimated.

As the acid-base reactions (3) indicate, particle surfaces in contact with aqueous solutions will in general be electrically charged, and this charge will depend on the pH value. The charge density in the solid surface, σ_s (C/m²), depends on the specific surface area, A (m²/g), the solid concentration, S (g/l), and the extend of ionisation and sorption, according to:

$$\sigma_s = \frac{F}{SA} \left([\text{SOH}_2^+] - [\text{SO}^-] + (z-1)[\text{SOMe}^{(z-1)}] + \dots \right) \quad (13)$$

where $[]$ represent the molar concentration for surface sites. The total concentration of surface sites (mol/l) for the chemical system of interest, can be calculated from the solid concentration, specific surface area, and site density:

$$[\text{SOH}]_{\text{TOT}} = S A N_s 10^{18} / N_A \quad (14)$$

where N_s is the site density (sites/nm²) and N_A is the number of Avogadro (6.02214·10²³ mol⁻¹). The mass-balance constrain for all different surface sites "I" (compare with Eqn. 11) is:

$$[\text{SOH}]_{\text{TOT}} = \Sigma [I]$$

$$[\text{SOH}]_{\text{TOT}} = [\text{SOH}] + [\text{SOH}_2^+] - [\text{SO}^-] + [\text{SOMe}^{(z-1)+}] + \dots \quad (15)$$

The electrostatic long-range coulombic interactions between the aqueous ions and the electrically charged surface account for the variation of K_r^{app} (Eqn. 12) with pH, etc. The "apparent" equilibrium constant for a surface complexation (or acid-base) reaction is separated into the chemical ("intrinsic") and coulombic component as follows:

$$\log_{10} K_r^{\text{app}} = \log_{10} K_r^{\text{int}} - \frac{\Delta z_s F \Psi}{R T \ln(10)} \quad (16)$$

where Ψ is the electric potential (V) for the "mean plane of adsorption", and $\Delta z_s = \Sigma v_i z_i$, where "I" is taken for all surface species in the reaction. For example, $\Delta z_s = (z-1)$ for reaction (2), and $\Delta z_s = 1$ for reaction (3a). Eqn. (16) is equivalent to assume the following activity coefficient for the surface species,

$$\log_{10} \gamma_i = \frac{z_i F \Psi}{R T \ln(10)} \quad (17)$$

and therefore, for all surface species, the activity is defined as

$$\log_{10} \{I\} = \log_{10} [I] + \frac{z_i F \Psi}{R T \ln(10)} \quad (18)$$

These last two Eqns. are to be compared with Eqns. (8) and (10) for aqueous ions.

The electric potential for the adsorption surface, Ψ , can be estimated with several assumptions, giving rise to different activity coefficients (Eqn. 17). These estimation methods constitute the surface complexation models: constant capacitance, two-layer (or diffuse-layer), Stern, triple-layer, four-layer, etc.

In this work, the triple-layer model is used. This model assumes that protons and strongly binding cations are placed in the particle's surface plane (the o-plane), weakly binding ions are placed in a second β -plane, and the third is the diffuse-layer d-plane.

For the o- and β -planes, there are associated capacitances C_1 and C_2 (F/m²), and the relation between charge and potential at each plane is given by:

$$\Psi_0 - \Psi_\beta = \sigma_o/C_1 \quad \text{or:} \quad \sigma_o = (\Psi_0 - \Psi_\beta) C_1 \quad (19)$$

$$\Psi_\beta - \Psi_D = (\sigma_o + \sigma_\beta)/C_2 \quad \text{or:} \quad (\sigma_o + \sigma_\beta) = (\Psi_\beta - \Psi_D) C_2 \quad (20)$$

The formula of Gouy-Chapman is used to estimate the diffuse-layer charge σ_D , from the diffuse-layer potential, Ψ_D :

$$\sigma_d = (8 \cdot 10^3 \epsilon_o \epsilon_w R T)^{1/2} \sqrt{I} \sinh\left(\frac{F\Psi_d}{2 R T}\right)$$

where ϵ_o is the permittivity of vacuum ($8.854 \cdot 10^{-12}$ C²/Jm), ϵ_w is the dielectric constant of water, and the ionic strength, I (Eqn. 9), is in units of mol/l. At 25°C $\epsilon_w = 78.3$ and therefore,

$$\sigma_d = 0.1173 \sqrt{I} \sinh(19.46 \Psi_d) \quad (21)$$

The total electrical charge of the system is of course zero, and therefore, electrical charge densities for the different planes are also constrained by the following equations:

$$\sigma_d = -(\sigma_o + \sigma_\beta) = -\sigma_s \quad (22)$$

for the surface complexes, m, in the o-plane:

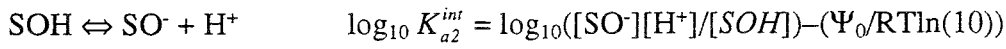
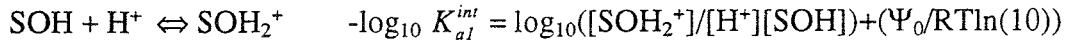
$$\sigma_o = \frac{SA}{F} \sum z_m [m] \quad (23)$$

for the surface complexes, n, in the β -plane:

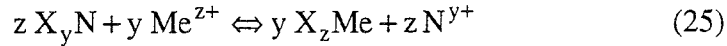
$$\sigma_\beta = \frac{SA}{F} \sum z_n [n] \quad (24)$$

The parameters needed in the model are: the values of $\log_{10}K_T^\circ$ for the formation of all aqueous species, $\log_{10}K_T^{\text{int}}$ for the formation of all surface species, the capacitances C_1 and C_2 , the site density N_s , and the specific surface area A . Furthermore, the pH, the redox potential and total concentrations are also needed.

