



TECHNICAL REPORT 96-05

Far-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in an Undisturbed Palfris Marl Host Rock

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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 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 Co-operative 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

A Palfris marl formation at Wellenberg (Gemeinde Wolfenschiessen, NW) has been chosen by NAGRA as a potential repository site for low- and intermediate-level radioactive waste, L/ILW. In the coming years a series of performance assessment studies will be performed for this site. One set of key data required for such safety analysis calculations is sorption data bases (SDB) for safety relevant radionuclides in the far-field. The purpose of this report is to describe the procedures used to generate sorption data bases appropriate for the in situ conditions existing along the different potential flow paths in an undisturbed marl host rock formation. An important aim was to document the sources of sorption data used and, in particular, the processes by which data selections were made. The main guiding principles here were "transparency" and "traceability". Inherent within this whole process is also the justification for, and defensibility of, the selected values.

Much of the sorption data used to generate the SDB for marl came from the open literature. A major part of this report is concerned with describing the procedures whereby these initial literature values are modified so that they apply to the actual marl mineralogies and groundwater chemistries. The resulting "reference R_d values" are then further modified using so called Lab -> Field transfer factors to produce sorption values which are appropriate to the in situ bulk rock conditions. The Lab -> Field transfer factors attempt to correct for the differences in sorption site availability between the crushed rock state used in batch tests and the intact rock state existing in reality in the host rock.

There are two main groundwater chemistries and five characteristic mineralogical compositions which cover the three broad types of flow paths which have been identified in the Palfris marl formation. A sorption data base corresponding to the in situ conditions for each of these groundwater/mineralogy combinations are given. In principle the methodology described here to construct sorption data bases for marl is applicable to any type of host rock.

ZUSAMMENFASSUNG

Als potentiell geeignetes Wirtgestein eines geplanten Endlagers für schwach- und mittelaktive Abfälle (SMA) hat die NAGRA den Palfris-Mergel am Wellenberg (Gemeinde Wolfenschiessen, NW) ausgewählt. Entscheidend für Sicherheitsanalysen sind Sorptionsdaten für sicherheitsrelevante Radionuklide im Fernfeld. In diesem Bericht werden die Verfahren beschrieben, mit denen Sorptionsdaten für die in situ Bedingungen entlang verschiedener potentieller Fliesswege in einer intakten Mergelformation erstellt werden. Wichtig dabei ist die Dokumentation der Quellen von relevanten Sorptionsdaten und insbesondere der Überlegungen, die zur Datenauswahl geführt haben. In diesem Zusammenhang waren die Leitkriterien Transparenz und Nachvollziehbarkeit der Datenauswahl sowie die Vertretbarkeit dieses Vorgehen.

Viele der Sorptionsdaten, die zur Erstellung von Datenbasen für Mergel berücksichtigt wurden, sind der offenen Literatur entnommen. Der vorliegende Bericht beschreibt, wie die ursprünglichen Literaturwerte an die tatsächliche Mergelmineralogie und die Grundwasserchemie angepasst werden. Die resultierenden "Referenz- R_d -Werte" werden dann mit sogenannten "Labor -> Feld"-Transferfaktoren weiter modifiziert, um Sorptionswerte zu berechnen, die für die in situ Bedingungen im Gestein relevant sind. Mit den "Labor -> Feld"-Transferfaktoren wird versucht, die unterschiedliche Verfügbarkeit von Sorptionsstellen an gemahlenem Gestein (Batch-Tests) und intaktem Gestein (in situ) zu korrigieren.

Die drei möglichen Fliesswege, die im Palfris-Mergel identifiziert wurden, können mit fünf charakteristischen Mineralzusammensetzungen sowie zwei Hauptgrundwassertypen beschrieben werden. Für jede Grundwasser/Mineralogie-Kombination wird eine Sorptions-Datenbasis erstellt, die die in situ Bedingungen beschreibt. Die in diesem Bericht beschriebene Methode der Erstellung einer "Mergel-Sorptions-Datenbasis" kann grundsätzlich auch für andere Gesteinstypen eingesetzt werden.

RESUME

La formation Palfris riche en marnes qui est située au Wellenberg (commune de Wolfenschiessen, NW) a été choisie par la Cédra comme site potentiel de dépôt final pour les déchets radioactifs de faible et moyenne activité. Des études de démonstration de sûreté de ce site sont programmées dans les prochaines années. Or, une des données clefs de ces études sont les bases de données de sorption dans le champ lointain concernant les radionucléides pertinents pour la sûreté. Ce rapport a pour but de décrire les procédures utilisées pour générer les bases de données de sorption adaptées aux conditions *in situ* existant le long des différents chemins potentiels d'écoulement hydrodynamique dans une roche d'accueil non perturbée composée de marnes. Un des objectifs importants de ce travail était de préciser l'origine des données de sorption utilisées et en particulier d'explicitier la procédure de sélection des données. Celle-ci repose sur la "transparence" et la "traçabilité" des données utilisées. Ainsi, la justification et la pertinence des données sélectionnées sont prises en compte tout au long de cette procédure.

La plupart des données de sorption utilisées pour construire les bases de données pour les marnes provient de la littérature ouverte. Une grande partie de ce rapport décrit les procédures utilisée pour modifier ces valeurs initiales issues de la littérature, afin de pouvoir les appliquer à la minéralogie précise de la formation étudiée et à la géochimie des eaux souterraines. Les "valeurs de référence R_d " qui en découlent, sont ensuite modifiées par un facteur de correction dénommé facteur de transfert "Laboratoire -> Terrain", afin d'obtenir les valeurs de sorption pertinentes pour les conditions *in situ* de la formation géologique. Ces facteurs de transfert "Laboratoire -> Terrain" essaient de corriger les différences d'accessibilité des sites de sorption entre la roche broyée utilisée pour les expériences de laboratoire et la roche d'accueil intacte.

Les chemins de circulation dans la formation marneuse de Palfris peuvent être décrits à partir de deux eaux souterraines de composition chimique différente et de cinq compositions minéralogiques. Une base de données de sorption *in situ* a ainsi été constituée pour chacune des combinaisons eau souterraine/minéralogie. Enfin, la procédure décrite et appliquée ici pour les marnes de la formation Palfris, permet en principe d'élaborer des bases de données de sorption pour n'importe quel type de roche d'accueil.

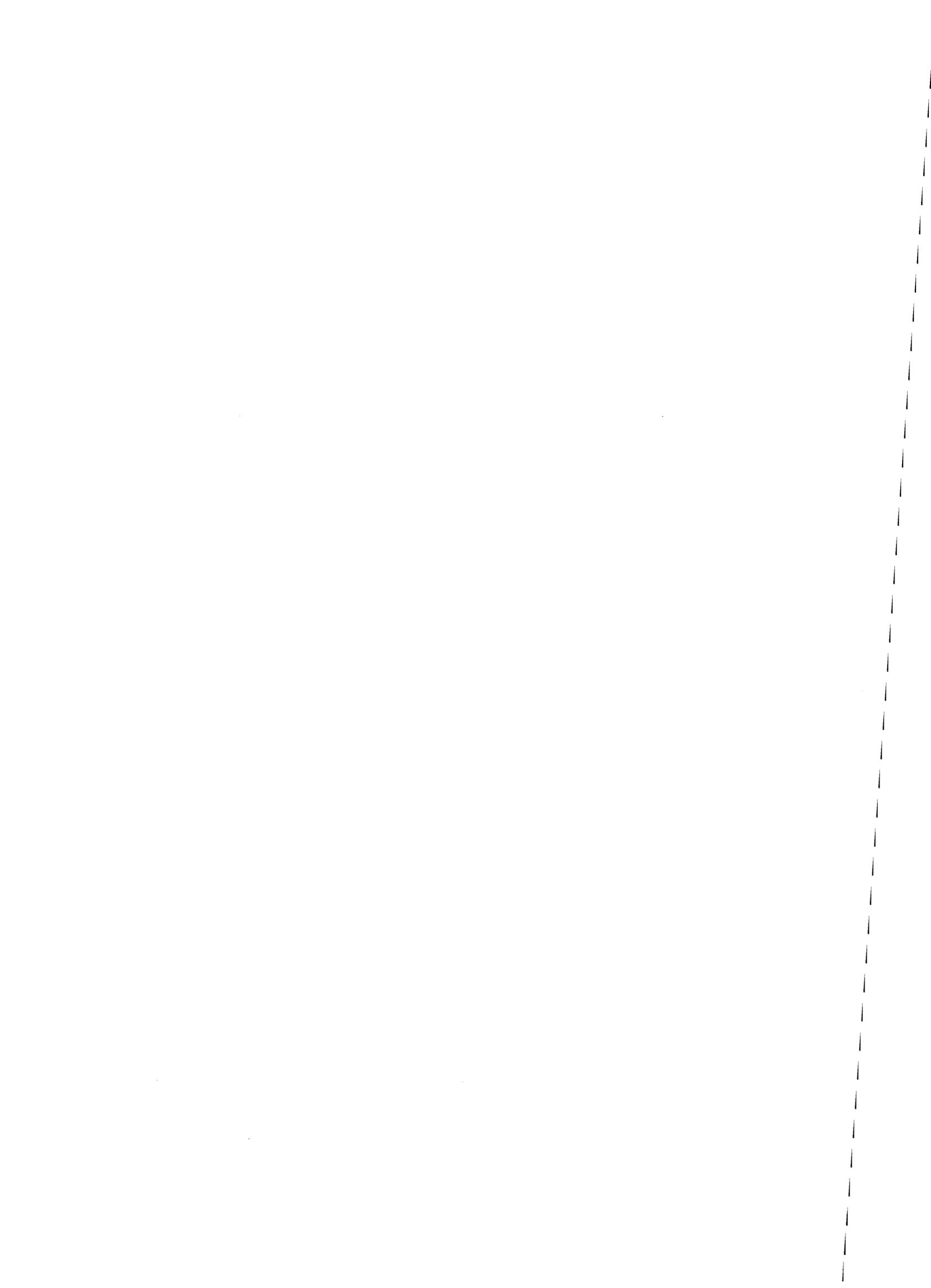


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1 INTRODUCTION

The Palfris marl formation at Wellenberg (Gemeinde Wolfenschiessen, NW) has been chosen by NAGRA as a potential host rock for the disposal of low- and intermediate-level radioactive waste, L/ILW (NAGRA 1994). In the coming years it is planned to carry out a series of performance assessment studies which form an important and integral part of the procedures for obtaining the necessary authorisations for the realisation of the repository. Certain critical data will be required for these safety analysis calculations. One such data set is a sorption data base (SDB) for safety relevant radionuclides in the far-field. The purpose of this report is to describe the procedures used to generate a sorption data base appropriate for the in situ conditions existing along the different potential flow paths in an undisturbed Palfris marl host rock formation. (In another report (BRADBURY & BAEYENS 1997) the potential influence of a pH plume, originating from the cementitious near-field, on the radionuclide retention characteristics of marl is considered.)

Irrespective of the particular host rock and groundwater chemistries involved, the basic principles underlying our procedures for setting up sorption data bases are very similar. The emphasis may be different, the details may be different, but the overall approach is essentially the same. Thus, the methodology adopted here is very similar to that developed previously to generate a SDB for the cementitious near field of a L/ILW repository, described in BRADBURY & SAROTT (1994). The discussions and arguments given in Chapters 1 and 2, and sections 4.1 and 4.2 in that report are equally relevant and valid for the current work and will not be repeated here, although selected important topics may be reviewed from the specific point of view of marl.

The approach adopted here was to select the best available laboratory sorption data which we consider to be the most relevant to the Wellenberg marl/groundwater system. As discussed in BRADBURY & SAROTT (1994) many factors play a role in the choices made, but, without doubt, "expert judgement" is an important component in the process. These initial values are then tailored to the marl mineralogies and water chemistries corresponding to the individual flow systems as described in Chapters 5 and 6 before finally being modified (see Chapter 7) to provide "in situ values", Chapter 10. This

SDB contains realistic sorption values applying to the in situ conditions in the Palfris marl formation.

An important aim of this work is to document the sources of sorption data used and, in particular, the processes by which data selections were made. The main guiding principles here are "transparency" and "traceability". The documentation will be such that any third party now, or in the future, can see clearly where the laboratory measured sorption data came from, why they were selected and how they were modified to correspond to the various specific "in situ" conditions. It should be possible, from the information provided, to make an independent judgement as to the "quality" of the selected data. Inherent within this whole process is also the justification for, and defensibility of, the selected values.

In addition to the usual single distribution ratio approach, there is an increasingly positive trend in radioactive waste management towards trying to understand sorption processes via mechanisms, and describing these mechanisms in terms of models which can be incorporated into computer codes. Wherever possible we will draw on this small but steadily increasing body of information to either directly calculate sorption values under the appropriate condition where confidence in the sorption model is justifiably high, or, use the basic model concepts as an additional aid in the selection of data.

