



TECHNICAL REPORT 02-17

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Coefficients Measured in Compacted
Kunigel V1 Bentonite with those
Calculated from Batch Sorption
Measurements and D_e (HTO) Data:**

**A Case Study for Cs(I), Ni(II),
Sm(III), Am(III), Zr(IV) and Np(V)**

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

PREFACE

The Laboratory for Waste Management of the Nuclear Energy and Safety Research Department at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Cooperative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

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ABSTRACT

Recently, a bentonite sorption data base, comprising values taken from batch sorption data, was developed for a performance assessment study for high-level waste and spent fuel (Entsorgungsnachweis). Thus distribution coefficients (K_d) determined on dispersed systems were used to calculate apparent diffusion coefficients (D_a) subsequently applied in diffusive transport calculations for the highly compacted system. Whenever such a procedure is adopted, questions invariably arise as to whether this is conservative or not.

On the occasions when K_d values have been extracted from (mainly) in-diffusion experiments and compared with those obtained from batch tests, apparent discrepancies have been found. In the majority of cases the batch values are larger, sometimes significantly. Hypotheses from "surface diffusion" to "double layer pore constrictivity effects" have been proposed to explain the inconsistencies. However, although such discrepancies have been reported periodically over the past twenty years or so, and have become generally accepted facts of life, there are surprisingly few quantitative studies directly dealing with this issue. Further, two other points are worthy of mention. The first is that a diffusion model (including the associated assumptions) is needed in order to deduce K_d values from diffusion measurements. Thus the sorption values calculated are model dependent. The second is that too little attention has been paid to the potential effects of water chemistry, i.e. a comparison between sorption values is only valid when the water chemistry in the batch tests is the same as, or very close to, the porewater chemistry in the intact material. In practice, this condition is difficult to achieve because of the uncertainties concerning the latter.

This report describes a study in which K_d values for Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) and Np(V) were calculated from in-diffusion data published in the open literature for a Na-bentonite (Kunigel V1) at dry densities between 400 and 2000 kg m⁻³. The range of oxidation states of the elements considered provides a good representation of those expected in a radioactive waste repository.

A porewater chemistry was calculated for each dry density and used in conjunction with sorption models and/or sorption data from batch measurements to produce blind predictions for K_d values for the compacted Kunigel V1 bentonite. These K_d values combined with effective diffusion coefficients (D_e) for tritiated water (HTO) were used to calculate D_a values as a

function of dry density and compared with the corresponding D_a values from diffusion measurements.

An important motivation for this study was to see whether discrepancies did in fact exist between calculated and measured D_a values originating from batch and diffusion experiments when "state of the art" knowledge concerning sorption processes and bentonite porewater chemistry was applied to a specific system.

The preliminary conclusion drawn is that, in general, the differences between D_a values calculated from batch K_d measurements and D_e (HTO) values, and those measured in-diffusion tests are not great. However, an important consideration is the bentonite porewater chemistry.

ZUSAMMENFASSUNG

Im Rahmen der Sicherheitsanalyse "Entsorgungsnachweis" für hochradioaktive Abfälle wurde aus Batch-Sorptionsexperimenten eine Sorptionsdatenbank für Bentonit erarbeitet. Die in dispersen Systemen bestimmten Verteilungskoeffizienten (K_d) wurden vorerst in scheinbare Diffusionskoeffizienten (D_a) umgerechnet, welche anschliessend für Berechnungen des diffusiven Transports in hoch-kompaktiertem Bentonit verwendet wurden. Diese Übertragung von Zahlenwerten aus verdünnten in kompaktierte Systeme ist zwangsläufig mit der Frage nach der Konservativität des Verfahrens verknüpft.

Der Vergleich von K_d -Werten abgeleitet aus Diffusionsexperimenten mit solchen aus Batchversuchen führt zu Diskrepanzen. In den meisten Fällen sind die "Batch"-Sorptionswerte grösser, in einigen Fällen sind sie wesentlich grösser. Obwohl in den letzten zwanzig Jahren solche Diskrepanzen immer wieder festgestellt und als generelle Tatsachen anerkannt wurden, gibt es erstaunlich wenig quantitative Studien, die sich direkt mit diesem Thema befassen. Verschiedenste Hypothesen, z.B. die "Oberflächendiffusion" oder auch der „Doppelschicht-Porenverengungs-Effekt“ führten bisher nicht zu befriedigenden Erklärungen. Zur Klärung dieser Diskrepanzen muss berücksichtigt werden, dass berechnete K_d -Werte modellabhängig sind. Zu ihrer Bestimmung sind sowohl ein Diffusionsmodell als auch die zugehörigen Annahmen notwendig. Ausserdem wurde dem möglichen Einfluss der Wasserchemie bisher zu wenig Aufmerksamkeit geschenkt. K_d -Werte können nämlich nur dann miteinander verglichen werden, wenn die chemischen Bedingungen in den Batchversuchen vergleichbar, oder aber der Porenwasserchemie des intakten Probenmaterials sehr ähnlich sind.

Die vorliegende Studie beschreibt K_d -Werte von Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) und Np(V) an Na-Bentonit (Kunigel V1, mit Trockendichten zwischen 400 und 2000 kg m⁻³), berechnet aus publizierten "in-diffusion"-Daten. Für die im Endlager erwarteten Oxidationszustände der Elemente ist diese Sequenz ein repräsentatives Abbild.

Die Porenwasserchemie wurde für jede Trockendichte einzeln berechnet. Zusammen mit den Sorptionsmodellen und/oder den Sorptionsdaten aus Batchversuchen wurden damit die K_d -Werte für kompaktierten Kunigel V1 Bentonit vorausgesagt. Aus diesen K_d -Werten und aus effektiven Diffusionskoeffizienten (D_e) von tritiiertem Wasser (HTO) wurden die D_a -Werte in

Funktion der Trockendichte abgeleitet und mit entsprechenden D_a -Werten aus Diffusionsexperimenten verglichen.

Batch-Sorptions- und Diffusionsexperimente scheinen unterschiedliche D_a -Werte zu liefern. Bleiben diese Unterschiede bestehen, wenn neueste wissenschaftliche Erkenntnisse auf Sorptionsprozesse und Porenwasserchemie spezifischer Systeme angewendet werden? Dies war eine der zentralen Fragen der vorliegenden Studie.

Es wird der vorläufige Schluss gezogen, dass sich in Diffusionsexperimenten gemessene und aus Batch- K_d / D_e (HTO) abgeleitete D_a -Werte im allgemeinen nicht sehr unterscheiden. Die detaillierte Kenntnis der Porenwasserchemie ist dabei von entscheidender Bedeutung.

RÉSUMÉ

Récemment, une base de données de sorption pour la bentonite, comprenant des valeurs obtenues à partir d'études de sorption en batch, a été développée pour une étude d'évaluation des performances concernant des déchets de haute activité "Entsorgungsnachweis". Des coefficients de distribution (K_d) déterminées pour des systèmes dispersés ont été utilisés pour calculer des coefficients de diffusion apparente (D_a), et utilisés en suite dans des calculs de transport par diffusion pour les systèmes hautement compactés. Lorsqu'une telle procédure est adoptée, la question de savoir si cela est prudent ou non se pose inévitablement.

Chaque fois que des valeurs de K_d ont été extraites, principalement d'expériences de "in-diffusion" et comparées avec celles obtenues à partir de tests en batch, des différences sont apparues. Dans la majorité des cas, les valeurs de K_d de batch sont plus élevées, parfois de façon significative. Des hypothèses telles que la "diffusion de surface" ou les "effets de constrictivité des couches doubles des pores" ont été proposées pour expliquer les incohérences. Néanmoins, bien que de telles différences aient été rapportées périodiquement durant les vingt dernières années et soient aujourd'hui généralement acceptées comme des faits avérés, il y a de façon surprenante peu d'études quantitatives qui traitent directement de ce problème. De plus, deux autres points doivent être mentionnés. Le premier est qu'un modèle de diffusion (incluant les hypothèses associées) est indispensable pour déduire des valeurs de K_d des mesures de diffusion. Donc, les valeurs de K_d calculées sont dépendantes du modèle. Le deuxième point est que trop peu d'attention a été portée aux effets potentiels de la composition chimique de l'eau, c'est-à-dire qu'une comparaison entre des valeurs de K_d est seulement valide quand la composition chimique de l'eau dans les tests en batch est la même ou très proche de la composition chimique de l'eau interstitielle dans le matériau intact. En pratique, cette condition est difficile à remplir à cause d'incertitudes concernant la composition chimique de l'eau interstitielle de la bentonite.

Ce rapport décrit une étude dans laquelle les valeurs de K_d pour Cs(I), Ni(II), Sm(III), Am(III), Zr(IV), et Np(V) ont été calculées à partir de données de "in-diffusion" publiées pour une bentonite sodique (Kunigel V1) avec une densité sèche entre 400 et 2000 kg m⁻³. La gamme des degrés d'oxydation des éléments considérés est représentative de ceux escomptés dans un dépôt de déchets radioactifs.

La composition chimique de l'eau interstitielle a été calculée pour chaque densité sèche et utilisée en conjonction avec des modèles de sorption et/ou avec des données de sorption en batch pour produire des prédictions en aveugle des valeurs de K_d pour la bentonite compactée Kunigel V1. Ces valeurs de K_d ont été utilisées avec des coefficients de diffusion effective (D_e) pour de l'eau tritiée (HTO) afin de calculer des valeurs de D_a en fonction de la densité sèche. Ces D_a ont été ensuite comparés aux valeurs correspondantes déduites des données expérimentales de diffusion.

Il s'agissait en fait surtout de déterminer si des incohérences existeraient entre les valeurs de D_a provenant respectivement des batch et des données de diffusion, lorsque l'on appliquait à un système spécifique des connaissances récentes concernant les processus de sorption et la composition chimique de l'eau interstitielle de la bentonite.

La conclusion préliminaire est que, en général, les différences entre des valeurs de D_a calculés/déduits des expériences de type batch avec des valeurs D_e (HTO), et celles provenant des tests de diffusion, ne sont pas grandes. Néanmoins, une considération importante à prendre en compte est la composition chimique de l'eau interstitielle de la bentonite.

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1 INTRODUCTION

Bentonites, in one compacted form or another, are almost the universal choice of backfill material in the designs of high-level waste repositories throughout the world. Compacted bentonite is an effective physical and chemical barrier to the movement of radionuclides. The swelling properties of the material ensure efficient sealing against tunnel walls upon re-saturation. Convective water flow through the repository is prevented, allowing only diffusive transport through the backfill. The majority of radionuclides interact with the bentonite system strongly, exhibiting high sorption and hence significant retardation. However, compacted bentonite is a very complex chemical and physical system in which the processes determining the transport of dissolved species are still relatively poorly understood in detail.