As explained elsewhere, e.g. in [44], experimentally determined values of K_T^{int} , depend on the assumptions used for the total number of sorption sites. Important parameters in the sorption models are thus, the specific surface area, A , the site density, N_s , and the acid-base properties:



Ion-exchange reactions are described elsewhere in the literature [45]. To simulate ion-exchange between two ions "Me" and "N" (usually two metal cations), at the ion-exchanger "X" (for example a clay), the following reactions are used:



assuming that the activity for ion-exchanged species is proportional to their molar concentrations,

$$\log_{10} K_x(N / \text{Me}) = z \log_{10} \{N^{y+}\} - y \log_{10} \{\text{Me}^{z+}\} + y \log_{10} [X_z \text{Me}] - z \log_{10} [X_y N] \quad (26)$$

The activity coefficients for the ion-exchanged species are thus assumed to be constant, and included in K_x . This assumption will be appropriate if only trace amounts of "Me" are ion-exchanged. The total concentration of ion-exchanger is given as the cation exchange capacity, and it is calculated with Eqn. (14).

3.2 THE CALCULATIONS

A chemical system is defined by the total concentrations of each component, which may be obtained by several analytical methods. The goal of the chemical model is to calculate the activities of the basis species corresponding to each component. Exceptionally, the activities of some components are experimentally measured with ion-sensitive electrodes (for H^+ , Cl^- , etc), or with a redox electrode (for the redox potential E_H).

For chemical components for which the total concentration is known, mass-balance equations must be solved (Eqn. 11). The total surface site-balance equation (15) must also be solved. The concentration of each aqueous complex is calculated from Eqns. (10) and (5), while concentrations of adsorbed species are calculated from Eqns. (12) and (16). The potentials in Eqn (16) are calculated from the charge densities and Eqns. (19) to (21), while charge densities are calculated from Eqns. (22) to (24). This has been performed with the computer program HYDRAQL [46].

Once the equations for the chemical system are solved (i.e., once the activities of the basis component species are known), the concentration of each species can be calculated with Eqns (10) (or 18), (7) and (26). Once the species fractionation has been calculated, the distribution coefficient is easily found.

For a given chemical element "Me", the distribution coefficient, K_D (m^3/kg , equivalent to dm^3/g), is calculated as the quotient between the concentration in the solid (mol/g) and the soluble concentration (mol/dm^3):

$$K_D = \frac{1}{S} \frac{[\text{SOMe}^{(z-1)+}] + [\text{SO-MeOH}^{(z-2)+}] + [\text{X}_2\text{Me}] + \dots}{[\text{Me}^{z+}] + [\text{MeOH}^{(z-1)+}] + [\text{MeL}^{z-y}] + \dots} \quad (27)$$

where concentrations are in units of mol/l and S is the solid concentration in g/l . For a given component "k", forming soluble complexes "j", and solid complexes "l", the distribution coefficient is then:

$$K_D = \frac{1}{S} \frac{\sum v_{l,k}[l]}{[k] + \sum v_{j,k}[j]} = \frac{1}{S} \frac{\sum v_{l,k}[l]}{[k]_{\text{TOT}} - \sum v_{l,k}[l]} \quad (28)$$

Modeling results are strongly dependent on the values chosen for $\log_{10}K_r^0$ for aqueous species (as defined in Eqn. 4) and $\log_{10}K_r^{\text{int}}$ for adsorbed species (Eqn. 6).

For aqueous complexation, the original data base supplied with the HYDRAQL program has been modified as follows. For uranium, the original HYDRAQL-values were replaced with those selected in the OECD-NEA review [47]. The data bases of Langmuir and Riese [48] for radium, Lemire and Garisto [49] for neptunium and Puigdomènech and Bruno [50] for plutonium, were used here.

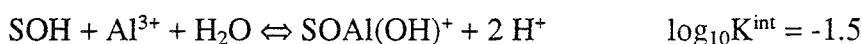
In order to simplify calculations involving actinide sorption, the ionic strength was kept constant at $0.1 \text{ mol}/\text{l}$ (NaCl electrolyte). Precipitation of solid phases was suppressed during the calculations, and equilibrium between the several redox couples was enforced by a prevailing redox potential, E_H . Due to the structure of the HYDRAQL program, the calculations had to be

repeated setting the main component equal to each of the possible redox states, for example, for plutonium, calculations had to be performed setting the main component successively to PuO_2^{2+} , PuO_2^+ , Pu^{4+} , and Pu^{3+} . The results were then collected and integrated into a single K_D -value using a spread-sheet program. The total concentration of radionuclides in the simulations were (in mol/l): 10^{-9} for Cs, 10^{-10} for Ra, 10^{-5} for U, 10^{-8} for Np and Pu.

There is a large scatter in the literature [51] about the protolysis constant of iron oxides and hydroxides.