2. MINERALOGY OF THE MAJOR FLOW PATHS

2.1 Simplified major mineralogy

MAZUREK (1994) describes the dominant flow paths in the Palfris marl formation and classifies them into three broad types viz. cataclastic zones (type 1), thin discrete shear zones (type 2), and jointed calcareous marl or limestone layers (type 3). The conceptual models of these zones are shown in Figures 1 to 3. Each of these water conducting zones or layers is further defined in terms of its geological features and characteristic mineralogical compositions. We have grouped the eleven rock compositions given into four classes, MIN-A to MIN-D, within which the mineralogies are the same or very similar. These classes are listed below together with the simplified mineralogies used later to scale sorption measurements, see Chapter 5. The geological features included in each class are given using the same nomenclature.

MIN-A

Fractured wall rock: Porosity ~3-4%, water conducting feature type 1

Mean wall rock: Porosity ~2%, water conducting feature type 2

Simplified mineralogy: ~53%, calcite/ankerite/dolomite
 ~31%, clay minerals
 ~14%, quartz

MIN-B

Argillaceous marl: Porosity ~3%, water conducting feature type 2

Argillaceous marl: Porosity ~3%, water conducting feature type 3

Argillaceous skin: Porosity ~2%, water conducting feature type 2

Fault gouge: Porosity ~10%, water conducting feature type 1

Simplified mineralogy: ~42%, calcite/ankerite/dolomite
 ~40%, clay minerals
 ~16%, quartz

MIN-C

Calcite/marl limestone: Porosity ~0.8%, water conducting feature type 1

Calcite/marl limestone: Porosity ~0.8%, water conducting feature type 3

Simplified mineralogy: ~71%, calcite/ankerite/dolomite

~16-17%, clay minerals

~10%, quartz

MIN-D

Fracture/vein infill: porosity ~0.8%, water conducting feature type 1

Calcite shear zone: porosity ~1%, water conducting feature type 2

Vein infill: porosity ~1%, water conducting feature type 3

Simplified mineralogy: ~95%, calcite

~5%, quartz

Note: The clay minerals are dominated by illite and illite/smectite mixed layers and chlorite.

2.2 Iron(hydr)oxide content of marl

Mineralogical analysis of marl samples have shown that the total iron content can be up to ~ 30 mg Fe g⁻¹ marl (MAZUREK, pers. comm.). Whether this iron is important for sorption processes or not depends upon its chemical and physical form and also upon its accessibility within the marl. Iron can be present as (hydr)oxides, within ankerite (Ca,Mg,Fe)CO₃, as pyrite and as lattice cations within clay minerals.

The results from a series of standard iron extraction procedures for amorphous iron and total iron on crushed Valanginian marl samples from Oberbauenstock (particle size <63 μm), yielded total extractable Fe levels of ~ 0.9 mg g⁻¹ (TITS et al. 1998). Thus, although iron (hydr)oxides appear to be present in marl, their levels are low and, even assuming that they have surface areas similar to hydrous ferric oxides (~ 600 m² g⁻¹), their surface area is only ~0.5 m² g⁻¹ compared to the total N₂-BET surface area of crushed marl of ~5 m² g⁻¹, see Table 3b. For marl samples containing only small quantities of clay minerals,

iron (hydr)oxides could become an important sorbent especially if they were to be present as amorphous coatings on mineral surfaces (JENNE 1977; BRADBURY & BAEYENS 1993). However, the different types of marl occurring along and within the active flow regions have not been analysed in sufficient detail for us to make any quantitative estimates of the importance of sorption reactions on iron (hydr)oxides on the overall sorption behaviour of marl. Consequently, Fe-oxides have not been considered further in this report, but it should not be forgotten that under certain circumstances their contribution to sorption could be significant. Thus the approach taken is a conservative one.

It is worth noting that up to an order of magnitude more iron could be extracted from decarbonated marl, or when the extraction procedure involved long times at pH values between 4 and 5 (TITS et al. 1998). This "additional Fe" is likely to have arisen from ankerite, or the oxidation of pyrite or even the partial dissolution of the clay mineral lattice. At pH values in the range 7 to 8 most of the pyrite in marl is armoured with calcite (BLÄSI, pers. comm.) and the ankerite is only sparingly soluble so that such potential sources of iron would not be available under normal circumstances. In addition, at the Eh values typical for the Palfris marl (NAGRA 1997) pyrite is most probably stable (GARRELS & CHRIST 1975).

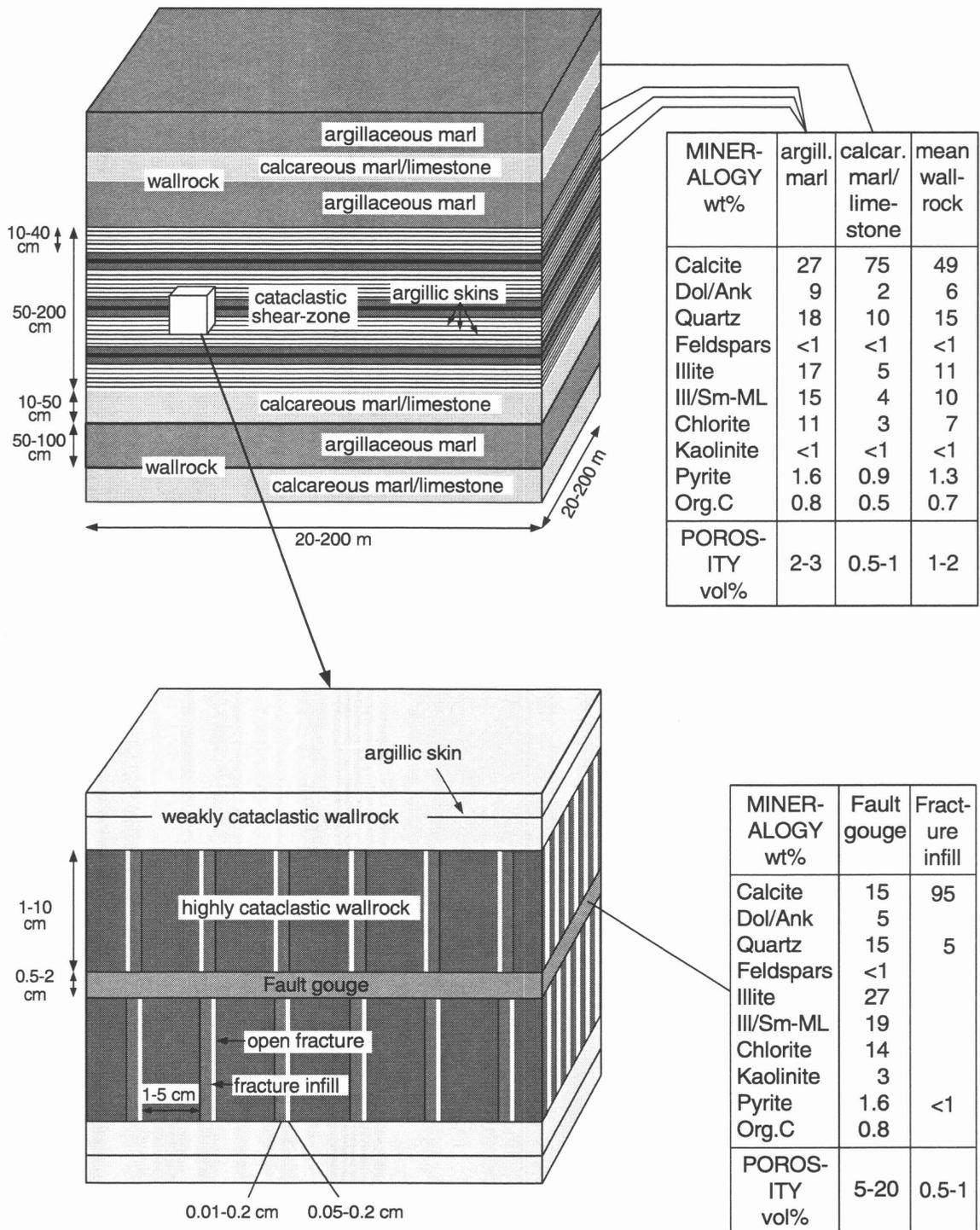


Figure 1: Conceptual model of cataclastic zones (water-conducting feature type 1), comprising geometric, mineralogic and porosimetric parameters. (Taken from MAZUREK 1994.)

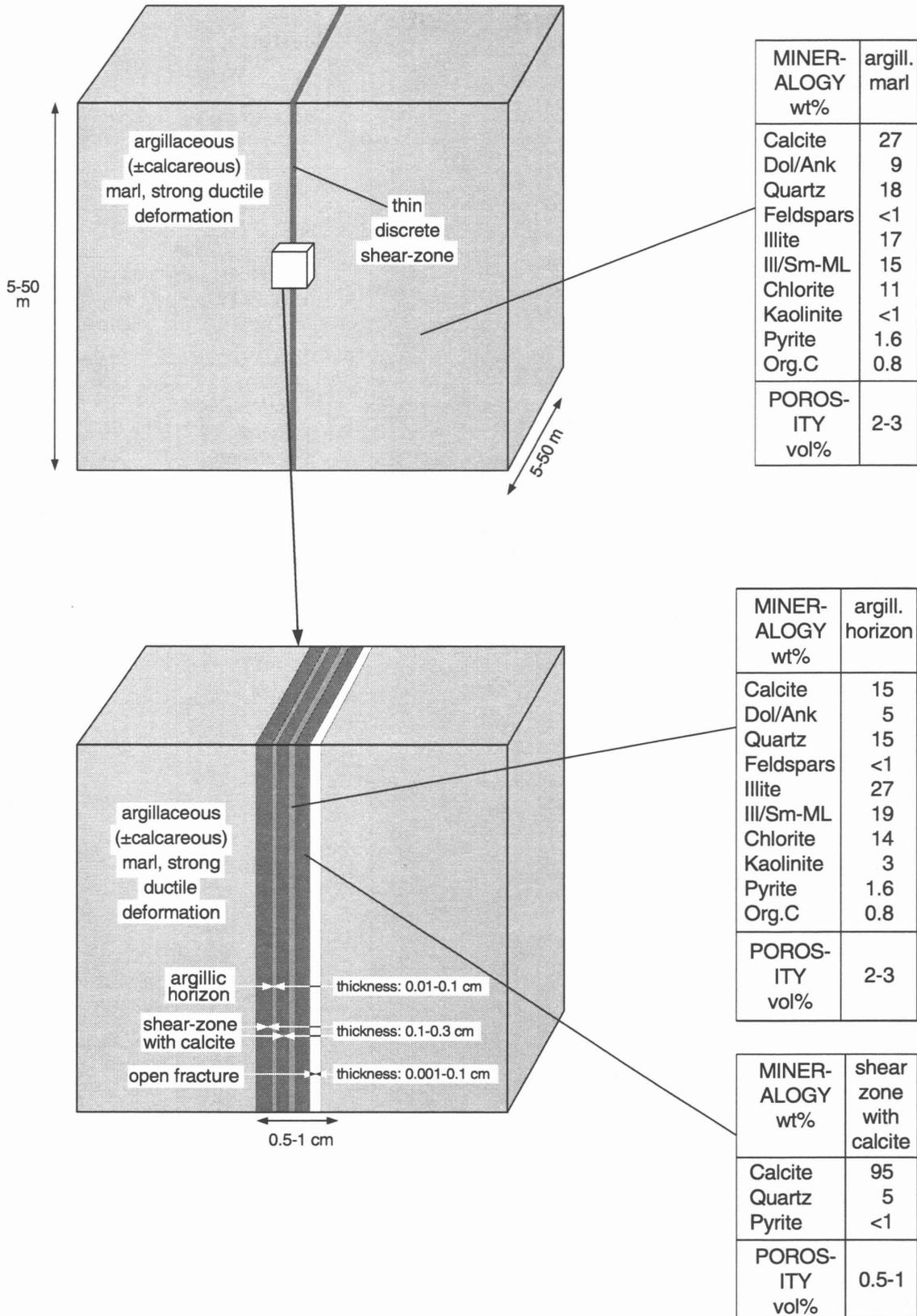


Figure 2: Conceptual model of thin discrete shear-zones (water-conducting feature type 2), comprising geometric, mineralogic and porosity data from MAZUREK 1994.)