The retention properties of the bentonite backfill play a very important role in the safety analyses of high-level radioactive waste repository facilities. In this respect the key parameter in the transport calculations is the apparent diffusion coefficient, D_a . Even in moderately compacted bentonite, for moderately sorbing species, diffusion rates are very low, $< 10^{-12} \text{ m}^2 \text{ s}^{-1}$. D_a values can be either directly determined from diffusion measurements, or they can be calculated from separately determined parameters, see later. According to the literature (see for example MIYAHARA et al., 1990, OSCARSON & HUME, 1994, MUURINEN & LEHIKONEN, 1995) these two approaches often result in different values: the directly measured D_a values are generally (significantly) higher than the corresponding calculated ones. This has led to the proposal that only measured D_a values should be used in performance assessment exercises because they are conservative with respect to the calculated values. The discrepancy is often qualitatively explained away by invoking additional processes e.g. surface diffusion (LEHIKONEN et al., 1996), or by arguments based on site accessibility (OSCARSON & HUME, 1994), or on the structure of water in compacted bentonite (e.g. TORIKAI et al., 1995) or by the absence of a distinct solution phase (ERIKSEN & JACOBSSON, 1984; PUSCH & HÖKMARK, 1990) or by additional constrictivity considerations in the pore structure due to double layer effects (SATO et al., 1995). However, this plethora of different explanations only serves to highlight the lack of understanding of transport processes through bentonite. Many open questions still remain and indeed both of the above approaches could be wrong. In rare cases consistency is found, as in the study by ERIKSEN & JANSSON (1996) using Sr and Cs. YU & NERETNIEKS (1997), in their review on sorption and diffusion in compacted bentonite, comment that

in many cases where differences are found this may simply be due to errors in measurement techniques!

Recently, a sorption data base (SDB) for compacted MX-80 bentonite based on batch sorption data measured "in house" and selected from the open literature was developed (BRADBURY & BAEYENS, 2003a). That is, the sorption values all came from experiments made on dispersed systems and from these, and other data, D_a values are calculated for use in performance assessment studies, (NAGRA, 2002). The discussion above is therefore very pertinent to the credibility and robustness of the sorption values selected. Important though these issues are, the purpose of this report is not to discuss the pros and contras of explanations for any (apparent) discrepancies. Rather, the idea is to assess whether such discrepancies do in fact exist, and, if so, how large they might be and what the consequences for the SDB development and performance assessment are.

2 DIFFUSION

2.1 General

In the vast majority of diffusion experiments in compacted and re-saturated bentonites and montmorillonites, the transport of radionuclides is treated as being pure Fickian diffusion into a homogeneous single porosity medium. Where radionuclide uptake onto the bentonite occurs it is assumed to be rapid, reversible and linear as a function of concentration i.e. constant sorption described by a solid/liquid distribution coefficient K_d . Diffusion measurements are often carried out at a series of dry densities. For neutral and positively charged species the whole of the porosity present in the original dry compacted material is considered to be available for diffusion whereas for anionic species the diffusion accessible porosity is less, due to anion exclusion processes. Experimental diffusion data, and radionuclide transport in performance assessment, are treated using the same simple model, NAGRA (2002). This is often quoted as a reason why directly measured D_a values are intrinsically preferred over D_a values calculated from batch sorption values.

Because most of the radionuclides of interest exhibit moderate to high sorption on montmorillonite, diffusion into compacted bentonite is very slow, as mentioned previously. This in turn implies that long experimental times are required in order for the radionuclide to diffuse distances of only a few millimetres. As a consequence, "in-diffusion" type tests predominate, and the diffusion profiles measured by sectioning techniques in the compacted solid yield apparent diffusion coefficients. (For more information on the different experimental methodologies and diffusion terminology, see for example YU & NERETNIEKS, 1997).

D_a is defined as:

$$D_a = \frac{D_e}{\varepsilon_{dry} + \rho_{dry} \cdot K_d} \quad (1)$$

where D_e = effective diffusion coefficient ($m^2 s^{-1}$)

ε_{dry} = total porosity at a compaction of ρ_{dry}

ρ_{dry} = dry compacted density ($kg m^{-3}$)

K_d = distribution coefficient ($m^3 kg^{-1}$)

$$\varepsilon_{\text{dry}} = 1 - \frac{\rho_{\text{dry}}}{\rho_{\text{s}}} \quad (2)$$

where ρ_{s} = grain density for Kunigel V1 (2700 kg m⁻³)

In the case of non-sorbing radionuclides, $K_{\text{d}} = 0$ and the apparent and pore diffusion coefficients have the same value i.e.

$$D_{\text{a}} = \frac{D_{\text{e}}}{\varepsilon_{\text{dry}}} = D_{\text{p}} \quad (3)$$

where D_{p} = pore diffusion coefficient (m² s⁻¹)

In order to calculate a distribution coefficient from Eqn. 1, values for the four parameters ε_{dry} , ρ_{dry} , D_{a} , and D_{e} are required. ρ_{dry} and ε_{dry} are known from the preparation of the diffusion sample and D_{a} is obtained from the analysis of the solid-state diffusion profile. The remaining parameter D_{e} for specific radionuclides is generally not known. A "through-diffusion" experiment (see YU & NERETNIEKS, 1997) is required to determine D_{e} and because of the impracticably long times which would be required, even for moderately sorbing species, such experiments are seldom carried out. Instead, the effective diffusion coefficient for tritiated water, HTO, is taken. In a general sense this is not unreasonable since D_{e} only depends on the pore space characteristics of the solid and the free water diffusion coefficient i.e.

$$D_{\text{e}} = D_{\text{w}} \varepsilon_{\text{dry}} \frac{\delta}{\tau^2} \quad (4)$$

where D_{w} = free water diffusion coefficient (m² s⁻¹)

δ = constrictivity

τ = tortuosity

Thus if the free water diffusion coefficients of HTO and the radionuclide in question are similar, and assuming that they both can access the same pore space, then the D_{e} values will also be similar. (Corrections for differences in D_{w} can also be made, but in most cases such changes lie within the uncertainty bands of the data.)

A few further important points need to be made.

The first is that a model for the diffusion process is used to extract a D_{a} value from the measured profile and to subsequently deduce a K_{d} value from the D_{a} value. Clearly the K_{d} value obtained in this manner is model dependent,

whereas the sorption values from batch measurements are directly measured values and model independent.

Secondly, it is known that many radionuclides exhibit non-linear sorption as a function of concentration and therefore the assumption of a constant sorption value may not always be appropriate. Such non-linearity in sorption will influence the diffusion profile and this is seldom, if ever, taken into account in the subsequent analysis. However, at low enough concentrations radionuclides do tend to exhibit linear sorption, but this is rarely utilised as an experimental design criteria.

Thirdly, nothing is known a priori about the chemical conditions under which diffusion is taking place. The diffusion experiment is a "black box" in this respect and the whole of the "chemistry" is contained in the K_d value.

Finally, and perhaps most important of all, there is the question of the compacted bentonite porewater chemistry. If directly measured K_d values¹ from batch tests are to be meaningfully compared with those deduced from diffusion experiments, then the chemistry of the porewater in the compacted bentonite needs to be defined, particularly the ionic strength, pH and Eh. Only in this way can it be ensured that the water chemistry in the batch tests is as similar as possible to the bentonite porewater. This condition for a valid comparison of K_d values is often overlooked. However, herein lies a significant uncertainty since the porewater chemistry of a compacted bentonite is not well known at all. In the case of alkali and alkali earth metals, the type of cations and their concentrations will be most important; for transition and heavy metals and lanthanides the pH; and for the actinides the pH and Eh. Thus, making a proper comparison between K_d values originating from batch and diffusion measurements is not a trivial exercise and many factors may influence the outcome.

¹ In batch tests solid/liquid distribution ratios, R_d values, are measured, since equilibrium and reversibility cannot normally be guaranteed. However, in order to avoid confusion, the same terminology as in the diffusion equations is used here also, i.e. distribution coefficient, K_d .

2.2 Diffusion data selection

In recent years the most systematic and comprehensive diffusion studies on compacted bentonites have been carried out in Japan (e.g. MIYAHARA et al., 1990; SATO et al., 1992; 1995; SATO & YUI, 1997; SATO, 1998). So, although there are diffusion data on the Swiss reference MX-80 bentonite (see the review of YU & NERETNIEKS, 1997), the Japanese investigations on Kunigel V1 bentonite are preferred and have been chosen for consideration in this study because of the breadth and completeness of the measurements. Furthermore, the mineralogies, chloride and sulphate inventories, cation loadings and cation exchange capacities for Kunigel V1 and MX-80 are rather similar, see Table 1.

In particular the diffusion data for Kunigel V1 presented in SATO & YUI (1997) and SATO (1998) will be examined in detail. Apparent diffusion coefficients for a range of radionuclides were determined as a function of the compacted dry density using the "in-diffusion" technique. The experimental data for HTO, Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) and Np(V) are given in Figure 1. (For details of the experimental procedures the reader is referred to the original publications.) The Ni diffusion data given in SATO & YUI (1997) were not considered since the tracer concentrations used in these experiments were very high (pers. comm, 1998) and instead a single point D_a (Ni) determination made at a dry density of 1800 kg m^{-3} and trace concentration is plotted. (D_a (Ni) = $1.6 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$)

A comparison of the sort envisaged between K_d values originating from batch and diffusion data can be carried out in one of two ways. Either, K_d values can be calculated from diffusion data and compared with sorption data from batch measurements, or predictions of D_a values can be made on the basis of sorption values from batch data and compared with the measured diffusion values. It was decided to do both for completeness, though the basic data used for the two comparisons are the same.

Table 1: Comparison between Kunigel V1 and MX-80 bentonites in terms of mineralogies, inventories, cation loadings and cation exchange capacities.

	¥MX-80	*Kunigel V1
Mineralogy (wt.%)		
Smectite	75	46 - 49
Calcite	0.7	2.1 - 2.6
Dolomite	-	2.0 - 3.8
Siderite	0.7	-
Quartz	15.2	29 - 38
Pyrite	0.3	0.5 - 0.7
Feldspar	5 - 8	2.7- 5.5
Zeolite	-	3.0 - 3.5
Kaolinite	<1	-
Mica	<1	-
Inventories (mmol kg⁻¹)		
Cl	#1.35	0.7
SO ₄	#23.5	28
Cation loadings (fractional occupancies)		
N _{Na}	#0.85	0.853
N _K	#0.017	0.015
N _{Mg}	#0.051	0.023
N _{Ca}	#0.084	0.109
Cation exchange capacity (meq. kg⁻¹)	#787	601

¥ Data from MÜLLER-VON MOOS & KAHR (1983)

* The data for Kunigel V1 were taken from Table 3 in OCHS et al. (1998)

Data from BRADBURY & BAEYENS (2002a)