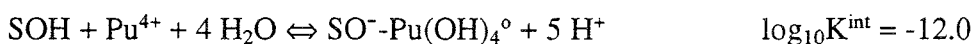
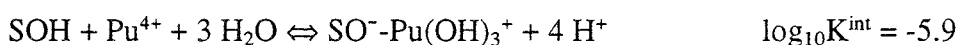
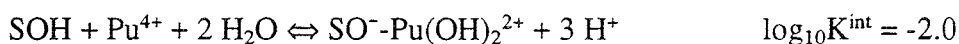
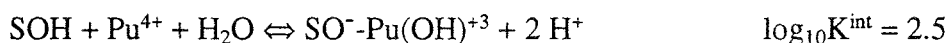
The properties of goethite selected here are those reported by [52], i.e., $A=39.9 \text{ m}^2/\text{g}$, $N_s=1.7 \text{ sites}/\text{nm}^2$, $\log_{10}K_{a1}^{int} = -7.5$, $\log_{10}K_{a2}^{int} = -9.5$, the swamping electrolyte constants reported by [44] ($\log_{10}K_{cat}^{int} = -9.3$, $\log_{10}K_{an}^{int} = 6.2$), and the TLM capacitances to $C_1=1.4 \text{ F}/\text{m}^2$ and $C_2=0.2 \text{ F}/\text{m}^2$. These values are adequate to model the general behaviour of actinide sorption in the environment.

For both Np^{3+} and Pu^{3+} , the surface complexation constants were set equal to those of the Al^{3+} -goethite system [52], i.e.,



which agree with other values obtained for Am^{3+} [53] and [54].

For U^{4+} , and Np^{4+} , the surface complexation constants were set equal to those for Pu^{4+} [55]:



Because of the uncertainty in the estimated carbonate and bicarbonate surface complexation constants, they were left out of the calculations. In order to simulate the experimental data for Pu(IV) sorption on goethite as a function of alkalinity (c.f., Fig. 5 in [55], the adsorption constant for



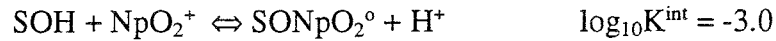
had to be adjusted to a value of $\log_{10}K^{int} = 8.0$, and this value was also used for uranium and neptunium.

Preliminary calculations showed anomalous results for uranium sorption. A comparison with plutonium calculations showed that the predicted stability of $U(OH)_4(aq)$ was unusually high. The NEA review [47] gives a large uncertainty for the formation of $U(OH)_4(aq)$. In p. 130 Grenthe et al. [47] note that the stability of $U(OH)_4(aq)$ "has been overestimated by orders of magnitude". Therefore, in our calculations the value $\log_{10}K_{eq} = -10$ was selected for



instead of the value -4.5 ± 1.4 selected by the NEA team [47]. This value is more in accordance with the equilibrium constants for Np^{4+} (-10.8), and Pu^{4+} (-9.2), and in better agreement with other reviews on uranium hydrolysis.

For PO_2^+ , surface complexation was modelled with the same constants as those for NpO_2^+ , i.e.,

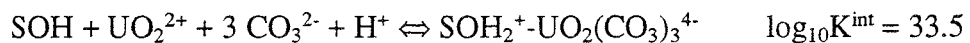
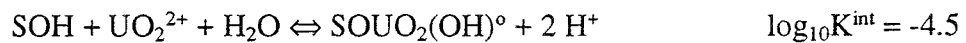


which is equivalent to the following reaction



as reported in [56] and [57]. The equilibrium constants was adjusted from the value reported in [56] ($\log_{10}K^{int} = -3.5$) and [57] ($\log_{10}K^{int} = 3.2$) in order to fit the curves in Fig. 5-2 of [56] and Fig. 2 of [57] with our data base of equilibrium constants for complexation in the aqueous phase.

When the U(VI) sorption data of Hsi and Lanmuir [58] were simulated with the sorption equilibrium constants reported by them, a clear disagreement was obtained. The reasons were both the use of a different data base for the aqueous complexation, and our different parameter values for goethite. Therefore, a slightly different model for UO_2^{2+} sorption was used, namely



This model approximates the effect of carbonate on both the percentage of adsorbed U(VI) (Fig. 8 in [58]) as well as on the total dissolved uranium (Fig. 4 in [58]). The same surface complexation equilibrium constants were used to simulate the sorption of NpO_2^{2+} and PuO_2^{2+} .

For Cs^+ , ion-exchange in competition with Na^+ , K^+ , Ca^{2+} and Mg^{2+} was modelled. The amount of clay was set to 1 g/l, and cation-exchange capacity was assumed to be 0.2 meq/g. The equilibrium constants for reaction of type

(25) are $\log_{10}K_X(\text{Na/K})=0.5$ and $\log_{10}K_X(\text{Na/Cs})=1.4$, as given in the Tables of Ref. [59]. For interchange between Na^+ and either Ca^{2+} or Mg^{2+} , the K_N values tabulated in [59] ($K_N \approx 4$ for Na/Ca and Na/Mg exchange) refer to ionic equivalent fractions in the ion-exchanger. If K_N is constant, then the value of K_X (as defined in Eqn. (26)) depends on the total cation exchange capacity of the system (*CEC*, in equivalents per litre of solution). Thus for



These selected constants for ion-exchange are similar to those reported in [60].