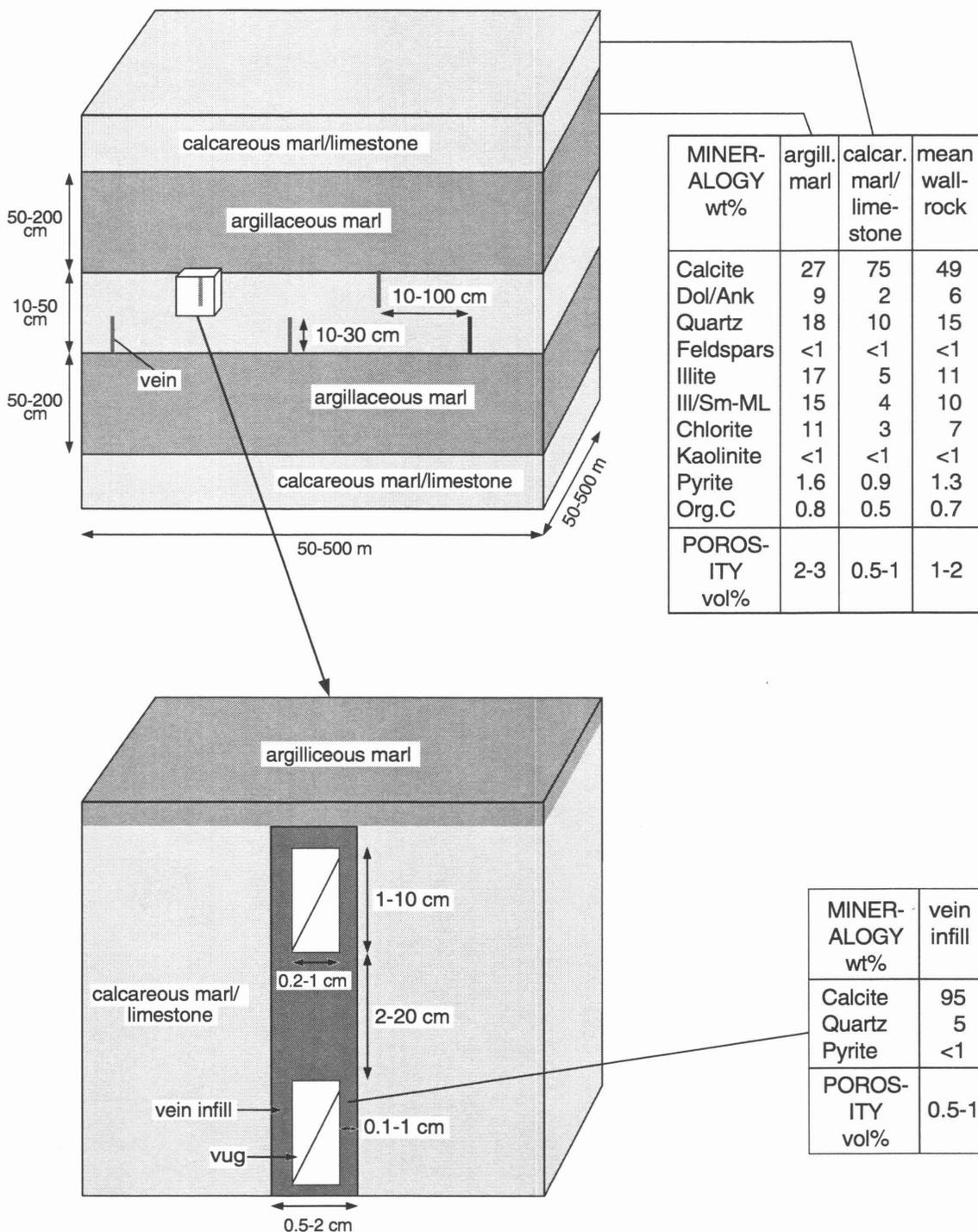


Figure 3: Conceptual model of joined calcareous marl/limestone layers (water-conducting feature type 3), comprising geometric, mineralogic and porosimetric parameters. (Taken from MAZUREK 1994.)

3 REFERENCE WATER CHEMISTRIES

3.1 NaHCO₃- and NaCl-type waters

Two dominant groundwater types have been sampled in the Palfris marl formation at Wellenberg. The first are NaHCO₃-type waters which are predominantly associated with high water yielding regions in the upper part of the marl formation and have dissolved solid contents of up to ~ 2 g L⁻¹. The second are NaCl-type waters occurring at depth in zones of very low water flow. These waters are relatively highly mineralised containing ~ 13 g L⁻¹ total dissolved solids of which ~ 7 g L⁻¹ is chloride (NAGRA 1997).

Based on water samples from boreholes drilled at Wellenberg (BAEYENS & BRADBURY 1991a; BLASER 1993; PEARSON 1994) and laboratory investigations (BAEYENS & BRADBURY 1991b, 1994) reference water chemistries for these two water types were developed (NAGRA 1997). The main cation and anion concentrations are summarised in Table 1. Although significant SO₄²⁻ concentrations are given for both reference waters, there is an increasing body of evidence which suggests that the SO₄²⁻ concentrations found in waters extracted from boreholes at Wellenberg and used to generate these water compositions may be artefacts, arising from the oxidation of aqueous sulphur species or pyrite, see PEARSON & SCHOLTIS (1994) and BAEYENS & BRADBURY (1994). The results from a long term down hole monitoring study of water chemistries tend to support the above, in that the measured concentrations of SO₄²⁻ continuously decrease with time (DEGUELDRE et al. 1994a).

3.2 Organics

Marl may contain up to ~ 2 wt.% solid organic matter (BURGER 1982,1985). Laboratory experiments (BAEYENS & BRADBURY 1991b; TITS et al. 1993) have shown that only a small fraction of the solid organic matter (~ 0.1 mg g⁻¹ marl, representing < 1% of the available solid organic matter) is soluble in the pH range from neutral to ~9.5. Organic ligands can undergo complexation reactions with radionuclides, thereby potentially influencing radionuclide sorption properties adversely.

Table 1: Marl reference groundwater compositions (NAGRA 1997).

	NaCl-type water pH= 6.7 Eh= -310 mV	NaHCO ₃ -type water pH= 8.3 Eh= -310 mV
Cations	Concentration (M)	Concentration (M)
Li	1.3 x 10 ⁻⁴	1.4 x 10 ⁻⁵
Na	1.9 x 10 ⁻¹	1.8 x 10 ⁻²
K	6.0 x 10 ⁻⁴	4.6 x 10 ⁻⁵
Rb	1.5 x 10 ⁻⁶	1.2 x 10 ⁻⁶
Cs	9.3 x 10 ⁻⁷	7.5 x 10 ⁻⁷
NH ₄ ⁺	5.6 x 10 ⁻⁵	3.3 x 10 ⁻⁵
Mg	4.8 x 10 ⁻³	4.0 x 10 ⁻⁵
Ca	6.2 x 10 ⁻³	5.0 x 10 ⁻⁵
Sr	5.8 x 10 ⁻⁴	5.7 x 10 ⁻⁶
Ba	-	4.6 x 10 ⁻⁷
Mn	1.4 x 10 ⁻⁵	2.0 x 10 ⁻⁷
Fe	6.6 x 10 ⁻⁷	1.0 x 10 ⁻⁵
Ni	-	1.3 x 10 ⁻⁷
Cu	-	1.3 x 10 ⁻⁷
Zn	-	5.4 x 10 ⁻⁷
Cd	-	8.9 x 10 ⁻¹⁰
Pb	-	2.4 x 10 ⁻⁸
Al	-	3.2 x 10 ⁻⁵
Anions		
F ⁻	2.0 x 10 ⁻⁴	9.4 x 10 ⁻⁴
Cl ⁻	2.0 x 10 ⁻¹	2.6 x 10 ⁻⁴
Br ⁻	1.2 x 10 ⁻³	2.9 x 10 ⁻⁶
I ⁻	2.7 x 10 ⁻⁴	1.3 x 10 ⁻⁵
P	1.2 x 10 ⁻⁵	2.4 x 10 ⁻⁶
SO ₄ ²⁻	< 10 ⁻⁶	< 7 x 10 ⁻⁵
Se	-	7.9 x 10 ⁻⁹
HCO ₃ ⁻	1.3 x 10 ⁻²	1.6 x 10 ⁻²
CO ₃ ²⁻	-	3.0 x 10 ⁻⁴

The extent of this influence depends on the types of organic ligand present, their concentrations and their complexation constants with each specific radionuclide. In view of this, a series of laboratory investigations (TITS et al. 1993) was carried out to determine the complexation characteristics of the dissolved organic carbon (DOC) extractable from marl samples SB1-203.9b, SB1-387.43a and SB1-1031.04b (MAZUREK et al. 1994). One of the main conclusions drawn from this work was that the soluble component of the solid organic matter was not composed of humic substances. Complexation constants and capacities determined by the Schubert method (SCHUBERT & LINDENBAUM 1952) for UO_2^{2+} indicated that the DOC comprised predominantly of small organic molecules with complexing properties similar to phthalic acid (1,2-benzenedicarboxylic acid).

The observations made during the long term in situ water chemistry monitoring programme carried out at Wellenberg in boreholes SB1 and SB6 (DEGUELDRE et al. 1994a), indicated that the DOC levels in NaHCO_3 -type waters are low ($\sim 0.5 \text{ mg L}^{-1}$). This, combined with the laboratory results given above, leads to the preliminary conclusion that the low concentrations of small organic molecules in the marl groundwaters are unlikely to have any adverse influence on radionuclide sorption. (However, further investigations over a wider range of conditions are required to check this.) Since the compositions of the marls in contact with NaCl -type waters are similar to those in contact with NaHCO_3 -type waters, we would argue that the above conclusion is also valid for deep marl groundwaters. In addition, the NaCl -type waters have a pH which is ~ 1.5 units lower than the NaHCO_3 -type waters which would imply, if anything, a weakening of any potential complexation reactions.

3.3 Redox

From the same long term in situ groundwater monitoring programme mentioned above, DEGUELDRE et al. (1994a) were also able to show that the initially measured redox potential of the groundwater fell continuously with time reaching a long term stable Eh value of $-320 \pm 30 \text{ mV}$. A value within this range i.e. -310 mV was chosen for both NaHCO_3 and NaCl reference waters (see Table 1), and implies that the in situ conditions are relatively strongly reducing.

Redox is an extremely important water chemistry parameter where sorption is concerned. It is difficult to measure in the field and stable reducing conditions are relatively difficult to reproduce in the laboratory. The latter accounts for the scarcity of sorption data available in the open literature measured under Eh conditions comparable with those given above. In the following we have implicitly assumed an Eh of -310 mV and attempted to discuss sorption in terms of those species likely to be stable under these reducing conditions. Although redox is not always specifically mentioned, the reducing conditions assumed to exist in the undisturbed marl far-field have influenced the sorption values selected.

3.4 Colloids

Long term down hole monitoring of the NaHCO₃-type water (DEGUELDRE et al. 1994a), revealed that the colloid population in the size range from 10 to 1000 nm reached a steady state value corresponding to an upper estimated limit for their concentration of 0.1 mg L⁻¹. The colloids in this system are mainly composed of illite, illite/smectite mixed layer and chlorite clay minerals (DEGUELDRE et al. 1994a).

For the NaCl-type groundwater, where the ionic strength and Ca concentrations are an order of magnitude higher, a considerably smaller colloid population might be expected since flocculation and attachment are favoured in systems where these parameters are large.

In order to estimate the potential influence of colloids on radionuclide transport we use similar arguments to those given in BRADBURY & SAROTT (1994) Chapter 12. In particular the relation,

$$m_c > \frac{V_{\text{pore}}}{R_{d,c}} \quad (1)$$

where

m_c = total mass of colloids present in solution per kg of rock

V_{pore} = pore volume per kg of material, L kg⁻¹

$R_{d,c}$ = radionuclide distribution ratio on the colloids, L kg⁻¹

is used as a condition on the value of m_c for judging whether colloids can have an impact on sorption. A typical value for V_{pore} in the fault gauge, where the porosity is approximately 10% (section 2.1), is $\sim 0.05 \text{ L kg}^{-1}$. (The density of the fault gauge was taken as $\sim 2 \text{ kg L}^{-1}$.) The selection of an $R_{d,c}$ value is somewhat tricky, but even for the most strongly sorbing safety relevant radionuclides, an extreme upper limit for colloids in the lower size bracket ($\sim 20 \text{ nm}$) would be an $R_{d,c}$ value of $\sim 10^6 \text{ L kg}^{-1}$ (see for example DEGUELDRE 1994). If we make a further conservative assumption that all colloids making up the concentration of 0.1 mg L^{-1} are in this size range, then putting these values into Eq. (1) yields a value for m_c of $5 \times 10^{-8} \text{ kg per kg rock}$, or, a colloid concentration of $\sim 1 \text{ mg L}^{-1}$. Even for the very conservative values taken, 1 mg L^{-1} is an order of magnitude higher than the measured in situ value for a NaHCO_3 -type groundwater. On this basis we would therefore conclude that colloids do not influence radionuclide migration in the marl system. However, an implicit assumption in the above argument is that sorption is reversible.