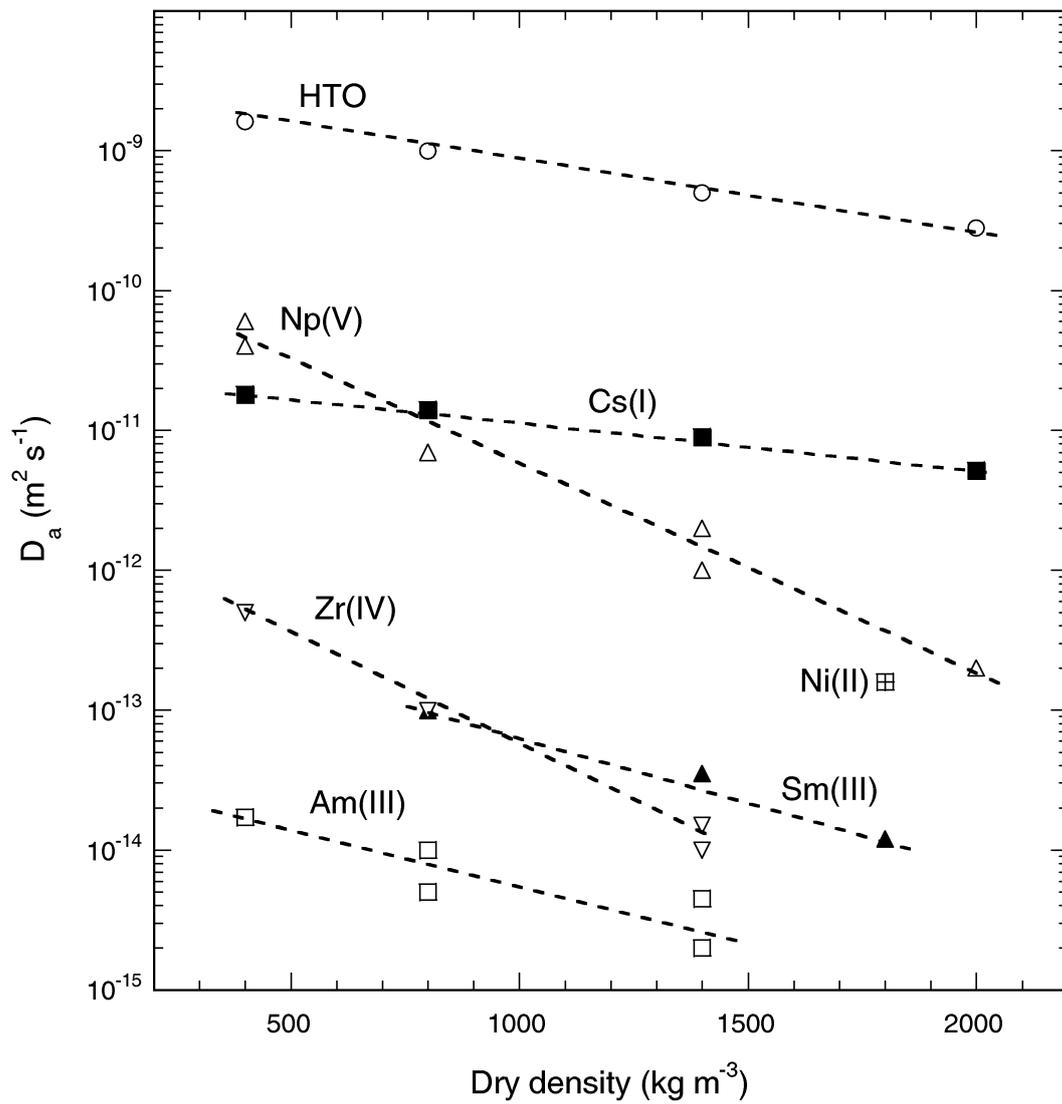


Figure 1: Diffusion data for HTO, Cs(I), Ni(II), Am(III), Zr(IV) and Np(V) (SATO & YUI, 1997) and for Sm(III) (SATO, 1998) on Kunigel V1 as function of dry densities.

3 CALCULATIONS OF DISTRIBUTION COEFFICIENTS FROM APPARENT DIFFUSION COEFFICIENTS

In order to calculate distribution coefficients from D_a values under the assumptions given earlier, an equation of the following form can be used.

$$D_a(\text{Rn}) = \frac{D_a(\text{HTO})}{1 + \frac{\rho_{\text{dry}}}{\varepsilon_{\text{dry}}} K_d(\text{Rn})} \quad (5)$$

where D_a , ρ_{dry} , ε_{dry} , and K_d have their usual meanings and
 HTO = tritiated water
 Rn = radionuclide

The parameters ρ_{dry} and ε_{dry} for Kunigel V1 as a function of dry density from 400 to 2000 kg m⁻³ are taken from OCHS et al. (1998) and are reproduced in Table 2 together with D_a (HTO) values from SATO & YUI (1997).

Table 2: Total porosity and D_a (HTO) data from SATO & YUI (1997) as function of dry density for Kunigel V1 bentonite.

Dry density, ρ_{dry} (kg m ⁻³)	Total porosity, ε_{dry}	D_a (HTO) (m ² s ⁻¹)
400	0.85	~1.6 x 10 ⁻⁹
800	0.70	~1.0 x 10 ⁻⁹
1400	0.48	~5.0 x 10 ⁻¹⁰
1800	0.34 [#]	3.4 x 10 ⁻¹⁰ [#]
2000	0.26	~2.8 x 10 ⁻¹⁰

[#]Interpolated values

D_a values read from Figure 1 are tabulated in Table 3. The K_d (Rn) values calculated using these values and the data in Table 2 in Eqn. 5 are summarised in Table 4.

For Cs the K_d values calculated from the D_a (Cs) data show a clear trend to lower values at the higher densities. (The K_d at 2000 kg m⁻³ is almost a factor of 30 lower than at 400 kg m⁻³.) This is broadly in accord with the trend which would be expected from the development of the porewater chemistry as a function of dry density and a cation exchange uptake mechanism for Cs.

The K_d values deduced from diffusion data for Sm(III), Zr(IV) and Np(V) can, to a first approximation, be considered to be constant within a factor of 2 across the whole range of dry densities (K_d (Sm) $\sim 5 \text{ m}^3 \text{ kg}^{-1}$, K_d (Zr) $\sim 17 \text{ m}^3 \text{ kg}^{-1}$, K_d (Np) $\sim 1.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$) However the extracted K_d values for Zr and Np do seem to exhibit a trend to higher values at higher dry densities.

The calculated sorption values for Am(III) are very high with a spread in values of approximately a factor of five and a trend to lower values at higher densities. Such a trend cannot be explained by changes in porewater chemistry, Table 5, and is opposite to the one exhibited by Zr(IV) and Np(V). For this reason, sorption site availability (fewer sites accessible at higher densities) is probably an unlikely explanation.

On the basis of the information available it is difficult to assess the errors associated with these diffusion experiments and the authors of the source data give little or no indications of what they might be. The uncertainty in D_a values must be at least a factor of two at the very best, and it is to be expected that it will increase significantly as D_a values decreases (higher sorption). All of the D_a values given for Am (even at $\rho_{\text{dry}} = 400 \text{ kg m}^{-3}$) must be approaching the limits of what is feasible to measure, and have a correspondingly high uncertainty associated with them. Using the simple relation that $\sqrt{(D_a \cdot t)}$ is the penetration depth at which the concentration is $\sim 1\%$ of the source value, this distance corresponds to $\sim 2 \text{ mm}$ in an "in-diffusion" test after one year for an apparent diffusion coefficient of $10^{-14} \text{ m}^2 \text{ s}^{-1}$.

Finally, as mentioned in section 2.1, linear sorption is assumed in the treatment of the experimental diffusion data. This is defensible only if the source concentration of labelled solution is low enough. In an attempt to create the most favourable measurement conditions i.e. high activity in the measurement samples, this criterion might be violated, or even worse, precipitation may occur at the surface of the diffusion specimen. (The predicted pH of the bentonite porewater is 8, and at this pH the solubilities of Ni(II), Am(III) and Zr(IV) are $\sim 2 \times 10^{-5} \text{ M}$, $\sim 4 \times 10^{-7} \text{ M}$ and $\sim 2 \times 10^{-10} \text{ M}$ respectively.)

Table 3: Apparent diffusion coefficients ($\text{m}^2 \text{s}^{-1}$) from “in-diffusion” measurements as a function of dry density for Kunigel V1.

	ρ_{dry} 400 kg m^{-3}	ρ_{dry} 800 kg m^{-3}	ρ_{dry} 1400 kg m^{-3}	ρ_{dry} 1800 kg m^{-3}	ρ_{dry} 2000 kg m^{-3}
D_a (Cs)	1.8×10^{-11}	1.4×10^{-11}	8.9×10^{-12}	6.5×10^{-12} *	5.2×10^{-12}
D_a (Ni)				1.6×10^{-13}	
D_a (Sm)		1.0×10^{-13}	3.5×10^{-14}	1.2×10^{-14}	
D_a (Am)	1.7×10^{-14}	1.0×10^{-14} 5.0×10^{-15}	4.5×10^{-15} 2.0×10^{-15}	1.3×10^{-15} #	
D_a (Zr)	5.0×10^{-13}	1.0×10^{-13}	1.5×10^{-14} 1.0×10^{-14}	3.0×10^{-15} #	
D_a (Np)	6.0×10^{-11} 4.0×10^{-11}	7.0×10^{-12}	2.0×10^{-12} 1.0×10^{-12}	4.0×10^{-13} *	2.0×10^{-13}

*interpolated

#extrapolated

Table 4: Distribution coefficients ($\text{m}^3 \text{kg}^{-1}$) derived from “in-diffusion” apparent diffusion coefficient measurements as a function of dry density for Kunigel V1.

	ρ_{dry} 400 kg m^{-3}	ρ_{dry} 800 kg m^{-3}	ρ_{dry} 1400 kg m^{-3}	ρ_{dry} 1800 kg m^{-3}	ρ_{dry} 2000 kg m^{-3}
K_d (Cs)	1.9×10^{-1}	6.2×10^{-2}	1.9×10^{-2}	9.7×10^{-3} *	6.9×10^{-3}
K_d (Ni)				4.0×10^{-1}	
K_d (Sm)		8.8	4.9	5.4	
K_d (Am)	200	88 175	17 34	49#	
K_d (Zr)	6.8	8.8	11 17	21#	
K_d (Np)	5.5×10^{-2} 8.3×10^{-2}	1.2×10^{-1}	8.5×10^{-2} 1.7×10^{-1}	1.6×10^{-1} *	1.8×10^{-1}

*interpolated

#extrapolated

4 CALCULATION/DERIVATION OF K_d (Rn) VALUES FROM BATCH SORPTION MEASUREMENTS

Any comparison of K_d (Rn) values from batch sorption experiments with values deduced from diffusion tests, or any predictions of D_a (Rn) values can only be meaningfully done when the batch K_d values relate to the same chemical conditions as those existing in the compacted bentonite at the dry density being considered. The first step in calculating/deriving appropriate K_d (Rn) values is therefore to define compacted bentonite porewater chemistries as a function of dry density.

4.1 Porewater compositions in compacted Kunigel V1

The water chemistry in a batch test is very easy to measure whereas that in a compacted bentonite is virtually impossible to determine experimentally. In almost all cases where compositions for bentonite porewaters are given, they have been calculated, using the procedures proposed by WANNER (1986). Recently, a new approach to this difficult problem has been put forward by BRADBURY & BAEYENS (2002a) and this procedure was used to calculate porewater compositions for Kunigel V1. Only an outline of the methodology will be given here and the reader is referred to the original report for a more detailed description.

Briefly, concepts are proposed and developed in this approach to the porewater chemistry in compacted bentonite that are different from those used in other previously published works. Consideration is given to factors such as the swelling properties of montmorillonite, the types of water associated with the re-saturated material, the semi-permeable membrane characteristics of montmorillonite, the exchangeable cation pool, the high buffering capacity afforded by the amphoteric $\equiv\text{SOH}$ sites and their role in determining the pH of the porewater. Of particular importance is the concept that the "as received" bentonite powder has been conditioned during the production process and during storage by the atmosphere. The pH in the moist bentonite powder will be that determined by carbonate/sulphate mineral equilibration at air P_{CO_2} i.e. $10^{-3.5}$ bar. The consequence is that the amphoteric hydroxy groups at the edges of montmorillonite platelets will also have been conditioned to a state reflecting air equilibration, and, any subsequent compaction of the bentonite will not alter the protolysis state of these sites. The result of this is that the amphoteric edge sites buffer the pH of the compacted bentonite porewater to a

value very close to 8. The above factors are considered together with physico-chemical characterisation data for Kunigel V1, Table 1. The calculated porewater chemistries for compacted Kunigel V1 are given in Table 5.