For Ra^{2+} , a combination of ion-exchange and surface complexation has been used. Ion-exchange competition with Na^+ , K^+ and Ca^{2+} was modelled, as described above for Cs^+ . Precipitation of calcite and aragonite was suppressed in the calculations. The sorbent was assumed to be 1 g/l of clay and 0.05 g/l of goethite, the later having the properties indicated earlier for the sorption of U, Np and Pu. Surface complexation constant for Ra^{2+} was assumed to be equal to those of Ca^{2+} , i.e.,



as reported in [61] and [44].

4 RESULTS

The calculations carried out have presented K_d -values as a function of environmental conditions such as pH, E_{HH} , alkalinity, concentrations of cations etc. The results are presented graphically in three dimensional plots against the major parameter influencing the K_d -values for the respective element handled. It could be worthwhile to point out that values of these parameters may be wider than the ranges normally occurring in the environment. Normal background values for soil porewaters are given in Table 2. Major changes for the sediment properties compared to soil is that reducing conditions may occur and the pH-values may be higher than in the soil, presumably about 7. The redox potential is positive in surface soil and upper sediment while reducing conditions occur in deeper situated sediment.

4.1 CESIUM

For cesium, ion-exchange is the main process for retaining this element on solid materials. The calculations show also this with decreasing K_d -values when the concentrations of cations increase, see Fig 1. However all values obtained seem to be lower than those obtained from experimental studies. This may be due to the fact that many measurements include the total irreversible bound Cs-pool and also to the experimental design. These two pools of bounded Cs^+ in soil are described in the literature [62] and [63].

4.2 RADIUM

Also for radium, ion-exchange is the main sorption process. The calculations show that the calcium concentration is the main parameter influencing the K_d -values, see Fig 2 and Fig 3 where the K_d -values are plotted against calcium concentration and the concentration of the alkali metals Na and K or pH, respectively. The influence of alkali metals is due to the competing properties of these elements because of their chemical similarity.

4.3 Uranium

The calculations show that pH, inorganic carbon and E_H are the major parameters influencing the K_d -values. The K_d -values against E_H and pH with a constant carbonate concentration of 1 mM are plotted in Fig 4. K_d -values, when keeping the redox-potential constant (0.6 V) but varying widely the content of inorganic carbon and pH are presented in Fig 5. As can be seen from Fig 4 reducing conditions give the highest K_d -values. The effect of pH increases considerably under oxidising conditions. Under such conditions in combination with pH-values above 6 the K_d -values obtained are about 0.1 m³/kg. At high concentrations of inorganic carbon and pH-values higher

than 6 the K_d -values decrease considerably. However, when looking at normal values for soil and sediments concerning the alkalinity and pH respectively, K_d -values for use should be about $0.1 \text{ m}^3/\text{kg}$. These values are in agreement with these earlier used in dose assessments as discussed in the "Nuclides" section and elsewhere [6].

4.4 NEPTUNIUM

The K_d -values are high under reducing conditions, see Fig 6. This is in agreement both with the few investigations made under reducing conditions [64] and [65] as well as the low solubility of the tetravalent Np, which is the dominating state under reducing conditions [66]. The pH dependence of K_d shown in Figure 6 is in agreement with experimental studies of the adsorption behaviour of Np in soil [67], [68], [69], [70] and [71].

4.5 PLUTONIUM

In contrast to neptunium the K_d -values obtained are not so sensitive to E_H at neutral and acid conditions, see Fig 7 where the K_d -values are plotted against pH and E_H for a constant total inorganic carbon content of 61 mg/l. However, the dependence on pH is clearly seen in Fig 7. Experimental studies of pH adsorption have also shown this, however not so fully pronounced as our calculations show [17] and [55]. The very extreme values are due to extreme combinations of chemical conditions not occurring naturally. There is a large scatter of values in the literature concerning K_d -values for Pu, see for example [72] and the recent compilation by Albinson [17].

5 ACKNOWLEDGEMENT

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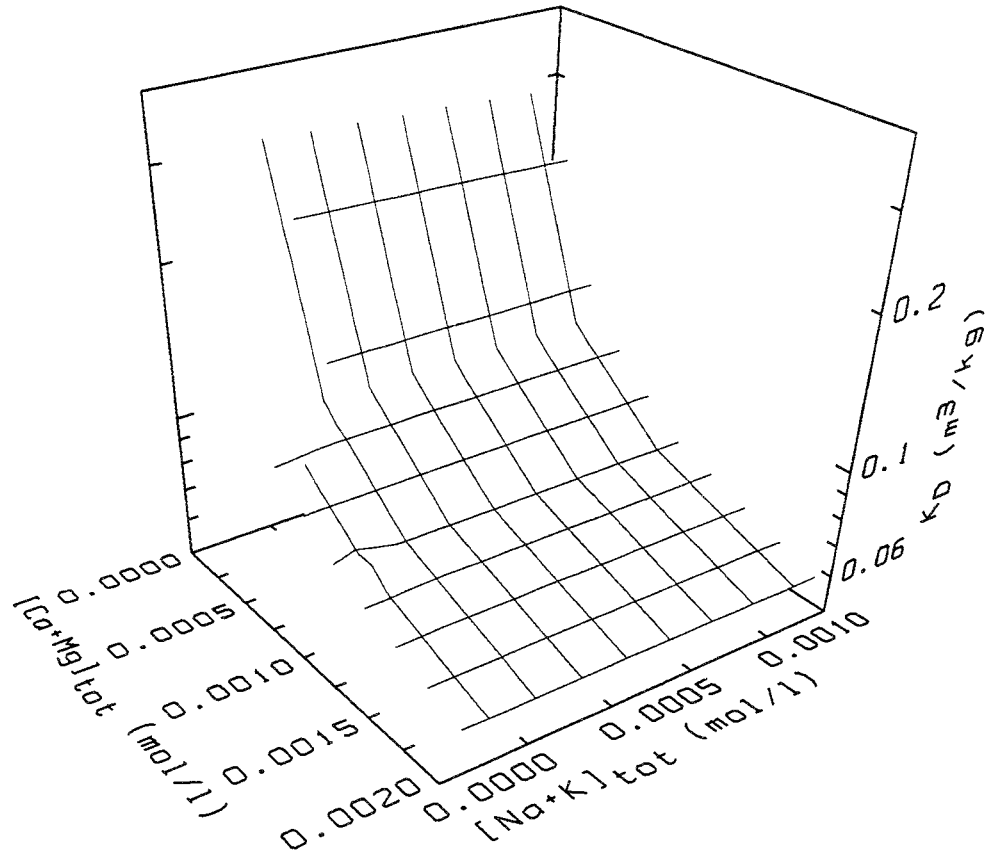