Deep slow moving groundwater systems are in general geochemically stable because of their long evolution times. They exhibit stable water chemistries and stable colloid populations. Rock/water interactions such as primary mineral dissolution, the build up of supersaturations with respect to secondary minerals and precipitation and growth of secondary minerals belong to a much earlier stage in their history. The weathering reactions, precipitation reactions and processes such as Ostwald ripening¹ (see for example STEEFEL & VAN CAPPELLEN 1990) which had previously determined the colloid size ranges and concentrations along the flow path have virtually ceased. The groundwater and rock mineralogies have reached a stage where changes are only occurring very slowly. However incorporation processes such as Ostwald ripening and/or colloid agglomeration could still be occurring, albeit very slowly. These processes might lead to otherwise reversibly sorbed radionuclides on the colloids becoming trapped. Since the radionuclides will remain trapped as long as the newly formed colloids remain intact, they may be considered to be "irreversibly sorbed". Release would then only occur when the larger particles, for whatever reason, become unstable and disintegrate or dissolve.

¹ Ostwald ripening is the process whereby smaller crystals with higher solubility dissolve and reprecipitate as larger crystals.

Ostwald ripening and colloid agglomeration, must, by definition, both lead to an increase in size of the colloidal material which increases the probability of them becoming trapped or filtered out of the moving groundwater. If radionuclides have become incorporated into the colloid structure during either its formation or subsequent growth then trapping/filtration is a permanent radionuclide removal mechanism which may have significant positive effects on the overall radionuclide transport.

Although an unambiguous answer to the "colloid question" is not feasible at this stage, we would argue, on the basis of the discussion given above and for the particular marl system presented here, that the balance of evidence indicates that irreversible uptake processes on colloids are not significant. If, however, irreversible sorption processes are invoked for colloids as a worst case scenario, then they must also be invoked for the immobile solid phases since there is no evidence to suggest that the sorption mechanisms are or should be different. It would be illogical to apply irreversibility in one case and not in the other.

3.5 Sorption reversibility/irreversibility

The question as to whether sorption is reversible or not is a generally important one in radioactive waste disposal. In the following a brief discussion with special reference to colloids is given.

On experimental time scales measured in months, it is virtually impossible to distinguish between irreversible sorption and very slow desorption kinetics. Thus, while it is possible to say that sorption is reversible within experimental error, it is not generally possible to show unambiguously that it is irreversible because the question is always, "On what time scale?". Very slow desorption kinetics can easily be interpreted as an "irreversible" uptake. (See for example COMANS et al. 1991.) In some cases the sorption of a radionuclide may be followed by some sort of surface re-arrangement processes (surface precipitation, incorporation into a hydrolysed surface region, formation of chelated complexes on the surface, or formation of very near surface solid solutions) which would make the radionuclide release kinetics considerably slower than the sorption kinetics.

The authors have carried out desorption measurements at pH values of 4.2, 6.7 and 8.3 for Ni sorbed at trace concentrations on Na-montmorillonite suspensions ($\sim 1 \text{ g L}^{-1}$) in which the particle sizes were less than 500 nm. Desorption experiments were carried out in the standard manner by reducing the aqueous radionuclide concentration under constant water chemistry conditions. The desorption behaviour was not straightforward, and only a simplified outline of the findings will be given here. At low pH values, where cation exchange was interpreted as being the dominant sorption mechanism, desorption was rapid and reversibility could be demonstrated, see Figure 4a. As the pH was increased, and the dominant mechanism changed to surface complexation (see BRADBURY & BAEYENS 1995), the extent and rates of desorption decreased significantly. The pattern was always similar in that a rapid initial desorption was followed by a much slower second stage of desorption. The quantity desorbed in the first stage, and the kinetics of the second, both decreased rapidly with increasing pH, see Figures 4b and 4c. At pH values > 9 , hardly any desorption occurred in the fast stage and thereafter the desorption rates were too slow to be measured over experimental times of a few months.

Following these "standard desorption tests" another type of experiment was carried out in which the method was to desorb, not by means of reducing the aqueous nuclide concentration, but by reducing the pH to a value lower than that at which sorption took place. The criterion for reversibility was then that the distribution ratio measured in the desorption test lay on the previously determined sorption edge ($\log R_d$ versus pH, see for example BAEYENS & BRADBURY 1995b). The measurements showed that the system behaved reversibly as a function of pH in accord with the equilibrium thermodynamic surface complexation model used to describe the data. Even so, these results do not prove unambiguously that the radionuclide uptake onto montmorillonite was reversible or not under the initial conditions.

Only when the radionuclide uptake processes are adequately understood can defensible statements regarding reversibility/irreversibility be made.

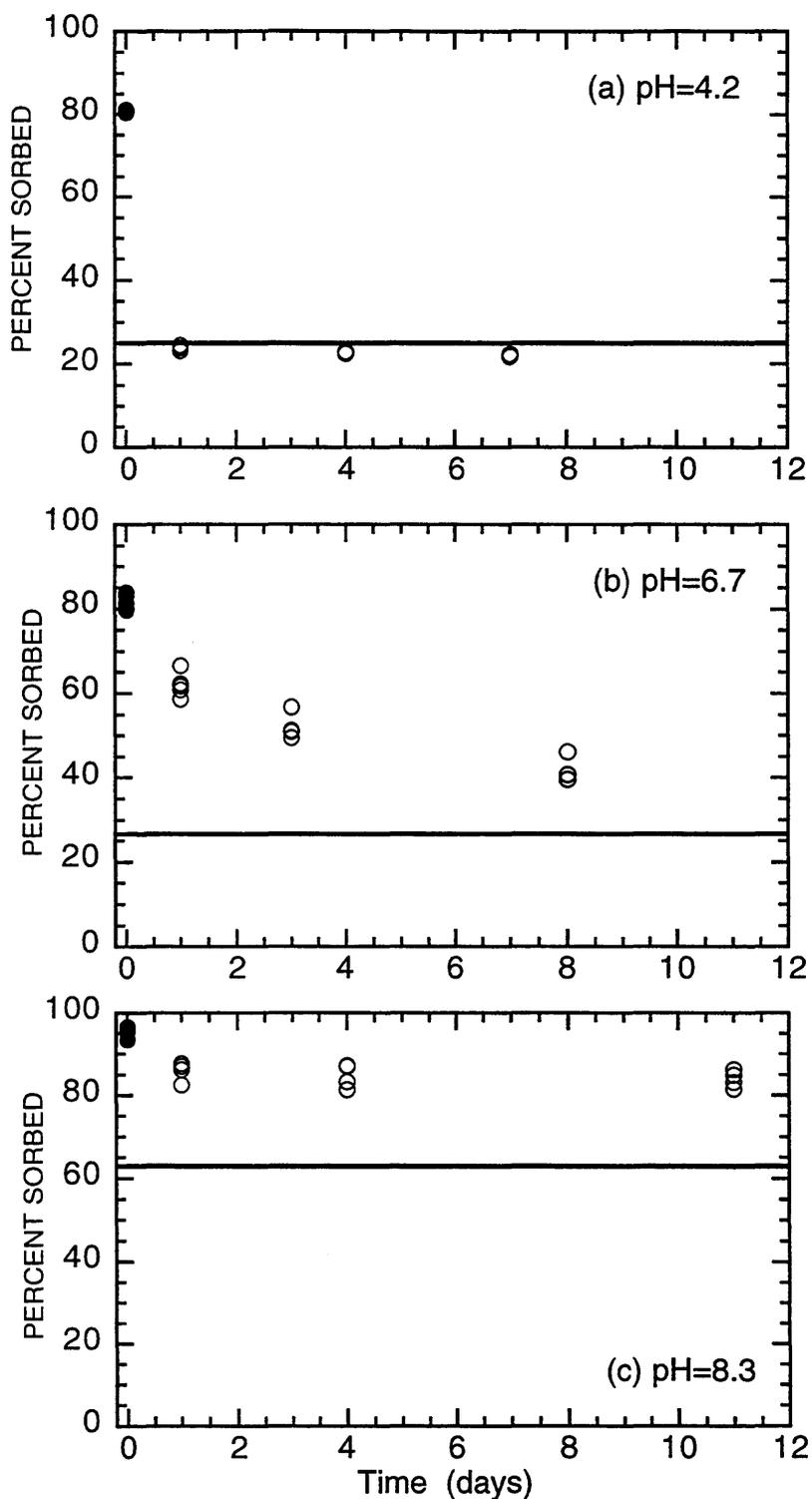


Figure 4: Sorption (●) and desorption kinetics (○) of Ni on conditioned Na montmorillonite at different pH values. The solid lines represent the % of Ni remaining sorbed after desorption under fully reversible conditions.

4 THE BATCH SORPTION TECHNIQUE

4.1 General remarks

Invariably, whenever laboratory generated sorption data are used in safety analyses, the question arises as to whether these data are appropriate for the "in situ" conditions. The answer to this question mainly revolves around the influence of two of the experimental conditions associated with batch sorption tests, namely, the solid to liquid (S:L) ratio and the use of crushed rock.

Generally, these two parameters are chosen for experimental convenience and, without further justification, batch tests can, at best, only claim to reflect the chemical conditions existing in the host rock formation. To a first approximation the liquid volumes available in an intact rock are comparable to the local porosity, normally a few volume percent. Even for flow paths containing fracture infill, porosities are not likely to exceed 20 vol.%. Solid to liquid ratios used in laboratory tests are often orders of magnitude smaller. Also, crushed rock can clearly not be taken a priori to be representative of bulk rock.

Since the major source of sorption data used in safety analyses is from batch type measurements on crushed rock carried out at some large, arbitrarily chosen S:L ratio, it is certainly worthwhile taking a closer look at the potential influence of these two variables.

4.2 Solid to liquid ratio

The potential influences of S:L ratio on laboratory sorption measurements have been discussed previously in BRADBURY et al. (1990) and BRADBURY & SAROTT (1994). The main conclusion reached was that there is no effect of the S:L ratio per se on sorption. We would maintain that this conclusion is generally valid and consequently also applies to marl. However, because there still seems to be a continuing confusion about the "solid to liquid ratio effect", and because this "effect" still appears to be used as an argument against the acceptability and relevance of batch sorption data used in safety analysis, we will briefly re-state the arguments here for completeness.

4.2.1 Water chemistry

Disequilibrium between solid and liquid phases is more often than not a starting condition in the majority of batch tests. Hence, when the two phases are brought into contact with one another, interactions will occur until a steady state/equilibrium condition is established. The kinetics of this process will depend on the system in question and the arbitrarily chosen S:L ratio, and will involve not only the aqueous composition but also the solid phase. Any major compositional changes in the liquid phase are relatively easy to detect and quantify, but this may not be the case for background impurities which might be competitive with the low concentrations of radionuclides often used in the batch tests. Changes occurring in the solid phase associated with surfaces are much harder to recognise and quantify. Changes can be driven by either the liquid phase or by the solid phase or indeed by both, depending again largely on the S:L ratio.

The sort of effects which may occur are dissolution/precipitation reactions and sorption/desorption of major/minor components. A minor mineral phase may change from being saturated to unsaturated if the volume of liquid added is sufficient to completely dissolve it. Sorption/desorption of nuclides may take place to different extents on different sorption site types; cation exchange sites, frayed edge sites, strong and weak $\equiv\text{SOH}$ edge sites, leading to changes in water chemistry and occupancies on the solid phase. A particularly serious case would be when (unknown) background impurity concentrations of one or more metal species in the added solution were to be sufficient to saturate the strong $\equiv\text{SOH}$ type sites for example, thus blocking them in the subsequent sorption tests. (This effect is more likely at low S:L ratios.) Also, if the solid phase contains soluble organic matter, its concentration in solution will depend upon the S:L ratio and therefore influence the speciation and thereby the sorption. The pH of the starting solution may not be the same than that of the equilibrated one, and may be influenced by the S:L ratio as well. (The pH is not always reported or determined at the end of batch sorption tests.) When sorption is occurring by surface complexation, small changes in pH within the sorption edge (often in the pH range 5-9) can result in significant changes in sorption.

The above is by no means an exhaustive list. (See in addition McKINLEY &

JENNE 1991.) The effects described are mainly associated with changes in the solid and liquid phases resulting when the two are not initially at equilibrium, and where the new equilibrium established will be dependent to a greater or lesser extent on the S:L ratio. Differences in S:L ratios may lead to sorption studies being carried out on effectively different systems. The situation may be even worse if the chemistry is still evolving in time during the sorption tests.

4.2.2 Non-linear sorption

The second major reason why people have been misled into believing that there is a "solid to liquid effect" has, in our view, to do with the sorption measurements themselves. Virtually all of the studies in which a sorption dependency on S:L has been (apparently) found, have relied on isolated single measurements i.e. in experiments where the initial concentration of radionuclide has been fixed and the S:L ratio varied. Under these circumstances changes in distribution ratio with S:L ratio are entirely expected when the radionuclide is sorbing non-linearly, since the equilibrium concentrations at the different S:L ratios are different. Cause and effect have been confused. The effect is an apparently inexplicable dependency of sorption on S:L ratio, whereas the cause is the non-linearity of the sorption process itself, a well known and well documented process.