Table 5: Calculated porewater chemistries for Kunigel V1 for initial dry densities from 400 to 2000 kg m⁻³.

Dry density (kg m ⁻³)	400	800	1400	1800	2000
P _{CO₂} (bar)	10 ^{-3.16}	10 ^{-3.52}	10 ^{-3.41}	10 ^{-3.91}	10 ^{-4.19}
pH	8.36	8.02	8.00	8.00	8.00
Ionic strength (M)	0.05	0.20	0.27	0.42	0.58
Na (M)	3.63 x 10 ⁻²	1.37 x 10 ⁻¹	2.05 x 10 ⁻¹	3.61 x 10 ⁻¹	4.86 x 10 ⁻¹
K (M)	1.78 x 10 ⁻⁴	6.89 x 10 ⁻⁴	9.40 x 10 ⁻⁴	1.60 x 10 ⁻³	2.14 x 10 ⁻³
Mg (M)	5.82 x 10 ⁻⁵	9.89 x 10 ⁻⁴	2.31 x 10 ⁻³	4.75 x 10 ⁻³	7.46 x 10 ⁻³
Ca (M)	4.49 x 10 ⁻⁴	9.60 x 10 ⁻³	9.21 x 10 ⁻³	1.82 x 10 ⁻²	2.91 x 10 ⁻²
Cl (M)	3.94 x 10 ⁻⁴	5.58 x 10 ⁻³	2.54 x 10 ⁻²	3.23 x 10 ⁻¹	5.07 x 10 ⁻¹
SO ₄ (M)	1.55 x 10 ⁻²	7.80 x 10 ⁻²	1.01 x 10 ⁻¹	4.26 x 10 ⁻²	2.74 x 10 ⁻²
C _{inorg.} (M)	3.07 x 10 ⁻³	7.16 x 10 ⁻⁴	9.02 x 10 ⁻⁴	3.13 x 10 ⁻⁴	1.79 x 10 ⁻⁴
Si (M)	1.87 x 10 ⁻⁴	1.83 x 10 ⁻⁴	1.83 x 10 ⁻⁴	1.84 x 10 ⁻⁴	1.84 x 10 ⁻⁴

The consequence of the above calculations is that the K_d (Rn) values taken from batch sorption experiments and used to calculate D_a values from Eqn. 5 at a specific dry density must be the ones which correspond to the porewater chemistry in the compacted Kunigel V1. Ideally, the K_d (Rn) values should have been measured in the appropriate water chemistry, but such data are seldom available. Hence, an alternative approach has to be adopted which is the subject of the following section.

A further potentially complicating factor is that implicit in the use of Eqn. 5 is the assumption that the sorption is linear i.e. that the sorption isotherm in the region of the concentration being used (in both batch and diffusion tests) is of the single Langmuir type at low sorbate loadings, far from any sorption site capacity saturation effects. This condition will depend on the water chemistry and is radionuclide specific. However, broadly speaking it may be said that for high

montmorillonite containing systems equilibrium radionuclide concentrations should be less than at most 10^{-6} M. Selection of batch sorption data on this basis is relatively easy, but what is often not so clear is whether the boundary conditions in the “in-diffusion” experiments also comply with this condition as mentioned previously.

4.2 Methodology

The K_d values given as a function of compaction for the Kunigel V1 bentonite are all based on laboratory batch sorption measurements i.e. on data from dilute systems (low solid to liquid ratios).

The distribution coefficients for Cs, Ni and Sm were calculated from sorption models while those for Am, Zr and Np were deduced from literature or in house data modified to the particular Kunigel V1 conditions. The procedures are briefly outlined below.

4.2.1 K_d values for Cs, Ni and Sm: Calculations from sorption models

A simple cation exchange model exists for the uptake of Cs in bentonite systems where the montmorillonite is predominantly loaded with Na (BRADBURY & BAEYENS, unpublished data). The Cs-Na, K-Na, Mg-Na and Ca-Na selectivity coefficients used in the calculations are those derived for the MX-80 bentonite system (BRADBURY & BAEYENS, 2002a). The cation exchange capacity and surface loadings are those given in Table 1.

The surface complexation/cation exchange sorption model for Ni and Eu due to BRADBURY & BAEYENS (1997a, 2002b) was used in the geochemical speciation code MINSORB to calculate the uptake of Ni and Sm (Eu as chemical analogue) in Kunigel V1. The site capacities used for Kunigel V1 are the values given for purified SWy-1 montmorillonite scaled over their respective cation exchange capacities.

In the MX-80 bentonite and the SWy-1 montmorillonite systems, the presence of transition metals, particularly Zn and Mn, was found to influence the sorption of Ni/Eu at trace concentrations through competition on the strong sites. These ubiquitous impurities were included as an integral part of the sorption model, BRADBURY & BAEYENS (1997a, 2002b). Zn and Mn are intrinsic to these systems but it is not generally known how prevalent and at what levels they exist in other montmorillonite/bentonite systems. Because of the similarity between the two

commercial bentonites Kunigel V1 and MX-80, Table 1, and in the absence of any Kunigel V1 specific data, the inventory values for Zn and Mn were assumed to be the same in the two cases to a first approximation and used in the sorption model applied to Kunigel V1 i.e. $(Zn) = 1.1 \times 10^{-3} \text{ mol kg}^{-1}$ and $(Mn) = 1.7 \times 10^{-3} \text{ mol kg}^{-1}$ (BRADBURY & BAEYENS, unpublished data).

It should be noted that it has been suggested that trivalent metals form silicate complexes (HUMMEL et al., 2002). Dissolved silica is present in all bentonite/montmorillonite systems. The existence of such complexes and their importance in the speciation of trivalent lanthanides and actinides are, at the moment matters of debate. Such complexes were not included in the modelling of the sorption data for Eu.

4.2.2 K_d values for Am, Zr, Np: Modification procedures

To the best of the authors knowledge, no batch sorption data for Am, Zr and Np have been reported in the open literature on Kunigel V1 in the water chemistries given in Table 5. In order to modify literature sorption data so that they apply to the mineralogy of Kunigel V1, Table 1, and the corresponding porewater chemistries, Table 5, the methodology developed by BRADBURY & SAROTT (1994) and BRADBURY & BAEYENS (1997b, 2003b) was used. In the following, brief descriptions are given of how mineralogy, pH and aqueous speciation are taken into account in modifying sorption data so that they correspond to the compacted Kunigel V1. In addition, chemical analogy is mentioned.

Mineralogy:

The major sorbing component in bentonites is montmorillonite. Scaling of the selected literature sorption values to the Kunigel V1 mineralogy is carried out over the cation exchange capacity (CEC).

The mineralogy conversion factor (CF-CEC) is defined as the ratio of the CEC value for the Kunigel V1 bentonite ($CEC_{\text{Kunigel V1}}$) and the CEC value for the montmorillonite/bentonite used in the literature studies (CEC_{lit}) i.e.

$$CF - CEC = \frac{CEC_{\text{Kunigel V1}}}{CEC_{\text{lit}}} \quad (6)$$

The CEC is a measure of the overall capacity of planar sites and if cation exchange is the main sorption mechanism then it is clearly a good scaling

factor for sorption. The selectivity coefficients governing sorption on the planar sites of montmorillonite are assumed to a first approximation to be the same irrespective of the source.

In the case where sorption is dominated by surface complexation, the scaling is still done over the CEC. It has been generally observed that the surface complexation site capacity for many clay minerals is approximately 10% of the exchange capacity e.g. GRIM (1953); YARIV & CROSS (1979); BAEYENS & BRADBURY (1997). Thus, the total $\equiv\text{SOH}$ site capacities of different rocks, and thereby the sorption, should also be proportional to their respective CEC values.

pH:

Wherever possible sorption data were selected as close as possible to the pH of the Kunigel V1 reference porewater (Table 5) thus making a correction for pH unnecessary. However, if a pH correction is necessary, sorption edge data measurements on purified montmorillonite in simple background electrolytes are available for many radionuclides (or their chemical analogues), and these are used directly to estimate the pH correction factors. The procedure is simple, and is illustrated with the aid of the schematic sorption edge given below.

The pH conversion factor (CF-pH) is defined as the ratio of distribution coefficients at the reference pH ($\text{pH}_{\text{Kunigel V1}}$) and the measurement pH ($\text{pH}_{\text{lit.}}$) as read off from the appropriate sorption edge, see Figure 2 i.e.

$$\text{CF-pH} = \frac{K_{d, \text{Kunigel V1}}}{K_{d, \text{lit.}}} \quad (7)$$

Speciation:

The complexation of radionuclides with inorganic and organic ligands can influence sorption and therefore corrections need to be made which reflect this when the water chemistries used in the literature measurements and the Kunigel V1 porewater are different. (A rigorous correction is only possible when a verified sorption model is available.)

In order to make a correction to sorption values taking into account the differences in radionuclide speciation in different water chemistries, species which are considered to sorb and those which do not sorb have to be distinguished.

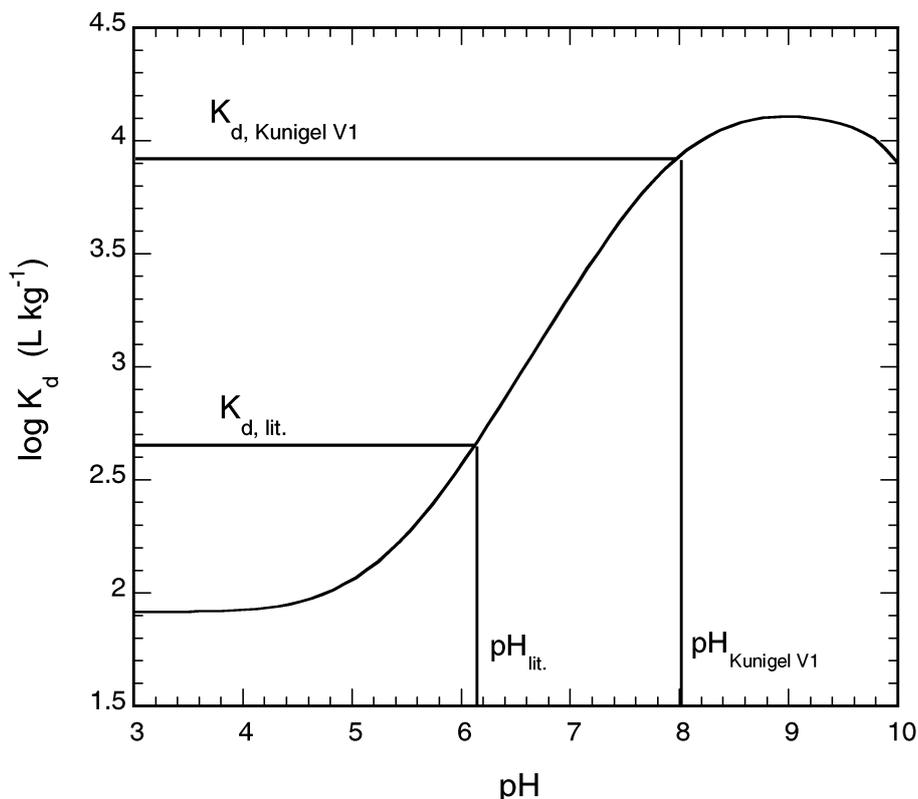


Figure 2: Schematic sorption edge indicating distribution ratios K_d Kunigel V1, and K_d lit. corresponding to $\text{pH}_{\text{Kunigel V1}}$ and $\text{pH}_{\text{lit.}}$ respectively for a particular radionuclide.