Figure 1. The relationship between calculated K_d -values for Cs by ion-exchange versus the concentrations of the alkali metals Na and K and the concentrations of Ca+Mg.

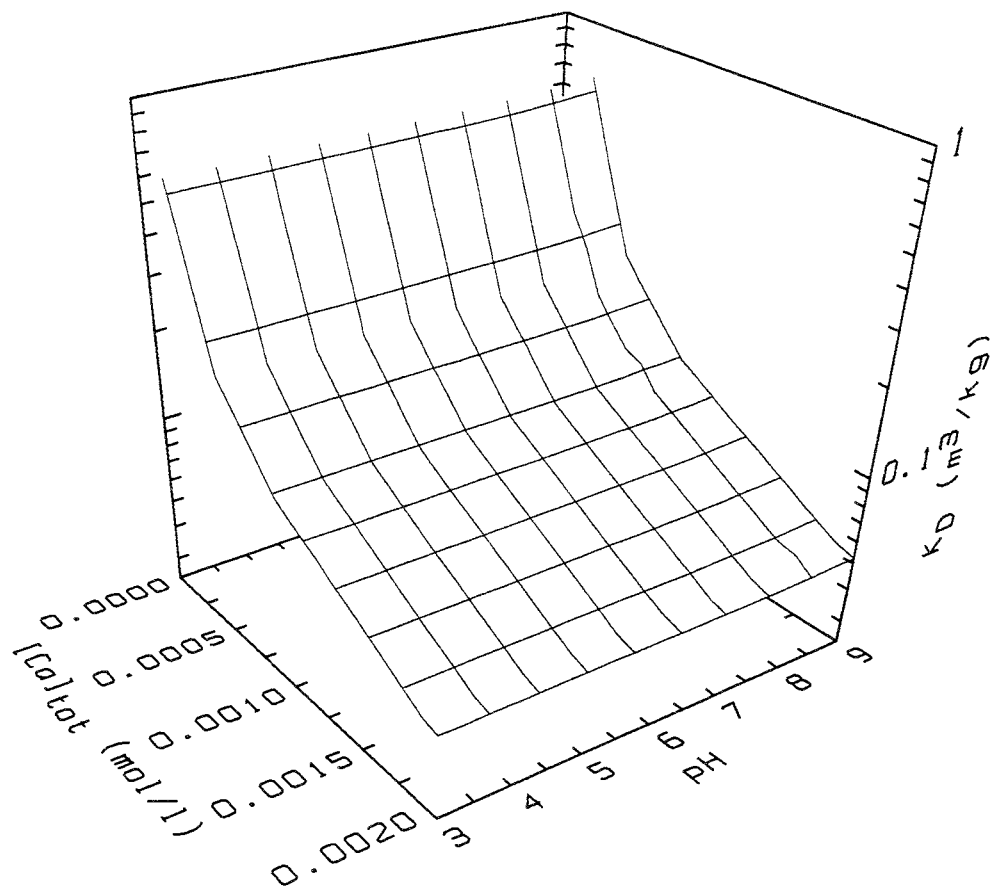


Figure 2. The relationship between calculated K_d -values for Ra by ion-exchange and surface complexation models versus pH and the concentration of Ca^{2+} for $[\text{Na}^+]_{\text{TOT}} + [\text{K}^+]_{\text{TOT}} = 0.00025 \text{ mol/l}$.