In addition, McKINLEY & JENNE (1991) quote cases where clear S:L effects appear to have been found, but point out that the sorption isotherms were incorrectly plotted in terms of the initial metal concentrations in the batch tests, instead of equilibrium concentrations. When the data are re-plotted in terms of equilibrium concentrations, then all of the measurements lie on the same isotherm as would be expected.

Thus, to conclude this section we would like to make the clear statement that the "S:L effect" on sorption measurements is an artefact and that in reality does not exist. An apparent dependency on the S:L ratio is only observed in batch sorption experiments which are not performed without due regard to the points mentioned above, or where the data reduction is carried out incorrectly.

4.3 Crushed rock

The vast majority of sorption data available in the open literature have been measured in the laboratory on rock samples which have been crushed to some degree. The rationale behind crushing is to make those internal pore surfaces, which are normally only accessible via diffusion, readily available as sorbing areas in batch tests. In this way sorption experiments can usually be completed on time scales of days rather than the months or years which would be required for determinations on intact rock via diffusion. Although in theory all sorption data could be generated from measurements on bulk rock samples, diffusion based sorption measurements remain the exception because of the time and resources required. Also, it should not be forgotten that in order to interpret such data a model is required, and the parameters might be model dependent whereas the direct measurement of distribution ratios is - per se - model independent.

Ideally, crushing merely leads to the exposure of internal sorption sites, which are present anyway, and allows their sorption characteristics to be measured conveniently, efficiently and relatively quickly over a wide range of conditions in batch tests. However, the question inevitably arises as to whether all of this surface area made available in the crushed rock really originates from the internal porosity. Additional sorbing surfaces (fracture surfaces) may be created during the crushing process, possibly leading to erroneously high sorption values. If anything, we would expect to measure larger values in the crushed rock, either because new surfaces have been created, or because closed porosity in the bulk specimen, which is normally inaccessible, has been exposed.

Minerals, depending on their hardness, crush down at different rates and to different degrees. Clay mineral components tend to occupy the lower end of crushed rock size distributions simply because of their fine grained nature. On the other hand, quartz and feldspar particles occupy the higher end of size distribution because of their hardness and originally coarse grain sizes. Thus in any mineral assemblage consisting of a mixture of clay minerals, quartz, orthoclase and calcite, it is often the case that clay minerals make the most significant contribution to the overall surface area although they may not be dominant in the mineralogical composition.

The relevance of laboratory sorption data, and the credibility of safety analysis calculations, are strongly dependent on whether data obtained on crushed rock are valid for intact rock (or whatever the form of the in situ rock). If the conclusion is that batch sorption data are not directly applicable, then some quantifiable and scientifically justifiable means must be found of making the conversion from "lab data" to "field data". This problem is addressed further in Chapter 7 where values for Lab -> Field transfer factors are given, and the question of the influence of new surfaces created during crushing (fracture surfaces) on sorption values is discussed.

5 CONVERSION FACTORS FOR LABORATORY SORPTION DATA: MINERALOGY

5.1 General

Experience shows that sorption values for all safety relevant radionuclides are not available from measurements made on host rock samples under the prevailing "in situ" groundwater chemistry conditions. Rather, the norm is that only a limited amount of such data is available. The rest (often the majority) must be obtained from other sources such as the open literature. The difficulty here is that the literature data were most probably measured under different conditions from those required. Therefore the problem is how to modify the literature data in a scientifically plausible and consistent manner so that they apply to the conditions in question. In the following sections we will outline the general methodology adopted and applied here to scale sorption values to the required mineralogy and water chemistry. An important component of this process is the application of knowledge regarding sorption mechanisms wherever this is appropriate.

5.2 Marl

As stated above, some data will be available on samples of the host rock, Palfris marl from Wellenberg in this particular case. The major mineral components in marl are clay minerals (notably illite, illite/smectite mixed layers and chlorite) and carbonates, see Chapter 2. For sorption occurring by cation exchange or surface complexation, the uptake of radionuclides is most likely to be dominated by the clay mineral components and, in general, will be proportional to the overall cation exchange capacity (CEC). The connection between sorption occurring via cation exchange and the overall exchange capacity is obvious. That there is a relation between sorption via surface complexation and the exchange capacity is perhaps less clear and exists because of the general observation that the surface complexation site capacity for many clay minerals is approximately 10% to 20% of the exchange capacity (GRIM 1953; YARIV & CROSS 1979; BAEYENS & BRADBURY 1995a).

In a series of experiments carried out at PSI, and later reported by WABER et al. (1994), cation exchange capacities on core material from boreholes SB1

and SB3 were determined using the nickel ethylenediamine method. (See for example BAEYENS & BRADBURY 1994.) A set of 20 determinations were made on samples chosen to cover most of the different types of marl within the Palfris formation. The relationship between the CEC and total clay mineral content of the samples is plotted in Figure 5.

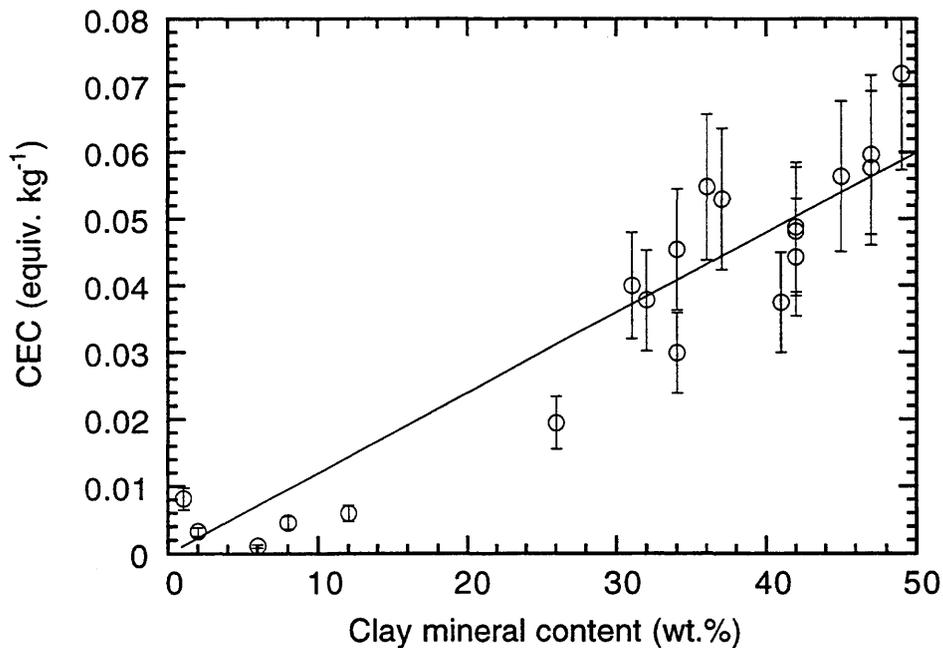


Figure 5: Correlation between CEC and clay mineral content for 20 samples selected from cores SB1 and SB3 drilled in the Palfris marl formation at Wellenberg.

On the basis of this plot we have assigned cation exchange capacities to the simplified mineralogies for the rock types grouped together in the categories MIN-A to MIN-C (Table 2). These CEC values can then be used as a basis for scaling sorption data, see Chapter 6. Note that the cation exchange capacities given in Table 2 for each of the simplified mineralogies listed, relate back to the mineralogies in the different flow paths, and hence to the information given in MAZUREK (1994). (To a first approximation we have assumed that no clay minerals are present in the MIN-D category of rocks and no CEC value was assigned.)

Table 2: Cation exchange capacities assigned to marl mineralogies in categories MIN-A to MIN-C (see section 2.1).

Marl category	Clay mineral content (wt %)	CEC (equiv. kg ⁻¹)
MIN-A	31	3.5 x 10 ⁻²
MIN-B	40	5 x 10 ⁻²
MIN-C	16-17	1.8 x 10 ⁻²

The data in Table 2 can be used to scale sorption data for different marl mineralogies where sorption is occurring predominantly on the clay mineral fraction by cation exchange or surface complexation. It is worth mentioning here that when sorption is viewed on this basis the wide range of mineralogies included in categories MIN-A to MIN-C should only exhibit sorption values differing by a factor of approximately three.

5.3 Illite

Illite, and illite/smectite mixed layers, make up the major clay mineral components in marl systems. Consequently, it is logical to look to illite as a source of sorption data, particularly when data measured directly on marl are sparse. Of course, such sorption data cannot be taken directly, and some sort of scaling is required. Again, in an analogous manner to that described above, we propose to use the CEC parameter as a means of scaling illite data so that they can be applied to the different marl mineralogies.

There is evidence in the literature which indicates not only that the above is a reasonable procedure but that it works practically. For example, BRADBURY & BAEYENS (1992) developed a two site cation exchange model to describe the non linear sorption of Cs using selectivity coefficient parameters deduced from literature data for illite. This model was used successfully to calculate the sorption measurements obtained for Cs in complex natural systems (marl, Grimsel granodiorite and Boom clay) where the main clay mineral in the rock was mica or illite.

Finally, we present here some as yet unpublished data from TITS et al. (1998)

showing nickel sorption isotherms on a marl and an illite equilibrated with a marl pore water composition described in BAEYENS & BRADBURY (1991b).

A marl sample from the Valanginian formation at Oberbauenstock (OBS-PSI-F4) was used and Ni sorption isotherms were measured at two different S:L ratios. In a separate series of experiments the Ni inventory of both solid phases was determined using diethylenetriamine-pentaacetate (DTPA) extractions at pH = 8.3 on the equilibrated marl and illite suspensions. The quantities of Ni extracted after 2 weeks contact with a 0.1 M DTPA solution was 4×10^{-5} mol kg⁻¹ for marl and 3.7×10^{-5} mol kg⁻¹ for illite. These inventories were taken into account in the calculations of the sorption isotherms.

The CEC of the marl and illite, determined using the nickelethylenediamine method, was $6.3 (\pm 0.2) \times 10^{-2}$ and $11.4 (\pm 0.3) \times 10^{-2}$ equiv. kg⁻¹, respectively. The data set for illite was scaled to the sorption measurements on marl via the ratio of their respective CEC values. The Ni sorption isotherms determined on marl at 2 different S:L ratios (open symbols) are shown in Figure 6. The scaled illite sorption values are represented by the filled circles. As can be seen, the isotherm predicted from Ni sorption measurements on illite is slightly conservative with respect to the real system.

The conclusion drawn here is that it is not only reasonable, but also justifiable, to deduce sorption values applicable to marl from measurements made on illite, via the procedure outlined above, provided that the main sorption mechanisms are cation exchange and/or surface complexation.

5.4 Calcite

There is a relatively large body of evidence (see for example: DAVIS et al. 1987; COMANS & MIDDELBURG 1987; WERSIN et al. 1989; MECHERRI et al. (1990); ZACHARA et al. 1991; CARROLL et al. 1992; STIPP et al. 1992; VAN CAPPELLEN et al. 1993) which indicates that carbonate minerals such as calcite, dolomite and ankerite can have a significant potential for the removal of radionuclides from solution.

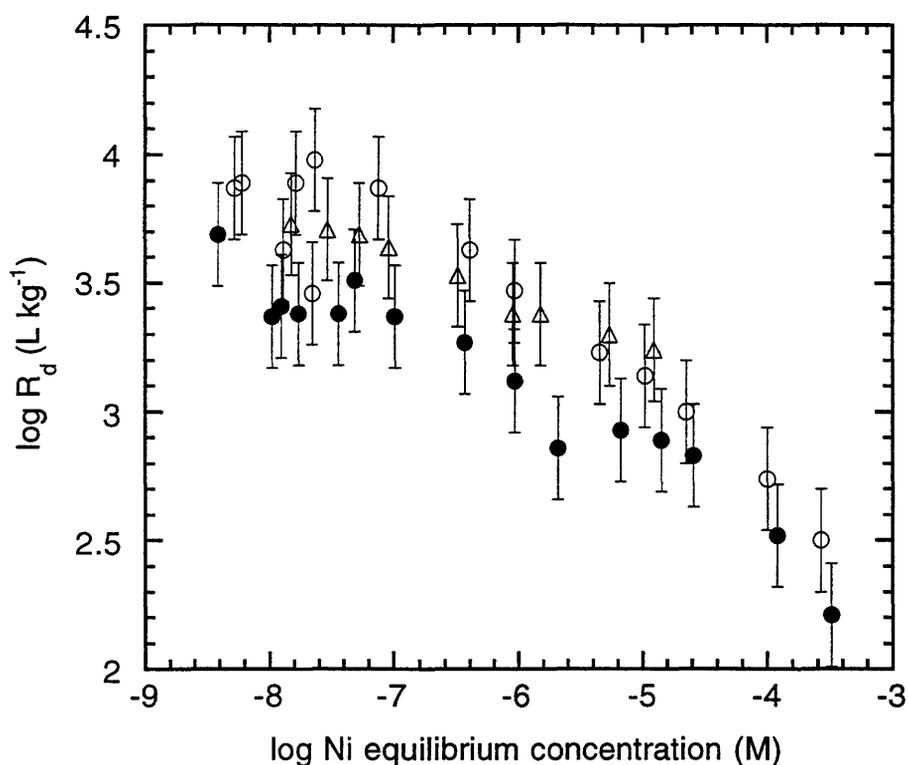


Figure 6: Ni sorption isotherms on marl, S:L=2.7 g L⁻¹ (O); S:L=23 g L⁻¹ (Δ). Scaled sorption data for illite (●). (TITS et al. 1998)

We have deliberately refrained from using the term "sorption" here since the mechanism of radionuclide uptake is often unclear. Proposed mechanisms have been variously described in terms of one, or combinations of the following: sorption, surface precipitation, co-precipitation, formation of solid solutions, lattice penetration plus recrystallisation, lattice penetration by diffusion, diffusion into a hydrated surface layer etc. The mechanism may also be radionuclide dependent. Although "sorption values" may be available, modifying these to apply to our specific conditions is difficult because of the relative large uncertainties concerning mechanisms.