The proposal put forward is to define free cations, positively charged and neutral hydrolysis species as sorbing. All other species are treated as being non-sorbing.

The conversion factor used for modifying sorption values according to the speciation in different water chemistries is simply:

$$\text{CF-speciation} = \frac{F_{\text{Kunigel V1}}}{F_{\text{lit.}}} \quad (8)$$

$F_{\text{Kunigel V1}}$ is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the reference Kunigel V1 porewater.

$F_{\text{lit.}}$ is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the literature sorption measurements.

Attempts to correct for speciation differences in this manner are of course sensitively dependent on the quality of the stability constants in the thermodynamic data bases. The updated Nagra/PSI thermodynamic data base (HUMMEL et al., 2002) was used throughout.

Chemical analogues:

In cases where chemical analogy is invoked, the reference sorption value for the analogue is taken. The selected literature sorption value for the analogue element is first modified to the Kunigel V1 reference conditions. The correction factor which then needs to be applied to obtain the $K_{d \text{ Kunigel V1}}$ value for the radionuclide in question is one which takes into account the differences in aqueous speciation i.e.

$$\text{CF-chemical analogue} = \frac{F_{\text{nuclide}}}{F_{\text{chemical analogue}}} \quad (9)$$

F_{nuclide} is the fraction of the radionuclide concentration calculated to be present in the aqueous phase as sorbing species in the reference Kunigel V1 porewater.

$F_{\text{chemical analogue}}$ is the fraction of the chemical analogue concentration calculated to be present in the aqueous phase as sorbing species in the reference Kunigel V1 porewater.

4.3 Illustrative procedures

In the following, sorption values for Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) and Np(V) have been calculated for Kunigel V1 compacted in the range 400 to 2000 kg m⁻³. In order to illustrate the procedures, worked examples are given below for a porewater chemistry corresponding to a compaction of 1400 kg m⁻³, Table 5. The methodology used to calculate K_d values corresponding to the other dry densities is essentially the same.

At the end of this section a summary of all sorption values as a function of the different dry densities is given as well as the apparent distribution coefficients calculated from them using Eqn. 5.

4.3.1 Caesium (mechanistic sorption model)

The uptake of Cs by smectites is predominantly via cation exchange. From measurements of Cs sorption on purified Na conditioned SWy-1 montmorillonite in 0.01 M NaClO₄ it was found that the isotherm could be modelled over a wide range of concentrations using a K_c (Cs-Na) value of 15 for the permanently charged sites, Figure 3.

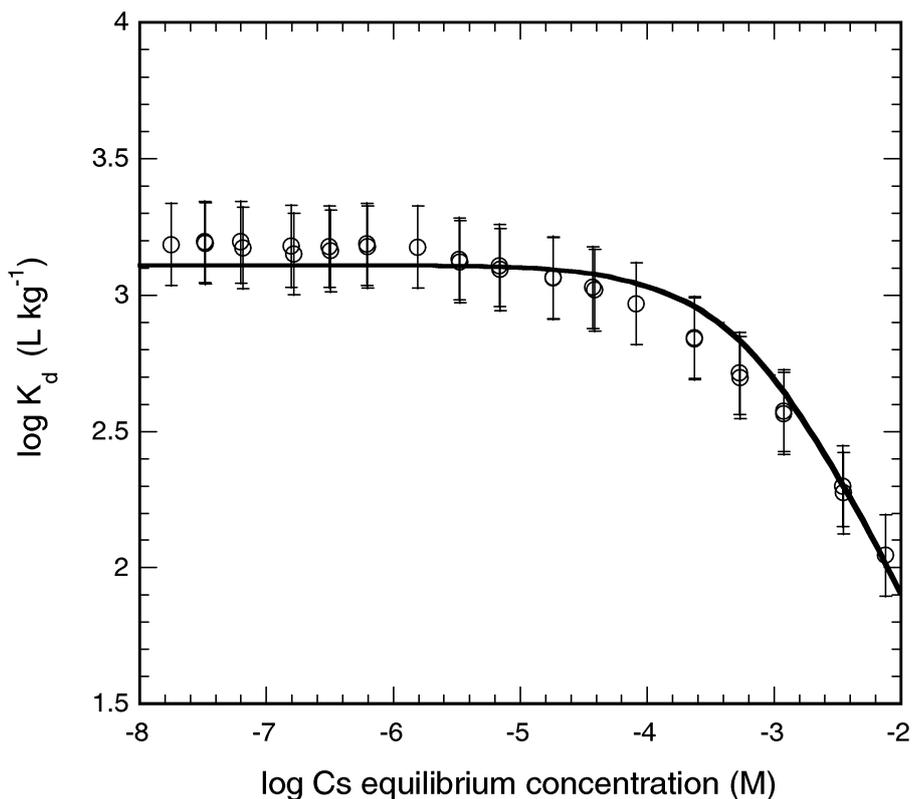


Figure 3: Cs sorption isotherm on conditioned Na montmorillonite (SWy-1) in 0.01 M NaClO₄. (Solid to liquid ratio = 1.2 g L⁻¹; equilibration time 21 days.) The continuous line was calculated using a Cs-Na selectivity coefficient of 15. (BRADBURY & BAEYENS, unpublished data).

The sorption of Cs on Kunigel V1 bentonite in the calculated porewater chemistry for the compacted material, Table 5, was modelled via a cation exchange mechanism using the geochemical code MINSORB, the selectivity coefficient data presented in Table 6 and the above selectivity coefficient for Cs-Na exchange.

A K_d of $4.1 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ was calculated at an equilibrium Cs concentration of 10^{-7} M for the compacted Kunigel V1 ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$).

Table 6: Cation exchange equilibria and selectivity coefficients for K-Na, Mg-Na and Ca-Na on MX-80 (BRADBURY & BAEYENS, 2002a).

Exchange reaction	K_c
$\text{Na-mont} + \text{K}^+ \rightleftharpoons \text{K-mont} + \text{Na}^+$	4.0
$2 \text{ Na-mont} + \text{Mg}^{2+} \rightleftharpoons \text{Mg-mont} + 2 \text{ Na}^+$	2.2
$2 \text{ Na-mont} + \text{Ca}^{2+} \rightleftharpoons \text{Ca-mont} + 2 \text{ Na}^+$	2.6

4.3.2 Nickel (mechanistic sorption model)

The surface complexation/cation exchange sorption model for Ni due to BRADBURY & BAEYENS (1997a) was used in the geochemical speciation code MINSORB to calculate the uptake of Ni in Kunigel V1. In the model calculations, Ni was assumed to be at trace concentrations and the uptake was occurring only on the strong sites (BRADBURY & BAEYENS, 1997a). As mentioned in section 4.2.1, Zn and Mn competition on the strong sites was included in the modelling.

A K_d value of $2.9 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ in the compacted Kunigel V1 bentonite ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$) was calculated. Ni equilibrium concentration = 10^{-8} M .

4.3.3 Samarium (mechanistic sorption model with Eu as chemical analogue)

Eu was taken as a chemical analogue for Sm and the surface complexation/cation exchange sorption model for Eu developed by BRADBURY & BAEYENS (2002b) was used to calculate the uptake of Sm in Kunigel V1. Intrinsic to the model is the inclusion of Zn and Mn aqueous species competing for uptake on the strong sites, see section 4.2.1.

A K_d value of $1.6 \text{ m}^3 \text{ kg}^{-1}$ in the compacted Kunigel V1 bentonite ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$) was calculated. Sm equilibrium concentration $< 10^{-8} \text{ M}$.

4.3.4 Americium (modified literature data)

GORGEON (1994) measured sorption edges for Am on a purified commercially available bentonite from Wyoming in a NaClO_4 background electrolyte at concentrations of 0.1 and 1 M, Figure 4. The solutions were in contact with air, but probably not long enough to reach equilibrium with CO_2 . Based on qualitative arguments, GORGEON (1994) estimated a total carbonate concentration of $1.3 \cdot 10^{-5}$ M. An Am sorption value at $\text{pH} = 8$ of $63 \text{ m}^3 \text{ kg}^{-1}$ was selected from these measurements. This value was tailored to the Kunigel V1 system according to the modification scheme laid out in section 4.2.2 and the accompanying data sheet documents these modifications.

The best estimate for the sorption of Am in compacted Kunigel V1 bentonite ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$) is $33 \text{ m}^3 \text{ kg}^{-1}$ at an Am equilibrium concentration of $\sim 5 \times 10^{-11}$ M.

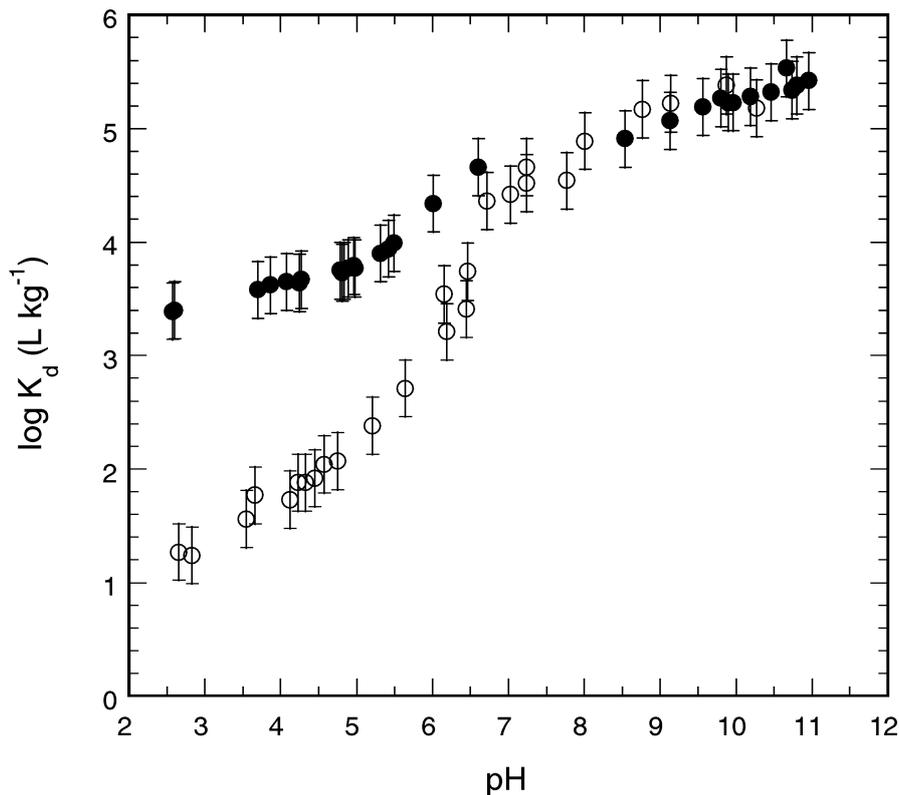


Figure 4: Am edges on Wyoming montmorillonite at 2 ionic strengths, GORGEON (1994): (●) 0.1 M NaClO_4 , (○) 1 M NaClO_4 .