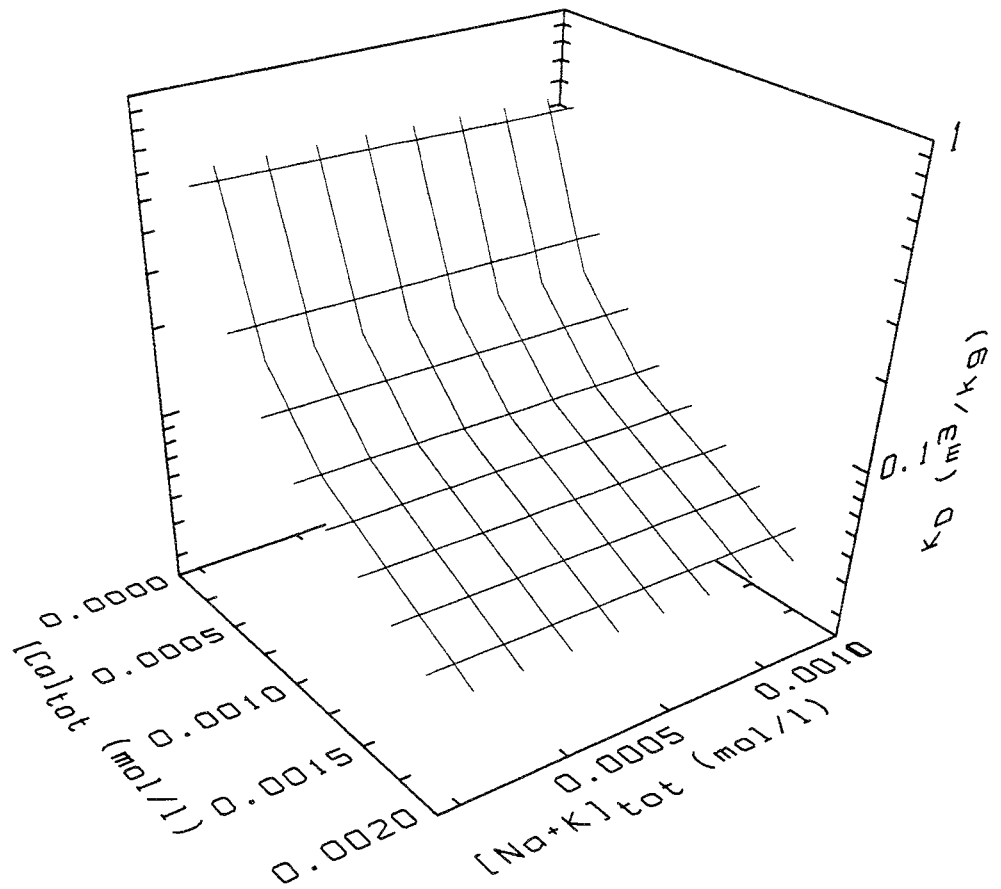


Figure 3. The relationship between calculated K_d -values for Ra both by ion-exchange and surface complexation models versus the calcium-concentrations and the alkali metals concentrations for $pH = 5$.

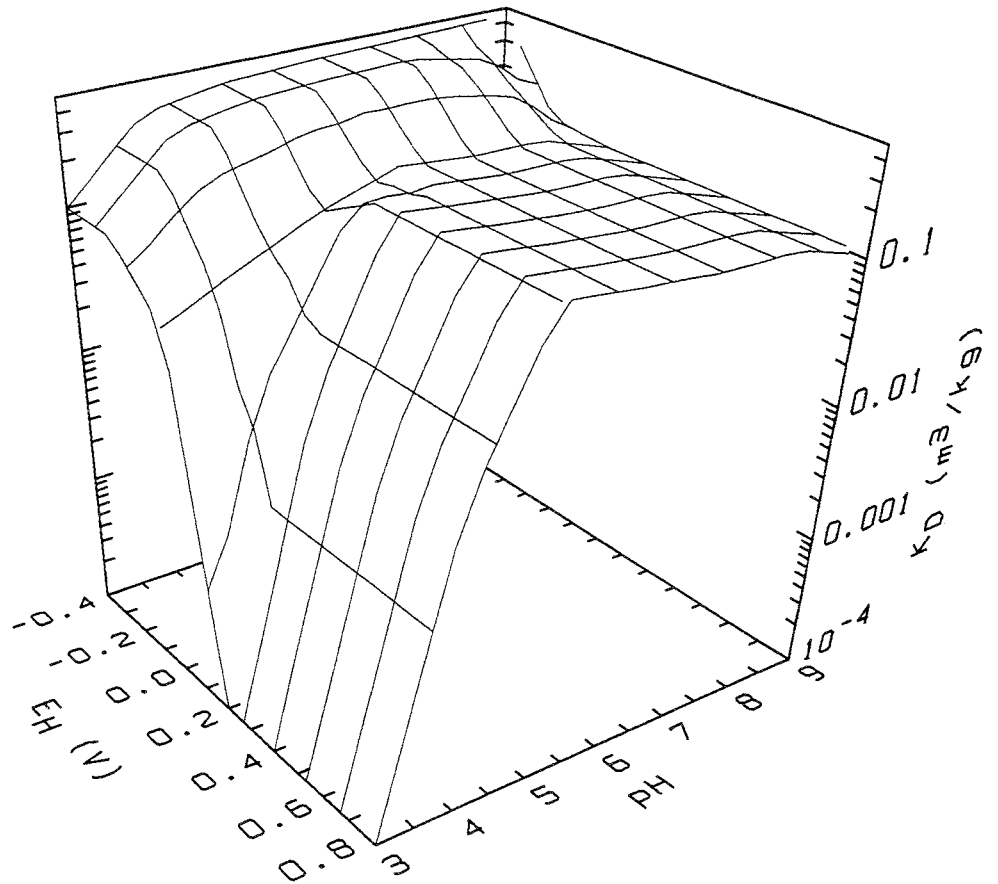


Figure 4. The relationship between calculated K_d -values by a surface complexation model versus pH and redox potential or $[\text{CO}_3^{2-}]_{\text{TOT}} = 0.001 \text{ mol/l}$.