In view of the above we suggest scaling literature sorption measurements on carbonates by the most straightforward method i.e. on the basis of the carbonate content of the simplified marl mineralogies given in Chapter 2. For the marl mineralogies classified under MIN-D, only sorption data on carbonates are relevant.

6 CONVERSION FACTORS FOR LABORATORY SORPTION DATA: SORPTION MECHANISMS AND WATER CHEMISTRY

6.1 General

The sorption data available in the literature are likely to have been measured for water compositions different from those defined for the reference waters in Table 1. If the literature values are to be used for the reference water conditions, corrections for the differences in water compositions should be made. This can only be done when the sorption mechanism and a model with the corresponding parameter values are available. Unfortunately, for most of the radionuclides of interest a quantitative mechanistic understanding of sorption is lacking. Nevertheless, some means needs to be found for quantifying the influence of the water compositions on the sorption values, and, since quantitative sorption models are not yet available, this can only be done in a semi-quantitative manner involving a number of assumptions. At the very least this enables an appreciation of the importance of the water composition to be realised to a first approximation.

In general, it is important to try to identify the most probable dominant sorption mechanism for each particular radionuclide since the influence of water chemistry on sorption is strongly linked to the sorption mechanism. Hence, both are taken together here. In the following we have chosen to discuss sorption in terms of two mechanisms: cation exchange and surface complexation. The interpretation given and scaling methodology suggested are based on this approach to sorption.

The processes by which radionuclides are taken up at carbonate surfaces are insufficiently well understood at the moment for us to be able to estimate the influence of water composition on sorption values. Consequently, no correction factors accounting for speciation differences were applied to sorption data on carbonates.

6.2 Sorption via cation exchange

The cation exchange mechanism applies predominantly to clay minerals

which in the marl system are dominated by illite, illite/smectite mixed layers and chlorite.

As mentioned previously, a cation exchange sorption model has been developed to describe the sorption of Cs on rock types where the major sorbing mineral component is illite, BRADBURY & BAEYENS (1992). Selectivity coefficient data have also been deduced for Ca, Sr and Na from experimental data on marl, see BAEYENS & BRADBURY (1991b, 1994). We have confidence in these parameters and models since they have been verified over a wide range of different conditions. Thus, sorption values on marl for the alkali and alkali earth metals such as Cs and Sr can be calculated simultaneously with the sorption model specifically for the reference water compositions, taking into account natural background concentrations of any inactive isotopes where necessary.

6.3 Sorption via surface complexation

The surface complexation mechanism predominantly applies here to the clay minerals in marl and to any metal (hydr)oxides present. Ionic strength and differences in major cation concentrations are not first order effects influencing sorption by surface complexation since cations such as Ca, Sr, Mg, Na, K are not generally competitive with the specifically sorbing heavy metals, transition metals, lanthanides and actinides for the surface sites.

6.3.1 Sorption of anionic species

Anions can sorb onto surfaces by undergoing ligand exchange with the hydroxyl groups of the $\equiv\text{SOH}$ type. Considerably less is known about anion uptake by surface complexation than cation uptake. Where anion sorption behaviour has been studied at trace levels in the concentration region below $\sim 10^{-6}$ M (see for example STUMM et al. 1980; SIGG & STUMM 1981; MOTTA & MIRANDA 1989) two clear features have emerged: (i) sorption increases with decreasing pH and (ii) sorption exhibits a Langmuir type behaviour. Iron (hydr)oxides, in particular, have a considerable potential for removing certain anionic species from solution (DZOMBAK & MOREL 1990).

The effect of water composition on the uptake of anionic species is likely to be

weak. However, there could be an influence on the sorption of anions such as SeO_3^{2-} and MoO_4^{2-} via competitive reactions from Cl^- , F^- and SO_4^{2-} (if present). The influence of such groundwater anions will only become important when they are able to saturate the available surface sites. All the evidence available on a large variety of minerals tends to indicate that sorption of Cl^- and F^- is either very weak or zero. The different Cl^- and F^- concentrations in the two reference waters are therefore unlikely to have an influence on anion sorption. The parameter of most importance is the pH.

The sorption characteristics of HCO_3^- and CO_3^{2-} on clay minerals is unknown, and hence their potential competitive effect on sorption of anionic species is difficult to quantify. In the pH range under consideration (6.5 to 8.5) the indications from the literature are that the sorption of all anions is weak. Thus we will assume to a first approximation that any competitive effects can be neglected.

6.3.2 Sorption of cationic species

Generally speaking, pH is probably the single most important parameter influencing the uptake of aqueous metal species via a surface complexation mechanism and can have an enormous influence on the magnitude of sorption. In the majority of cases the pH at which sorption data are available in the literature will be different from the pH values of the reference waters.

We have chosen three pH related aspects, which, in a simplified view of the system, are most likely to have potential influences on sorption. These are: (i) metal hydrolysis reactions as a function of pH, (ii) variation of sorption at trace levels ($< 10^{-6}$ M) as a function of pH (protonation/deprotonation reactions of surface $\equiv\text{SOH}$ sites), and (iii) the variation of $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentrations as a function of pH at calcite saturation and the formation of metal carbonate complexes. As stated previously, the treatment given here can only be regarded as semi-quantitative.

We can treat points (i) and (ii) together. When cation sorption at trace concentrations is investigated as a function of pH in the range from approximately 2 to 9, it is almost invariably observed that a strong increase in

sorption occurs. One of the main reasons for this is that the $\equiv\text{SOH}$ sites tend to become more deprotonated (formation of negatively charged surface sites) which favours the formation of surface complexes with positively charged metal aqueous species. In addition the proton concentration (activity) decreases by several orders of magnitude over the above pH range resulting in a considerable decrease in the effectiveness of proton competition for the surface sites. Both of these effects tend to favour the uptake of metal species by the surface.

It is also a general observation that the easier a metal hydrolyses the stronger are the surface complexes which it can form (DUGGER et al. 1964; SCHINDLER et al. 1976; DZOMBAK & MOREL 1990). The formation of positively charged or neutral hydrolysed species does not, in itself, tend to adversely influence sorption behaviour. For example, Eu, and other trivalent metals such as Am and Cm, begin to hydrolyse at relatively low pH values (~ 5), but the sorption increases rapidly with increasing pH. (GORGEON 1994, BRADBURY & BAEYENS: unpublished data on the sorption of Eu on Na- and Ca-montmorillonite.) Only when higher order negatively charged hydrolysed metal species begin to become significant is there the possibility of an adverse influence on sorption.

In the cases of tetravalent radionuclides where data for sorption at trace concentrations as a function of pH are available, there are strong indications that the rapid increase of sorption with pH (so called sorption edges) already occurs at relatively low pH values. Thereafter the sorption remains virtually constant over a broad pH range before tending to decreasing at high pH values where the effect of negatively charged hydroxy species becomes significant. A few examples of the admittedly sparse pool of measurements are illustrated below.

Studies of Th(IV) sorption on Al_2O_3 in the pH range ~ 5 to 13 showed only a weak pH dependency above $\text{pH} = 5$ (ALLARD et al. 1983a), Figure 7.

HUNTER et al. (1988) measured Th sorption edges on iron and manganese oxides. The edges occurred at very low pH values and "100% sorption" was achieved at $\text{pH} \sim 5$ (Figure 8).

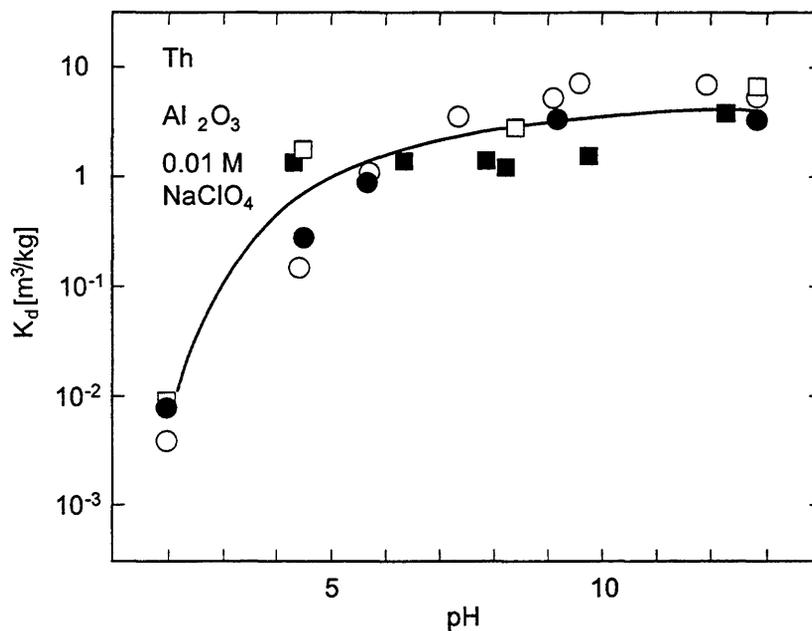


Figure 7: Distribution coefficients for Th(IV) on Al₂O₃. (Taken from ALLARD et al. 1983a, Figure 3.)

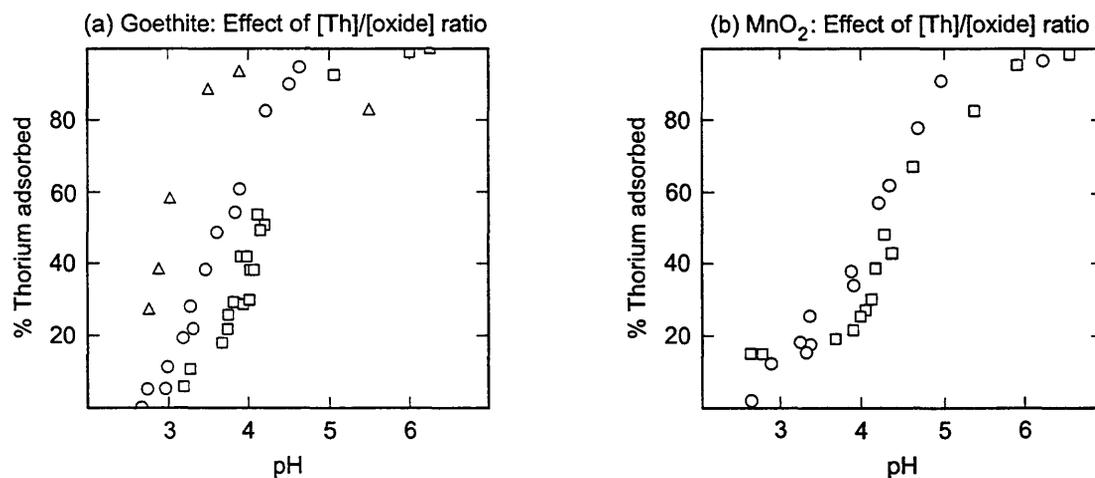


Figure 8: Sorption of Th as function of pH and different [Th/oxide] ratios on (a) goethite and (b) δ -MnO₂. (Taken from HUNTER et al. 1988, Figure 1.)

ALLARD et al. (1983a) also published Pu(IV) sorption data measured on Al_2O_3 as a function of pH (Figure 9). The results were similar to those determined for Th(IV) in that the sorption edge rose sharply at low pH values and reached a plateau between pH ~ 6 and 12.