Am DATA SHEET FOR KUNIGEL V1

Literature source: GORGEON (1994)

Selected $R_{d \text{ lit.}}$: $63 \text{ m}^3 \text{ kg}^{-1}$ (Am(III) equilibrium concentration: $\sim 5 \times 10^{-11} \text{ M}$)**SOURCE DATA SUMMARY**

Solid	$\text{CEC}_{\text{lit.}}$ (equiv. kg^{-1})
Smectite Wyoming	0.79

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	NaClO_4 (M)	$F_{\text{lit.}}$ speciation
8.0	1.3×10^{-5}	0.1	0.098

KUNIGEL V1 REFERENCE CASE DATA SUMMARY: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

$\text{pH}_{\text{ref.}}$	$F_{\text{ref.}}$ speciation	$\text{CEC}_{\text{ref.}}$ (equiv. kg^{-1})
8.0	0.067	0.60

CONVERSION FACTORS

CF-pH	CF-speciation	CF-CEC
1	0.68	0.76

KUNIGEL V1 REFERENCE SORPTION VALUE: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
33

4.3.5 Zirconium (chemical analogue)

No relevant sorption data measured under well-defined conditions could be found for Zr(IV). Consequently, the only means of estimating a sorption value is by chemical analogy.

Zr(IV) is a tetravalent element and has a similar hydrolysis behaviour to Sn(IV) except that the negatively charged hydroxy species begin to become significant already at $\text{pH} \leq 6$. The Sn(IV) sorption data presented in Figure 5 indicate that sorption is reduced when the negatively charged hydroxy species forms. The assumption is made here that only the neutral hydroxy species sorb and that Sn(IV) is an appropriate chemical analogue for Zr(IV).

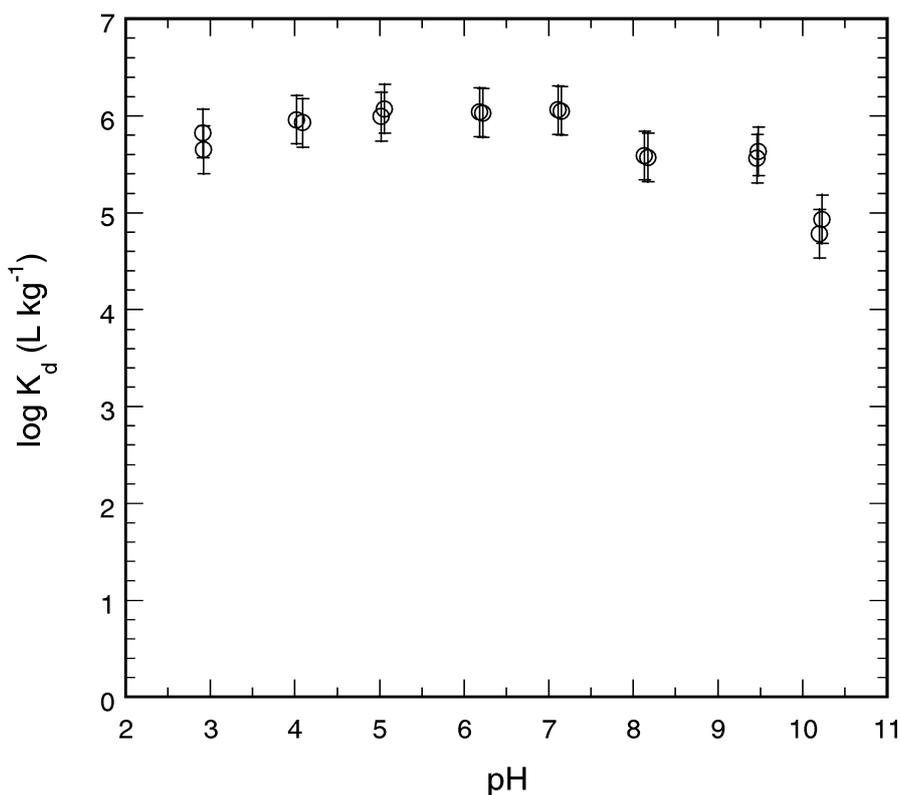


Figure 5: Sn(IV) sorption edge on conditioned SWy-1 Na-montmorillonite in 0.1 M NaClO₄. (Equilibration time 21 days.) BRADBURY & BAEYENS (unpublished data).

From Figure 5, a Sn sorption value of $890 \text{ m}^3 \text{ kg}^{-1}$ at $\text{pH} = 8$ was selected. The first of the two following data sheets documents the modification of this value to the Kunigel V1 system. In the second data sheet, the Sn sorption value for Kunigel V1 ($614 \text{ m}^3 \text{ kg}^{-1}$) is used as a chemical analogue for Zr and modified further to account for the differences in aqueous speciation.

(Note that Zr carbonate and hydroxy-carbonate complexes are not included in any of the calculations because no thermodynamic data are given for these complexes in the data base (HUMMEL et al., 2002).)

A K_d value of $22 \text{ m}^3 \text{ kg}^{-1}$ is estimated for Zr in compacted Kunigel V1 bentonite ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$) at an equilibrium concentration of $< 10^{-7} \text{ M}$.

Sn(IV) DATA SHEET FOR KUNIGEL V1

Literature source: BRADBURY & BAEYENS (unpublished data).

Selected $R_{d \text{ lit.}}$: $890 \text{ m}^3 \text{ kg}^{-1}$ (Sn(IV) equilibrium concentration: $\sim 5 \times 10^{-8} \text{ M}$)

SOURCE DATA SUMMARY

Solid	$CEC_{\text{lit.}}$ (equiv. kg^{-1})
Swy-1 montmorillonite	0.87

$\text{pH}_{\text{lit.}}$	$C_{\text{inorg.}}$ (M)	NaClO_4 (M)	$F_{\text{lit.}}$ speciation
8.0	-	0.1	1

KUNIGEL V1 REFERENCE CASE DATA SUMMARY: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

$\text{pH}_{\text{ref.}}$	$F_{\text{ref.}}$ speciation	$CEC_{\text{ref.}}$ (equiv. kg^{-1})
8.0	1	0.60

CONVERSION FACTORS

CF-pH	CF-speciation	CF-CEC
1	1	0.69

KUNIGEL V1 REFERENCE SORPTION VALUE: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

$R_{d \text{ ref.}}$ ($\text{m}^3 \text{ kg}^{-1}$)
614

Zr(IV) DATA SHEET FOR KUNIGEL V1

Selected chemical analogue: Sn(IV)

Source of chemical analogue sorption data: BRADBURY & BAEYENS (unpublished data).

KUNIGEL V1 REFERENCE CASE Sn(IV) DATA

$R_d \text{ Sn(IV)}_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$	$F \text{ Sn(IV)}_{\text{ref.}} \text{ speciation}$
614	0.42

KUNIGEL V1 REFERENCE CASE Zr(IV) DATA: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

$F \text{ Zr(IV)}_{\text{ref.}} \text{ speciation}$
0.015

CONVERSION

$$R_d \text{ (Zr)}_{\text{ref.}} = R_d \text{ (Sn)}_{\text{ref.}} \times [F \text{ (Zr)}_{\text{ref.}} \text{ speciation} / F \text{ (Sn)}_{\text{ref.}} \text{ speciation}]$$

KUNIGEL V1 REFERENCE SORPTION VALUE

$R_d \text{ Zr(IV)}_{\text{ref.}} \text{ (m}^3 \text{ kg}^{-1}\text{)}$
22

4.3.6 Neptunium (modified literature data)

Sorption values for Np(V), measured at trace concentrations on purified montmorillonite in simple background electrolytes, were chosen at pH = 8 from the sorption edge data given in GORGEON (1994), $0.13 \text{ m}^3 \text{ kg}^{-1}$, and TURNER et al. (1998), $0.1 \text{ m}^3 \text{ kg}^{-1}$, Figures 6 and 7 respectively. The two selected values are modified as shown in the following data sheets to yield distribution coefficients appropriate for the Kunigel V1 system.

The K_d Np(V) values calculated for compacted Kunigel V1 at $\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$, from the data of GORGEON (1994) and TURNER et al. (1998) are $7.5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ and $3.8 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ respectively. Np equilibrium concentration is $\sim 5 \times 10^{-7} \text{ M}$.

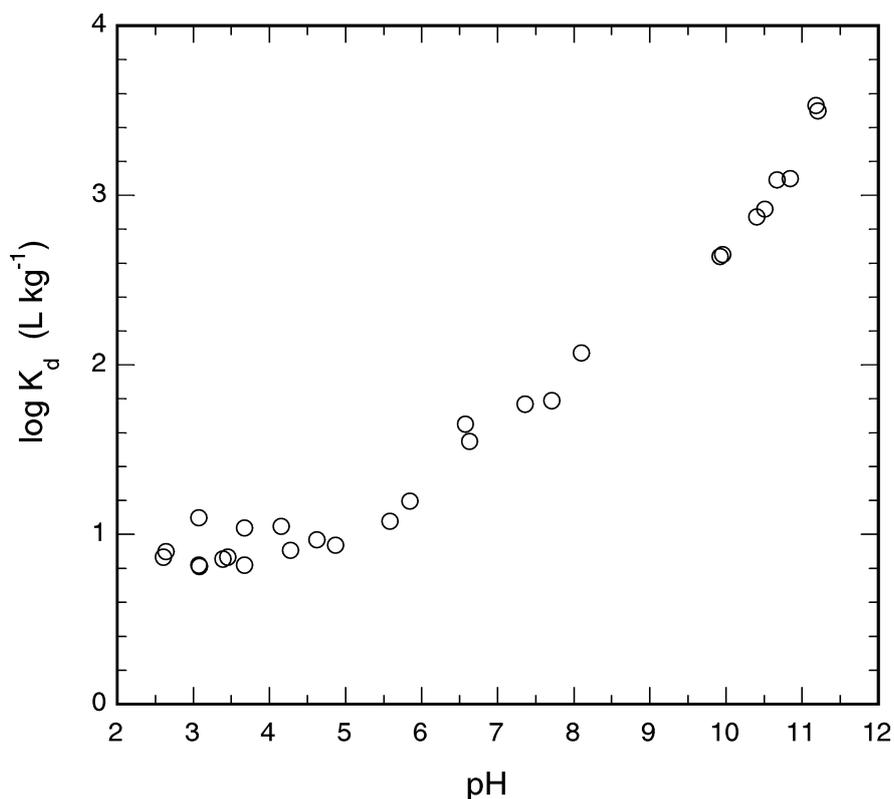


Figure 6: Np(V) sorption on a Wyoming smectite at 0.1 M NaClO_4 . Initial Np concentration $\sim 10^{-6} \text{ M}$. (Taken from GORGEON, 1994).