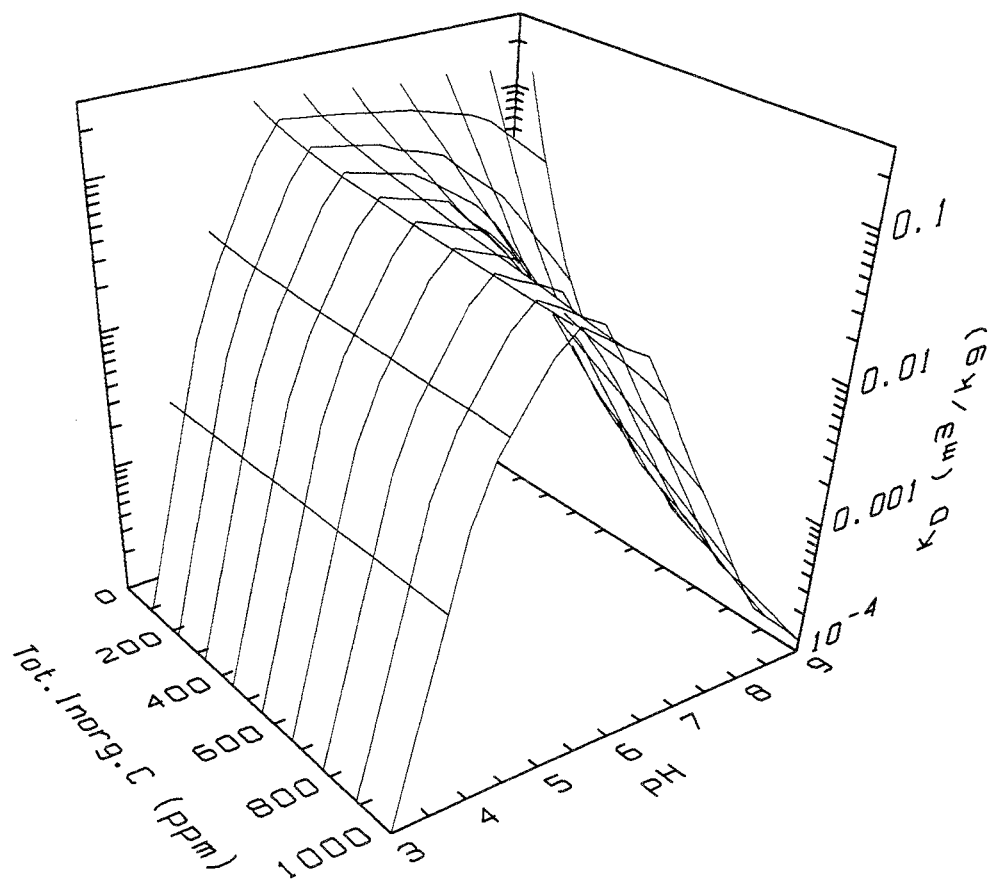


Figure 5. The relationship between calculated K_a -values for U by a surface complexation model versus pH and inorganic carbon concentrations for $E_H = 0.6$ V.