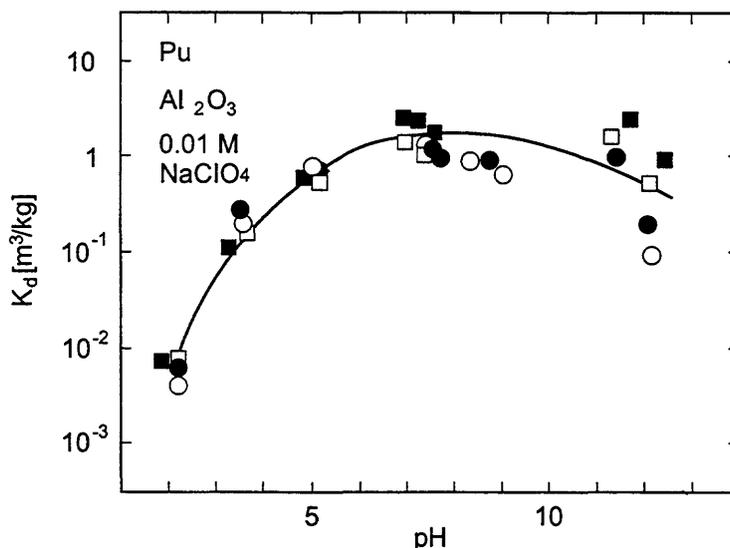


Figure 9: Distribution coefficients for Pu(IV) on Al_2O_3 . (Taken from ALLARD et al. 1983a, Figure 7.)

Taking the maximum pH as being ~ 8.3 for the marl reference waters, most actinides tend to form negatively charged hydroxy species only at higher pH values. To a first approximation therefore, we would maintain that hydrolysis reactions do not adversely affect sorption in the pH range of interest i.e. at pH values less than 9. Because of this, it is considered likely that actinides will already have reached their respective sorption plateau values at the pH values of the reference water chemistries. Thus, provided the selected literature sorption data were measured between pH ~ 6 and ~ 9, no correction for pH is required.

The situation for transition, heavy and trivalent metals is different since they tend to exhibit the strongest variation in sorption in the pH range from ~ 4 to ~ 9. A correction for pH is certainly needed for these radionuclides. For clay minerals such as illite and montmorillonite it has been experimentally observed that the slope of the sorption edge, expressed in the form of $\log R_d$ versus pH has a value of approximately unity i.e. the distribution coefficient

within the sorption edge increases (decreases) by at least one order of magnitude for each unit increase (decrease) in pH. (see for example GORGEON 1994; BAEYENS & BRADBURY 1995b; BANGASH et al. 1992). For oxides the dependency of sorption on pH is considerably stronger, increasing by up to two orders of magnitude per unit rise in pH (DZOMBAK & MOREL 1990). Since for the marl system we are primarily concerned with the uptake of radionuclides via surface complexation on clay minerals, we would propose that modifications to sorption values accounting for differences in pH are made according to the following relation,

$$R_{d,ref.} = R_{d,lit.} \cdot \frac{1}{10^{-(pH_{ref.} - pH_{lit.})}} \quad (2)$$

or

$$\log R_{d,ref.} = \log R_{d,lit.} + (pH_{ref.} - pH_{lit.}) \quad (3)$$

where

$R_{d,ref.}$ = marl reference sorption value.

$R_{d,lit.}$ = selected literature sorption value.

$pH_{ref.}$ = pH value of the marl reference groundwater.

$pH_{lit.}$ = pH value at which the selected literature sorption value was measured.

6.4 Linear free energy relationships

There are some strong indications in the open literature that sorption of transition metals is correlated positively with their tendency to hydrolyse, see for example the studies of SCHINDLER et al. (1976) on SiO_2 and DZOMBAK & MOREL (1990) on hydrous ferric oxides. ALLARD (1982) studied the sorption of Am, Np and Pu on 40 different minerals as function of pH and concluded that "...for all systems the sorption is drastically increased when hydrolysis starts. Sorption maxima are generally obtained in the pH range where neutral hydroxy complexes would dominate in solution".

Related to the above is a plot given in BAES & MESMER (1976) and reproduced here in Figure 10. The first hydrolysis constant (K_{11}) is correlated with the ratio of charge to bond length (z/d) for a wide range of metal hydroxy species. The z/d value can be taken as a "bond strength" indicator i.e. large (small) z/d ratios represent "strong" ("weak") bonding. It was noticed in some previous work (BRADBURY & SAROTT 1994) that where measured sorption

data were available, the values qualitatively correlated with the position of the elements in Figure 10. A strong tendency to hydrolyse (high K_{11} value) coupled with a large value for z/d was associated with high distribution ratios and vice versa. Though this is somewhat empirical, it could make sense in terms of a surface complexation sorption mechanism. Figure 10 proved to be very useful as a guide for helping in the selection of sorption values based on chemical analogy i.e. for those radionuclides where no measured data were available.

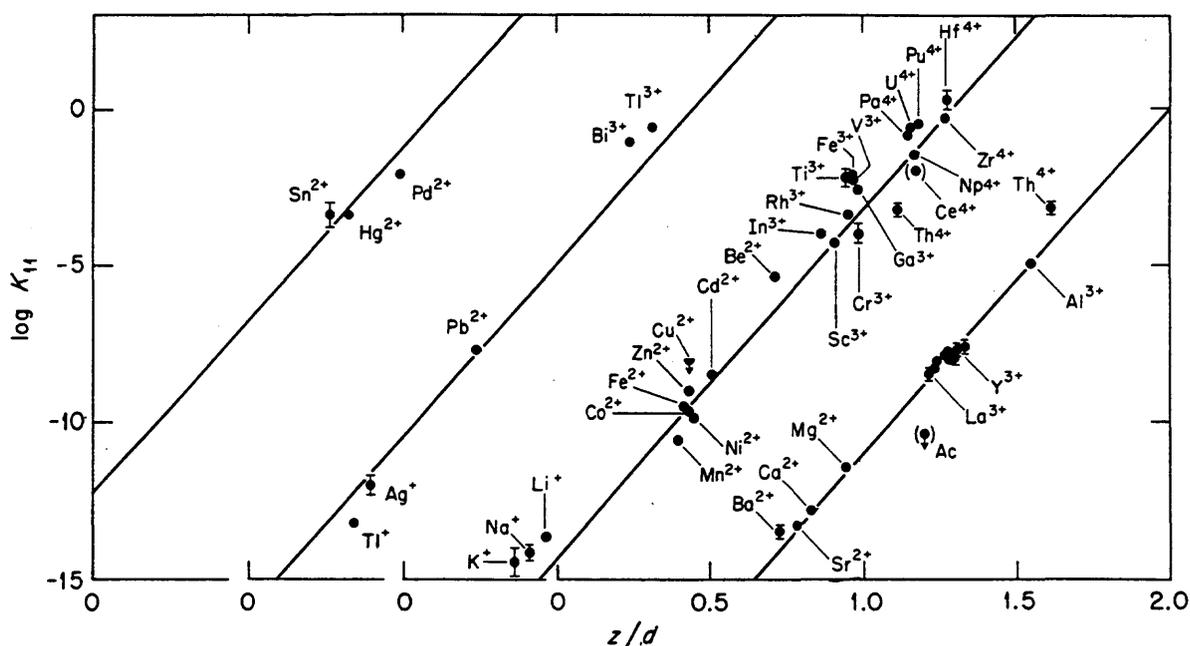


Figure 10: The linear dependence of $\log K_{11}$ on the ratio of the charge to the M-O distance for four groups of cations. (From BAES & MESMER 1976, Figure 18.4.)

6.5 Complexation

The complexation of radionuclides with inorganic and organic ligands can influence sorption. Thus, if the chosen literature value was measured in a water composition different of that of the marl reference waters (see section 3.1) a correction to the selected value needs to be made which reflects the differences in chemical composition of the respective waters. A rigorous correction is only possible when a verified sorption model is available, which is seldom the case. Indeed, for the majority of the radionuclides in most rock

water systems the major sorbing species is not even known. Nevertheless some attempt should be made to correct for different water chemistries. Since the main complexing anions in the reference water are carbonate/bicarbonate we propose to modify sorption values according to the extent to which carbonate complexes are formed. We assume that such complexes cannot sorb whereas all other species can potentially be taken up by the solid phase. This leads to a modification of sorption values based on the fraction of the equilibrium radionuclide concentration existing as carbonate complexes in a particular water composition. The basic equation used to make the correction for speciation is given below.

$$R_{d,ref.} = R_{d,lit.} \cdot \frac{1 - F_{ref.}}{1 - F_{lit.}} \quad (4)$$

$R_{d,lit.}$ is the selected literature sorption value.

$F_{lit.}$ is the aqueous fraction of radionuclide calculated to be present as carbonate complexes in the solution used to make the sorption measurements.

$F_{ref.}$ is the aqueous fraction of radionuclide calculated to be present as carbonate complexes in the reference water at the same radionuclide equilibrium concentration as given in the literature data.

$R_{d,ref.}$ is the corresponding sorption value for the reference water composition calculated according to Eq. 4.

In systems where there are a number of organic and/or inorganic ligands which complex significantly with a particular radionuclide, $F_{lit.}$ and $F_{ref.}$ can be taken as the aqueous fractions of that radionuclide existing in a complexed form in the respective solutions. (The potential influence of organic ligands arising from the marl itself was discussed in section 3.2 where it was concluded that their effects could be ignored to a first approximation.)

6.6 Summary of conversion factors

We propose to apply three scaling parameters to literature sorption values in order to convert them to values appropriate for marl mineralogies and groundwater chemistries. (See data sheets given in Appendixes B and C.)

- (i) A conversion factor is calculated which accounts for the differences in mineralogy between the solid phase for which the literature sorption data were measured, and the mineralogies given in Chapter 2. For the cases where sorption is occurring by cation exchange or surface complexation and where the literature data were obtained for clay minerals or argillaceous rocks, the conversion factor is taken to be the ratio of the respective CEC values e.g. $CEC_{\text{min-A}}/CEC_{\text{lit}}$. The CEC values for MIN-A, MIN-B and MIN-C were derived as shown in section 2.1 and are fixed values. If the literature sorption data are taken from measurements made on calcite, the conversion is made over the weight % of calcite in the Palfris marl, again according to the values given in section 2.1. For the flow paths having the simplified mineralogy "MIN-D", only sorption values for calcite are relevant.
- (ii) Given that the in situ conditions are taken to be reducing ($E_h = -310$ mV, Table 1) the most important water chemistry parameter is the pH. Literature sorption data are converted to values appropriate to the pH of the two types of groundwater. This is carried out by assuming that when sorption is dominated by a surface complexation mechanism, its magnitude increases or decreases by a factor of 10 per unit rise or fall respectively in the pH within the range ~4 to ~9 (see Eq. 3). Ionic strength is of secondary importance for surface complexation. For sorption via a cation exchange mechanism, ionic strength variations must be taken into account but pH differences can be neglected to a first approximation. No pH corrections are applied for tetravalent actinides (see section 6.3.2).
- (iii) Finally, we propose to correct for differences between aqueous speciation in the solution chemistry used in the literature measurements and the marl groundwaters via the radionuclide carbonate complexes according to Eq. 4 above. From the literature pH and total C_{inorg} ($H_2CO_3/HCO_3^-/CO_3^{2-}$) concentrations, the aqueous fraction of radio-

nuclide existing in the form of carbonate/bicarbonate complexes, F_{lit} , is calculated using MINEQL and the thermodynamic data compilation of PEARSON & BERNER (1991) and PEARSON et al. (1992). (F_{ref} values for the two reference water compositions are calculated in a similar manner.) The conversion factor is then calculated via Eq. 4. In sorption reports a pH value is almost always given but it is not necessarily so that $C_{inorg.}$ concentration data are available. For argillaceous rocks we assume calcite saturation at the pH given in order to calculate the F_{lit} value since calcite is ubiquitous in such natural systems. In purified mineral systems we assume equilibrium with the local P_{CO_2} , taken to be $10^{-5.5}$ bar in an inert atmosphere glove box and $10^{-3.5}$ bar in air atmosphere. Each reference groundwater composition, defined in Table 1, is treated separately. Under the heading of either "Conversion factor for NaCl-type water" or "Conversion factor for $NaHCO_3$ -type water" the conversion factors accounting for pH and total $C_{inorg.}$ differences are given.

These proposed modifications are intended to tailor the literature sorption data to the Palfris marl/groundwater systems by correcting for the major differences in mineralogy and water chemistry. However, this is not the end of the process since we must also consider the very important general question of the relevance of laboratory sorption values generated from crushed rock batch sorption tests to the "in situ" condition of the rock. This topic is discussed in the following chapter where so called Lab -> Field transfer factors are derived.

7 LAB->FIELD TRANSFER FACTORS

"Are laboratory sorption values measured in crushed rock batch sorption tests relevant and applicable to the in situ rock?"

The question is a long standing and difficult one (see for example HADERMANN & JAKOB 1987) which has a fundamental significance for safety analyses but for which there is, as yet, no simple answer. In most SDB compilations the question is hardly ever specifically addressed. However the problem is clearly too important to be ignored. An approach is suggested based on the hypothesis that the magnitude of sorption measured at equilibrium in any system under a constant set of conditions is directly proportional to the accessible surface area. We would argue that this is a reasonable and justifiable working hypothesis since sorption is essentially a surface phenomena. The problem of comparing crushed rock and intact rock with respect to their sorption then reduces, at least in a first approximation, to measuring the surface areas in both cases. (The proviso is that the crushed rock has had sufficient time to equilibrate with the water chemistry in the batch sorption test.)