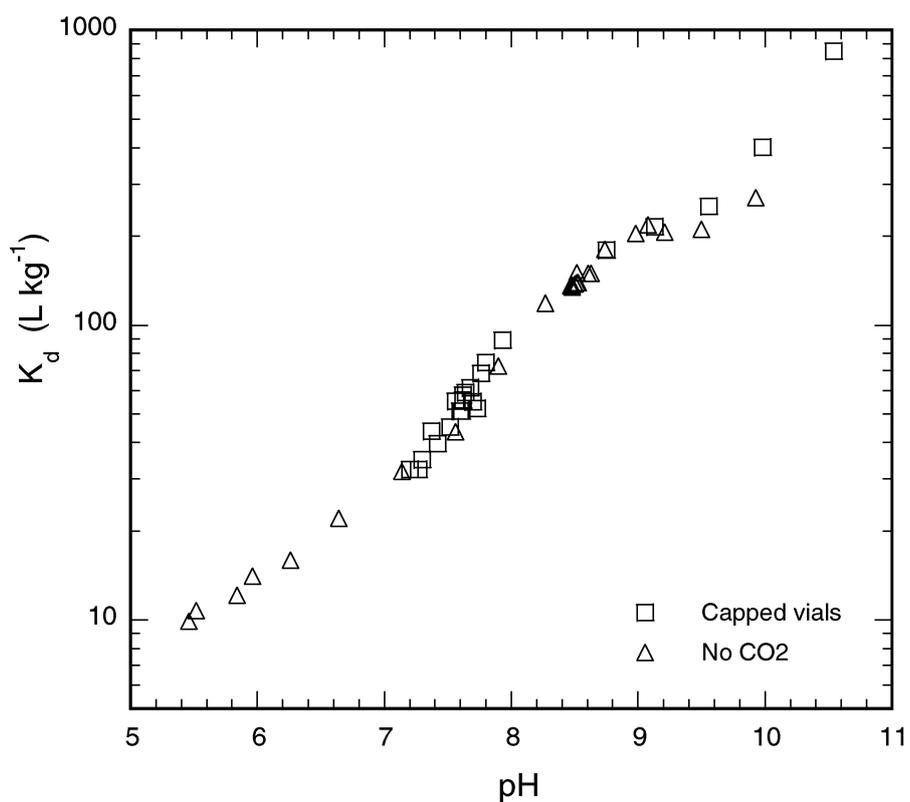


Figure 7: Np(V) sorption on Na-montmorillonite (SAz-1) in CO₂ free conditions equilibrated with 0.1 M NaNO₃. Initial Np concentration is $\sim 9 \times 10^{-7}$ M. (Taken from TURNER et al., 1998).

Np(V) DATA SHEET FOR KUNIGEL V1

Literature source: GORGEON (1994)

Selected R_d lit.: $1.3 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Np(V) equilibrium conc.: $\sim 5 \times 10^{-7} \text{ M}$)

SOURCE DATA SUMMARY

Solid	CEC _{lit.} (equiv. kg ⁻¹)
Smectite Wyoming	0.79

pH _{lit.}	C _{inorg.} (M)	NaClO ₄ (M)	F _{lit. speciation}
8.0	1.3×10^{-5}	0.1	1

KUNIGEL V1 REFERENCE CASE DATA SUMMARY: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

pH _{ref.}	F _{ref. speciation}	CEC _{ref.} (equiv. kg ⁻¹)
8.0	0.76	0.60

CONVERSION FACTORS

CF-pH	CF-speciation	CF-CEC
1	0.76	0.76

KUNIGEL V1 REFERENCE SORPTION VALUE: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

R_d ref. (m ³ kg ⁻¹)
7.5×10^{-2}

Np(V) DATA SHEET FOR KUNIGEL V1

Literature source: TURNER et al. (1998)

Selected $R_{d \text{ lit.}}$: $1.0 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ (Np(V) equilibrium conc.: $\sim 6 \times 10^{-7} \text{ M}$)**SOURCE DATA SUMMARY**

Solid	#CEC _{lit.} (equiv. kg ⁻¹)
SAz-1 montmorillonite	1.2

#Van Olphen & Fripiat (1979)

pH _{lit.}	C _{inorg.} (M)	NaNO ₃ (M)	F _{lit. speciation}
8.0	-	0.1	1

KUNIGEL V1 REFERENCE CASE DATA SUMMARY: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

pH _{ref.}	F _{ref. speciation}	CEC _{ref.} (equiv. kg ⁻¹)
8.0	0.76	0.60

CONVERSION FACTORS

CF-pH	CF-speciation	CF-CEC
1	0.76	0.5

KUNIGEL V1 REFERENCE SORPTION VALUE: ($\rho_{\text{dry}} = 1400 \text{ kg m}^{-3}$)

$R_{d \text{ ref.}}$ (m ³ kg ⁻¹)
3.8×10^{-2}

5 RESULTS AND DISCUSSION

The aim of this exercise was to compare sorption values and apparent diffusion coefficients derived/calculated from compacted and dispersed bentonite systems with a view to evaluating their compatibility.

In the above, distribution coefficients for Cs(I), Ni(II), Sm(III), Am(III), Zr(IV) and Np(V) were calculated from diffusion measurements in compacted Kunigel V1 bentonite as a function of dry density, Table 4. In order to derive corresponding values from batch tests for comparison, and from these to predict apparent diffusion coefficients, it was first necessary to calculate the porewater chemistry for the Kunigel V1 as a function of compacted density. In addition, it is important to realise that for this comparison a wide variety of sorption data from different sources measured on different montmorillonite materials had to be used. A further complicating factor in this whole procedure is that the modified batch based sorption values deduced, and those calculated from a sorption model, are sensitively dependent on the quality of the available thermodynamic data, e.g. see section 4.2.2.

Table 7 summarises the distribution coefficients calculated from diffusion measurements on Kunigel V1 and the corresponding ones derived for the Kunigel V1 system from batch sorption tests. Table 8 summarises the comparison of D_a values. The measured apparent diffusion coefficients (solid symbols) and calculated values (continuous lines) as a function of dry density are shown pictorially in Figure 8.

An overview of the basic assumptions and procedures used are given below in terms of a list of key points.

- (i) As a basis, diffusion data for Kunigel V1 presented in SATO & YUI (1997) and SATO (1998) were taken, primarily because of the breadth and completeness of the measurements. In order to extract distribution coefficients simple Fickian diffusion into a homogeneous single porosity medium was assumed in which the radionuclides either do not sorb at all or sorb rapidly, reversibly and linearly (constant K_d).
- (ii) For neutral and positively charged species the effective diffusion coefficient for HTO was used and the whole of the porosity present in the original dry compacted material was considered to be available. (Radionuclide transport in performance assessment is calculated with the same simple model, NAGRA, 2002)

- (iii) Sorption values calculated from diffusion measurements are model dependent whereas sorption values from batch sorption tests are directly measured.
- (iv) A comparison between K_d data from intact and dispersed systems is only meaningful when it is made for the same water chemistry (pH, Eh and aqueous composition) which can have an important influence on sorption. The methodology proposed by BRADBURY & BAEYENS (2002a) was used to calculate porewater chemistries as function of dry density for compacted Kunigel V1 bentonite, see Table 5.
- (v) Batch sorption data were taken from a wide variety of sources where different types of purified montmorillonites were used. The selected K_d values were modified to the Kunigel V1 porewater using the methodology outlined in section 4.2.2.
- (vi) The pathways for deriving distribution ratios for the Kunigel V1 system for the radionuclides under consideration were different.
 - Sorption models were used to calculate distribution ratios for Cs(I), Ni(II) and Sm(III) (by chemical analogy with Eu(III)).
 - Am(III) and Np(V) sorption values were derived by modifying K_d values obtained for different purified montmorillonites (section 4.2).
 - In the case of Zr(IV), chemical analogy with Sn(IV) was invoked where the source data were Sn(IV) sorption measurements on a purified montmorillonite.

The important point being made here is that the K_d values calculated/derived from batch data in Table 7 have been produced by a combination of different procedures most of which are also used in the derivation of sorption values in the sorption data base for MX-80 (BRADBURY & BAEYENS, 2003a). They are blind calculations/predictions for the sorption in compacted Kunigel V1.

For the K_d and D_a data compared in Tables 7 and 8 respectively, corresponding values lying within factors of 2 to 3 of one another must be regarded as being in very good agreement. In this context it should be realised that a realistic uncertainty factor for batch sorption measurements carried out under controlled conditions in the laboratory is considered to be approximately ± 1.6 , see BAEYENS & BRADBURY (1997). Further, estimates for the maximum uncertainty factor associated with modifying batch sorption data so that they apply to a reference compacted bentonite (specified mineralogy and water chemistry),

using the methodology described previously, can be considerably greater (BRADBURY & BAEYENS, 2003a).

Judging on the above basis, the agreement between K_d and D_a values for Cs in Tables 8 and 9 must be regarded as being excellent both in terms of the magnitudes of the corresponding data and the clear trend in the data.

There is only one diffusion datum for Ni measured at 1800 kg m⁻³. For this one point the D_a and K_d diffusion based values and those based on batch data are in excellent agreement.

No batch sorption data are available for Sm and hence Eu was taken as a chemical analogue. Sorption values for Sm were calculated using the Eu sorption model (BRADBURY & BAEYENS, 2002b). The agreement here ranges from excellent at 1800 kg m⁻³ to very reasonable at 800 kg m⁻³ and 1400 kg m⁻³ where the values are within factors of 3 to 4.

For Am, the degree of correspondence between diffusion and batch data is somewhat erratic. At the highest dry densities (1400 kg m⁻³ and 1800 kg m⁻³) the agreement is very good, whereas at the two lowest dry densities the agreement can only be regarded as poor. (Even so, the differences are only factors of 5-6). Am is a difficult case since penetration depths for the D_a values given can only be of the order of a millimetre, making data analysis very difficult and the uncertainties high, Chapter 3.

Even though the K_d values for Zr(IV) were estimated using Sn(IV) as a chemical analogue and then modifying the data to the Kunigel V1 system, they are predominantly within a factor of 2 of the K_d values derived from the diffusion data. Again the agreement is better at the higher dry densities.

Finally the agreement between the Np(V) values must also be regarded as good over the whole compaction range for Kunigel V1.

Table 7: Comparison of K_d values ($m^3 kg^{-1}$) derived from “in-diffusion” data and K_d values modelled/predicted from batch sorption measurements as a function of dry density for Kunigel V1.

	ρ_{dry} 400 kg m^{-3}		ρ_{dry} 800 kg m^{-3}		ρ_{dry} 1400 kg m^{-3}		ρ_{dry} 1800 kg m^{-3}		ρ_{dry} 2000 kg m^{-3}	
	from diffusion data	from batch data	from diffusion data	from batch data	from diffusion data	from batch data	from diffusion data	from batch data	from diffusion data	from batch data
K_d Cs(I)	1.9×10^{-1}	2.0×10^{-1}	6.2×10^{-2}	5.4×10^{-2}	1.9×10^{-2}	4.1×10^{-2}	$9.7 \times 10^{-3}^*$	2.2×10^{-2}	6.9×10^{-3}	1.6×10^{-2}
K_d Ni(II)		9.0×10^{-1}		3.3×10^{-1}		2.9×10^{-1}	4.0×10^{-1}	4.3×10^{-1}		4.1×10^{-1}
K_d Sm(III) ϕ		9.2×10^{-1}	8.8	1.9	4.9	1.6	5.4	5.0		8.5
K_d Am(III)	200	25	88 175	35	17 34	33	49 [#]	44		45
K_d Zr(IV)	6.8	16.5	8.8	21.0	11 17	22	21 [#]	21		22
K_d Np(V)	5.5×10^{-2} 8.3×10^{-2}	$2.9 \times 10^{-2}\phi$ $1.7 \times 10^{-2}\swarrow$	1.2×10^{-1}	$7.8 \times 10^{-2}\phi$ $4.0 \times 10^{-2}\swarrow$	8.5×10^{-2} 1.7×10^{-1}	$7.5 \times 10^{-2}\phi$ $3.8 \times 10^{-2}\swarrow$	$1.6 \times 10^{-1}^*$	$9.0 \times 10^{-2}\phi$ $4.6 \times 10^{-2}\swarrow$	1.8×10^{-1}	$9.4 \times 10^{-2}\phi$ $4.8 \times 10^{-2}\swarrow$

* Interpolated

Extrapolated

ϕ Chemical analogue for Eu(III)

ϕ GORGEON (1994)

\swarrow TURNER et al. (1998)

Table 8: Comparison of measured apparent diffusion coefficients ($\text{m}^2 \text{s}^{-1}$) and values calculated from batch sorption based K_d and D_e (HTO) data as a function of dry density for Kunigel V1.