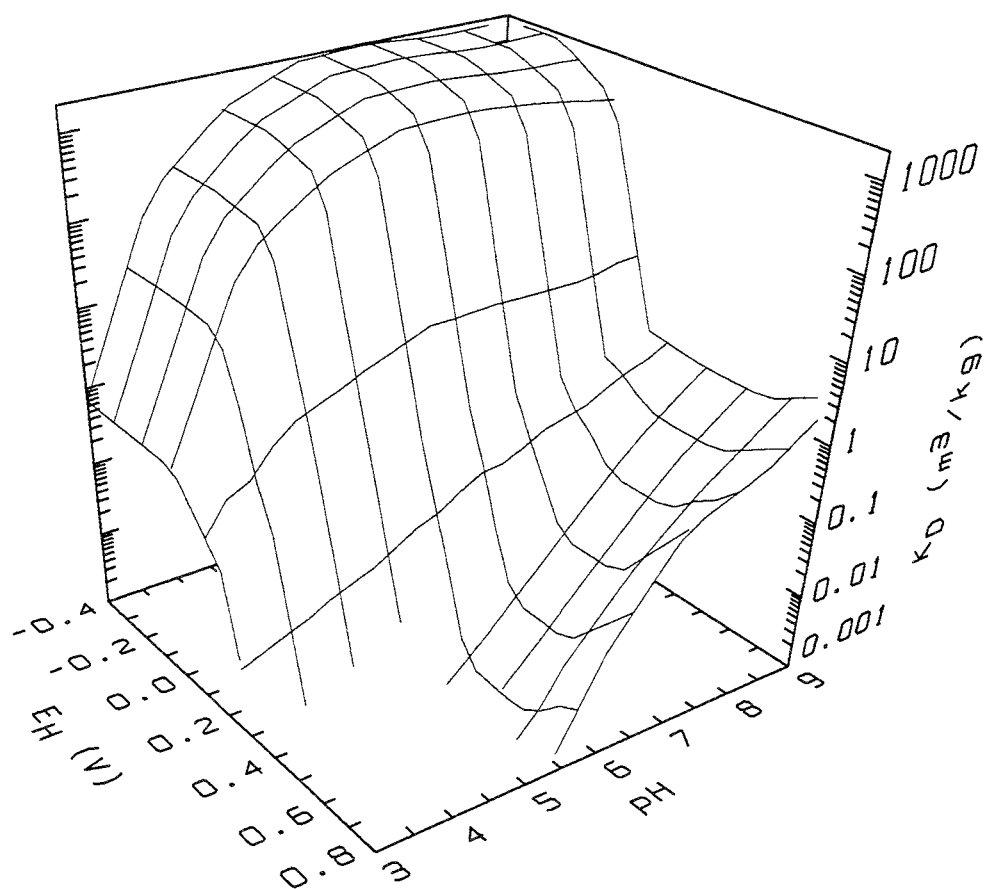


Figure 6. The relationship between calculated K_d -values for Np by a surface complexation model versus pH and redox potential for $[\text{CO}_3^{2-}]_{\text{TOT}} = 0.001 \text{ mol/l}$.

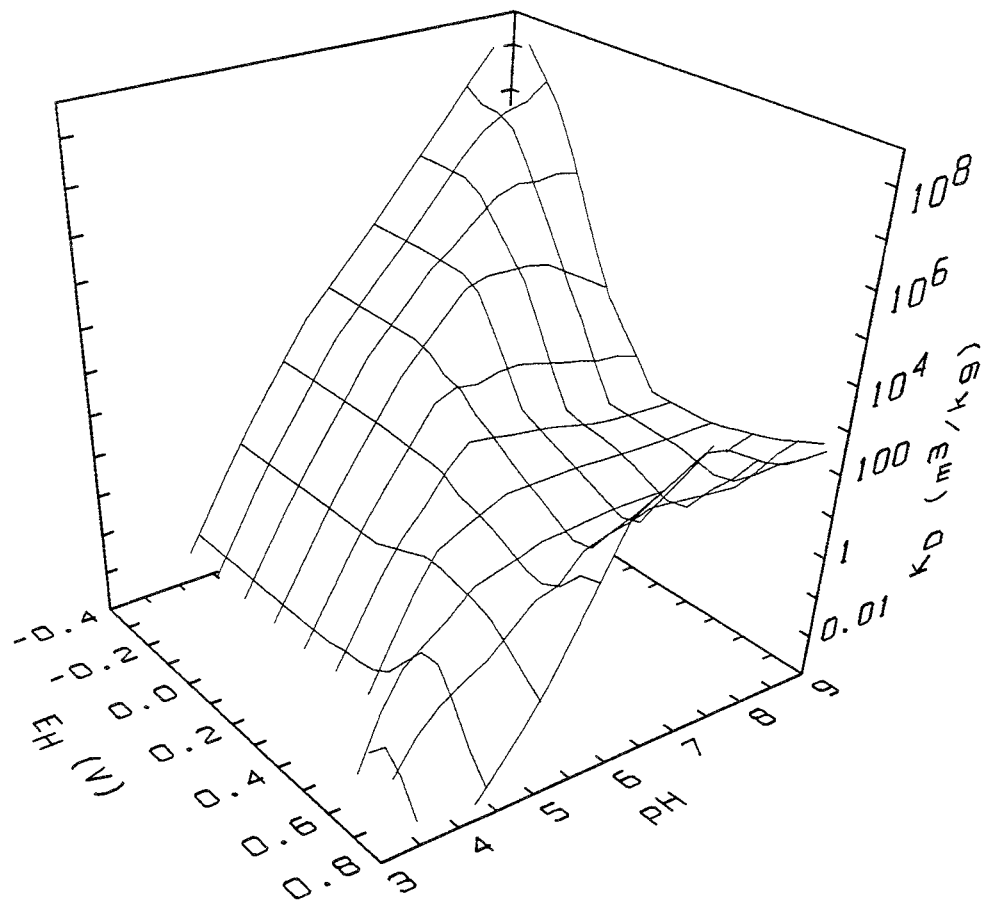


Figure 7. The relationship between calculated K_d -values for Pu by a surface complexation model versus Eh and pH for $[\text{CO}_3^{2-}]_{\text{TOT}} = 0.001 \text{ mol/l}$

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² Section for Solid Earth Physics, Department of Geophysics, Uppsala University, Sweden
³ Conterra AB, Uppsala, Sweden
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Jan Cramer (ed.)¹, John Smellie (ed.)²
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² Terralogica AB
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Swedish Nuclear Fuel & Waste Management Co, SKB
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Peter Andersson (ed.)¹, Anders Winberg (ed.)²
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² Conterra, Göteborg, Sweden
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Kjell O Wannäs, Tom Flodén
Institutionen för geologi och geokemi, Stockholms universitet
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Hans Wanner¹, Yngve Albinsson², Erich Wieland¹
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A R Hoch, S M Sharland
Chemical Studies Department, Radwaste Disposal
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² Svensk Kärnbränslehantering AB,
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Ignasi Casas¹, Jordi Bruno¹, Esther Cera¹,
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³ Imatran Voima Oy, Helsinki, Finland
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Karl-Erik Almén (ed.)¹, Pär Olsson², Ingvar Rhén³,
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¹ KEA GEO-Konsult
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³ VBB/VIAK
⁴ RS Consulting
⁵ SKB
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