	ρ_{dry} 400 kg m^{-3}		ρ_{dry} 800 kg m^{-3}		ρ_{dry} 1400 kg m^{-3}		ρ_{dry} 1800 kg m^{-3}		ρ_{dry} 2000 kg m^{-3}	
	from diffusion data	from batch data								
D_a Cs(I)	1.8×10^{-11}	1.7×10^{-11}	1.4×10^{-11}	1.6×10^{-11}	8.9×10^{-12}	4.1×10^{-12}	6.5×10^{-12} *	2.9×10^{-12}	5.2×10^{-12}	2.3×10^{-12}
D_a Ni(II)		3.8×10^{-12}		2.6×10^{-12}		5.9×10^{-13}	1.6×10^{-13}	1.5×10^{-13}		8.9×10^{-14}
D_a Sm(III) ϕ		3.7×10^{-12}	1.0×10^{-13}	4.6×10^{-13}	3.5×10^{-14}	1.1×10^{-13}	1.2×10^{-14}	1.3×10^{-14}		4.3×10^{-15}
D_a Am(III)	1.7×10^{-14}	1.4×10^{-13}	1.0×10^{-14} 5.0×10^{-15}	2.5×10^{-14}	4.5×10^{-15} 2.0×10^{-15}	5.2×10^{-15}	1.3×10^{-15} #	1.5×10^{-15}		8.1×10^{-16}
D_a Zr(IV)	5.0×10^{-13}	2.1×10^{-13}	1.0×10^{-13}	4.2×10^{-14}	1.5×10^{-14} 1.0×10^{-14}	7.8×10^{-15}	3.0×10^{-15} #	3.1×10^{-15}		1.7×10^{-15}
D_a Np(V)	6.0×10^{-11} 4.0×10^{-11}	$1.1 \times 10^{-10}\phi$ $1.8 \times 10^{-10}\swarrow$	7.0×10^{-12}	$1.1 \times 10^{-11}\phi$ $2.1 \times 10^{-11}\swarrow$	2.0×10^{-12} 1.0×10^{-12}	$2.3 \times 10^{-12}\phi$ $4.5 \times 10^{-12}\swarrow$	4.0×10^{-13} *	$7.1 \times 10^{-13}\phi$ $1.4 \times 10^{-12}\swarrow$	2.0×10^{-13}	$3.9 \times 10^{-13}\phi$ $7.6 \times 10^{-13}\swarrow$

* Interpolated

Extrapolated

ϕ Chemical analogue for Eu(III)

ϕ GORGEON (1994)

\swarrow TURNER et al. (1998)

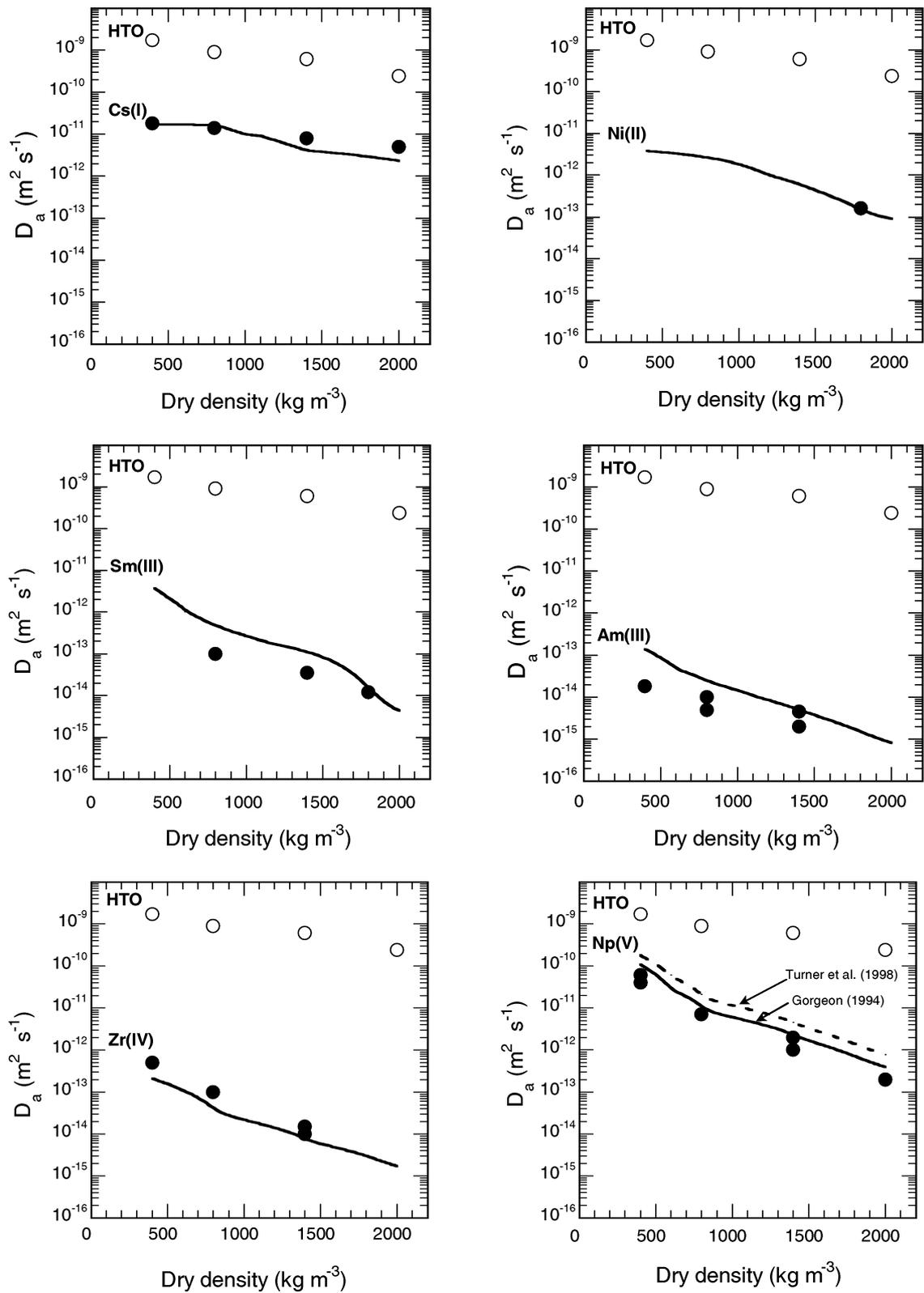


Figure 8: Measured apparent diffusion coefficients (symbols) and D_a values calculated from batch sorption based K_D values (continuous lines) as a function of dry density for Kunigel V1.

6 PRELIMINARY CONCLUSIONS

When all of the above factors are taken into account, the correspondence between the sorption values derived from diffusion data and those calculated from batch sorption measurements is generally good to very good with no significant trends. Only the data for Am at 400 kg m⁻³ and 800 kg m⁻³ show serious discrepancies between diffusion and batch derived data. Agreement tends to be better for dry densities above 1400 kg m⁻³ than below this dry density. The estimated D_a values generally lie above the measured ones i.e. the D_a values estimated from batch sorption measurements tend to be conservative. The one exception to this is Zr where the predictions for apparent diffusion coefficients are slightly less than the measured D_a values. (Note that even for batch sorption measurements carried out under controlled conditions in the laboratory and for diffusion measurements, realistic uncertainty factors are approximately ± 1.6 and $\geq \pm 2$ respectively).

The preliminary conclusion drawn from the results of the above exercise is that to a first approximation values calculated from sorption models or suitably modified data from batch sorption type measurements on dispersed bentonite/montmorillonite systems do not appear to differ in any significant way from K_d values derived from "in-diffusion" measurements carried out at high dry densities. The proviso is that the appropriate water chemistry for the particular compacted system is considered.

The corollary to this is that the use of batch sorption data, calculated and/or modified according to the procedures outlined before, can be used in the diffusion equations used to calculate the mass transport of radionuclides through bentonite in performance assessment studies. Also, based on the evidence presented, the authors see no justification or need to invoke additional processes, such as surface diffusion, to describe diffusive transport through compacted bentonite.

It needs to be emphasised that the conclusions are preliminary. Although based on the best available data, the data set itself is relatively small (6 elements). Clearly, further research is required to confirm these findings.

7 FINAL REMARKS

Two further remarks regarding this work need to be made.

Data on the diffusion of anions was not considered since this is a topic which should be considered separately. Anion exclusion effects undoubtedly occur in compacted bentonite systems implying that the diffusion accessible porosity is considerably smaller than the initial porosity and will vary with initial dry density. If Eqn. 1 is considered with a porosity value which for anions is probably at least an order of magnitude less than ε_{dry} , then it can be appreciated that even very small K_d values can have an effect on apparent diffusion coefficients. If for example the hypothetical case of an anion accessible porosity of 0.004 (MUURINEN et al., 1987) and an initial dry density of 1800 kg m^{-3} is considered, then even anion K_d values of about $10^{-5} \text{ m}^3 \text{ kg}^{-1}$ would have a significant effect on D_a values. (In this example the decrease in the apparent diffusion coefficient would be a factor of ~ 5 .) The measurement of such low K_d values in batch test is difficult and requires specifically designed experiments. At the moment sorption for most anions is taken to be zero and hardly any measured values exist. However, in view of the above, the intention in the future is to set up sorption experiments in which it is possible to measure such low sorption values. Also, the anion diffusion accessible porosity is an important parameter in this context which needs to be checked.

The second remark applies principally to redox sensitive elements such as Np, U, Pu and Tc. Here, the agreement between deduced sorption values and those extracted from diffusion tests carried out under reducing conditions appears not to be particularly good. (The D_a values calculated with the deduced sorption values tend to err on the non-conservative side.)

Diffusion measurements exist for these redox sensitive radionuclides in various compacted bentonite systems and it is claimed that the measured D_a values can be associated with a particular redox state. For oxidising conditions this may well be so, but under "reducing conditions" the situation is far from certain. Any sort of measurements at near neutral pH values and a well-defined redox state are notoriously difficult to perform. In most cases no measurements were carried out to check the redox state of the nuclide. If different oxidation states co-exist then the diffusion coefficient measured is some sort of value which is influenced by the different valence states, speciation and sorption characteristics. Claims that diffusion measurements have been carried out at a "fixed redox state" should be treated with the utmost caution. In addition, there

is always the question of possible precipitation effects and whether the assumption of constant K_d is valid.

On the other hand, there are also uncertainties in the sorption values in the sorption data bases (BRADBURY & BAEYENS, 2003a) deduced for Np(IV), U(IV) and Tc(IV) from batch data. The sorption mechanisms for elements in the tetravalent state are not understood. Sorption values were based on chemical analogy with Th(IV). Assumptions had to be made concerning the sorbing species and the aqueous speciation which, especially with respect to hydroxy-carbonate species for tetravalent actinides, and silicate species for the trivalent actinides, is not well established. The procedures used in the sorption data base work to convert laboratory batch sorption values to values appropriate to a given reference system are not applicable in every case, as has been noted previously (BRADBURY & BAEYENS, 2003a).

Making a valid comparison between sorption values originating from batch and diffusion measurements is a tricky exercise and requires a great deal of information. Situations where important information is lacking and/or where precise experimental conditions are difficult to establish, can lead to large uncertainties. This is especially so in the case of the actinides. At the moment the uncertainties are such that it is unclear which of the approaches leads to the most "correct" sorption values.

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