The methodology adopted can be briefly summarised as follows. Multipoint N₂-BET surface areas were measured on intact pieces of clay minerals, sedimentary rock and crystalline rock samples (approximately 2.0 x 1.0 x 0.5 cm³) using the Micromeritics Gemini 2360 apparatus. The same samples were then crushed, passed through a sieve with a mesh size of <63 µm, and the surface areas re-determined. The transfer factor for converting sorption measurements from crushed rock to values appropriate to intact ("in situ") rock is then given by the ratio of the intact rock area to the crushed rock area. In this context the N₂-BET surface area should in no way be taken as an absolute value for the area available for sorption but rather as a measure proportional to this area.

The surface area determinations on intact and crushed specimens are summarised in the Tables 3a and 3b below. Data for single minerals are presented in Table 3a, and the results for compacted bentonites, sedimentary and crystalline rocks in Table 3b.

Table 3a: Surface areas (SA) of intact and crushed samples of single minerals and their associated transfer factors (TF)

Mineral	Source	SA.of intact rock (m ² kg ⁻¹)	SA of crushed rock (m ² kg ⁻¹)	TF
<u>Clay minerals</u>				
Illite (IMt-1) ^a	Silver Hills, Montana Cambrian shale	24.8	31.7	~0.8
Illite/Smectite mixed layer (ISMT-1) ^a	Mancos shale (Ordovician)	25.6	27.8	~0.9
<u>Zeolite:</u>				
Clinoptilonite	Kranz (Germany)	42.0	41.5	~1.0
<u>Primary minerals</u>				
Calcite	Wellenberg WLB-SB2 979.04	0.12	2.3	~0.05
Orthoclase Monoclinic K-feldspar	Kranz (Germany)	0.16	1.2	~0.1

^a Source Clay Minerals Repository, University of Missouri-Columbia

From the data given in Tables 3a and 3b some clear trends are evident. For the clay minerals (illite and illite/smectite mixed layer) and the zeolite (clinoptilonite) the surface areas measured on intact and crushed materials are practically identical. Only minor increases in surface areas (<30 %) result from crushing. A similar trend is also seen in the compacted bentonites and clay rich sediments (Palfris and Valanginian marls, Schimberg shale, Opalinus clay).

For the remaining single minerals (calcite and orthoclase) and Grimsel granodiorite, which are in general hard, brittle materials, very pronounced differences are observed. The surface areas of the intact pieces are between ~0.1 and ~0.05 times smaller than those of the crushed samples.

The main observation from these data is that the clay mineral content of the material effectively determines the transfer factors. Or, in other words, for clay minerals and clay mineral rich rocks, crushing to particle sizes of $\leq 63 \mu\text{m}$ results in little or no significant increase in the N₂-BET surface area compared with that available in the intact rock.

Table 3b: Mineralogical compositions, porosities and surface areas (SA) of intact and crushed rock samples together with their associated transfer factors (TF).

Rocks	Mineralogy	Porosity vol. %	SA of intact rock (m ² kg ⁻¹)	SA of crushed rock (m ² kg ⁻¹)	TF
<u>Compacted Bentonite</u>					
MX-80 (Bulk density: ~2000 kg m ⁻³)	Na-mont. (75); quartz (15); feldspar (7); carbonates (1.4)	~40	28.6	31.3	~0.9
Montigel (Bulk density: ~2000 kg m ⁻³)	Ca-mont. (66); quartz (8); mica (13); feldspar (3); carbonates (4); kaolinite (2)	~40	86.8	88.8	~1.0
<u>Sedimentary rocks:</u>					
Valaginian marl OBS F4	calcite (42); quartz (18) ankerite (5); chlorite (8); kaolinite (3); illite & illite/smectite mixed layer (23)	1-2	2.3	5.3	~0.4
Palfris marl WLB SB4 525.3 Wall rock	calcite (32); ankerite/dolomite (10) quartz (16); albite (1); pyrite (2); illite (16); illite/smectite mixed layer (14); chlorite (9)	1-2	6.5	9.5	~0.7
Palfris marl WLB SB4 525.3 Fracture infill	calcite (35); ankerite/dolomite (7); quartz (15); albite (1); pyrite (1); illite (14); illite/smectite mixed layer (12); chlorite (11); kaolinite (3)	~10	15.4	17.2	~0.9
Schimberg shale WLB SB4 562.1 Wall rock	calcite (36); ankerite/dolomite (2); quartz (29); albite (2); pyrite (1); illite (11); illite/smectite mixed layer (10); chlorite (9)	1-2	5.0	7.2	~0.7
Schimberg shale WLB SB4 619.4 Fracture infill	calcite (36); ankerite/dolomite (2); quartz (29); albite (2); pyrite (1); illite (11); illite/smectite mixed layer (10); chlorite (9)	~10	14.3	15.2	~0.9
Opalinus clay Mt. Terri	illite (18-36); chlorite (6-12); kaolinite (10-20); illite/smectite mixed layer (6-12); quartz (18), feldspars (1); carbonates (5-20); pyrite (1)	~12	35.2	36.2	~1
<u>Crystalline rock</u>					
Grimsel granodiorite (AU126 GTS)	quartz (30); plagioclase/albite (20); K-feldspar (13); biotite (13); muscovite (21); epidote (2)	1-2	0.14	1.0	~0.1

^a values in parenthesis are wt. %

For such rock types the surface area transfer factors are approximately unity. (The lowest TF measured so far for a clay rich sediment was ~0.4 for a sample of Valanginian marl.)

The porosity of the intact rock does have an effect, but its influence appears to be secondary to that of the clay mineral content. For example, the Palfris marl wall rock and fracture infill, and Schimberg shale wall rock and fracture infill, have respectively very similar mineralogies, but the wall rocks have porosities of 1-2 % whereas for the fracture infill materials the values lie around 10 %. A factor of more than 5 difference in porosity changes the value of the TF from ~0.9 to only ~0.7.

For systems where the transfer factors are of the order of unity there is essentially no difference in surface areas between crushed and intact material, and hence crushing is not expected to have any influence on the R_d value. Where the TF is significantly less than unity, this value represents the minimum factor by which crushed rock sorption data should be reduced for application to the intact rock.

Transfer factors of 0.05, 0.4 and unity are chosen for MIN-D (calcite), MIN-A, MIN-B, MIN-C and fracture infill material respectively.

Transfer factors calculated on the above basis may not be the whole answer to the problem since there is an implicit assumption in the argument that any newly created surfaces (fracture surfaces) have the same sorption characteristics as the original surfaces present. If the sorption affinities on the fresh surfaces are the same as or less than those on the original surfaces, then transfer factors calculated over surface areas are at least realistic and quite possibly conservative. However, if they happen to have higher affinities, then the relative contributions to the overall sorption of the two different surface types is unknown in the cases where an increase in surface area is measured for the crushed rock. The results in Table 3 above, indicate that such an effect is only likely to be of any consequence when sorption on one of the "harder" minerals (quartz, orthoclase, calcite) is dominant. (Crushing has little or no effect on clay minerals.) In the case of marl, only the flow paths associated with mineralogy MIN-D would be potentially affected.

Of course this approach to the problem has to be tested. A comparison

between the sorption characteristics of crushed freshly fractured material with the same crushed source rock equilibrated over different times with the appropriate groundwater is one possibility. Another, more exacting test, would be a comparison between sorption values derived from field tests and those measured in the laboratory to which a transfer factor has been applied. However, it must be remembered that whereas sorption values are directly measured, the R_d values extracted from field measurements are model dependent, and clearly an inadequate or bad model for the hydraulics and the transport will lead to inconsistent values, which has often been the case in the past.

There are a few, and only a few investigations which might be considered in this context.

- (i) High pressure infiltration tests with uranium and granodiorite core samples from the Grimsel migration test site (HADERMANN & JAKOB 1987, 1991; SMITH 1992).

Due to certain experimental shortcomings in these tests, the conclusions drawn cannot be considered to be very strong. Nevertheless, the batch and "dynamic" sorption values were within an order of magnitude.

- (ii) The Finnsjon tests (JAKOB & HADERMANN 1994)

Again, though there were problems with the quality of the experimental data, the batch and "dynamic" sorption values were within an order of magnitude.

The tentative conclusions which can be drawn from both of these experiments is that a transfer factor of 0.1, as given above in Table 3b for Grimsel granodiorite, is probably not unreasonable for crystalline rock types.

- (iii) The Grimsel migration experiment (HEER & HADERMANN 1994)

These series of tests have produced one of the best field migration data sets currently available in the world. Taking all of the associated uncertainties into account, a transfer factor of 0.2 to 0.4 might be extracted (HADERMANN, pers. comm. 1997). The slightly higher value than that given in Table 3b might be rationalised in terms of the nature of the material "seen" by the radionuclides in the migration fracture i.e. a

more disaggregated rock than the wall rock with a porosity of ~10% compared with 1-2% of the bulk rock.

The main point about the above (admittedly limited) comparison is that we are not dealing with orders of magnitude differences between batch R_d values and R_d values deduced from intact rock and field migration experiments. Rather the differences are probably at most approximately one order of magnitude. It might even be said that the magnitude of this (apparent) "difference" is strongly correlated with our understanding of the system and the migration processes.

8 SELECTED SORPTION VALUES FOR MIN-A, MIN-B AND MIN-C MINERALOGIES

8.1 General remarks

Before beginning the discussion on sorption data it may be worthwhile to restate that the aim of this work is to select sorption data which are specifically appropriate for a L/ILW repository in a marl formation. For many radionuclides the maximum possible aqueous concentrations conceivable are inventory and not solubility limited which, together with strong sorption on the cementitious near-field materials, implies that the concentrations entering the far-field may be quite low. In some cases they may be below the background groundwater concentrations of the corresponding element or, where sorption is via cation exchange and/or surface complexation, the corresponding site capacities of the solid phases may be large in comparison with the solution concentrations. In both cases this would lead to an uptake mechanism characterised by linear sorption. The point here is that although the sorption data bases are composed of simple R_d values, the processes of selection have often involved considerations of sorption mechanisms, isotherm data and trace element concentrations in the groundwater i.e. based on a broad understanding of the system and the processes taking place. In many cases the choice of a single linear sorption value is justified because of the prevailing conditions even though the particular radionuclide may well exhibit complex, generally non-linear overall sorption characteristics. (A typical example is that of Cs, discussed in the following section.)

8.2 Alkaline and alkaline-earth metals

8.2.1 Caesium

Practically all measurements of Cs uptake as a function of concentration in systems containing a significant illite component indicate that the sorption is non-linear. (SAWHNEY 1972; BROUWER et al. 1983; DE PRETER 1990). Because Cs has such a simple water chemistry, only being present as the hydrated monovalent cation Cs^+ , non-linear sorption characteristics imply that sorption is occurring on at least two different sorption sites with different affinities and probably different site capacities. Also, it is well established in

the literature that Cs sorbs predominantly by cation exchange (COLEMAN et al. 1963).

Taking the above into consideration, we have developed a simple two site cation exchange sorption model for Cs which we consider to be appropriate for systems where the illite clay mineral phase is dominating the sorption characteristics (BRADBURY & BAEYENS 1992). The first set of sites, frayed-edge sites, have a capacity of only a few percent of the cation exchange capacity (MAES & CREMERS 1986) but have high affinities (selectivities) for monovalent cations such as K^+ , Rb^+ and Cs^+ and are responsible for the uptake of these ions at low concentrations, (See for example, SAWHNEY 1972; CREMERS et al. 1988). The second set of sites, with considerably lower sorption affinity for Cs but a much higher sorption capacity are the normal "planar" cation exchange sites. A set of parameters were deduced from literature measurements and used in the model to calculate Cs sorption isotherms in diverse rock-water systems including sediments such as Boom clay and Valanginian marl from Oberbauenstock. (It should be noted that there were no adjustable parameters in the model for these calculations.) In general, the agreement between the calculated and measured isotherms were found to be good. A full description of the Cs sorption model is given in BRADBURY & BAEYENS (1992).

As an example, this model together with the associated parameter values summarised in Table 4, was used to calculate Cs sorption isotherms in the two reference groundwater chemistries for the MIN-B system. The main cations competing with Cs^+ for the exchange sites are K^+ , Rb^+ and NH_4^+ , and in the calculations the concentrations of these cations in the groundwaters were added together and the exchange behaviour treated as being the same as for K^+ . The results of these calculations in the absence of any Cs background concentration are shown in Figure 11. The vertical "sorption cut-off line" drawn in Figure 11 corresponds to the natural Cs background levels in the reference groundwaters (Table 1). Note that when total Cs concentrations are considered, the isotherm ceases at the Cs background concentration. It is this concentration which determines the overall Cs sorption value and not the radio-caesium concentration released from the repository, which will be considerably less. (The Cs sorption values given in the SDB's for the other marl mineral systems were calculated in a similar manner using the

corresponding CEC values given in Table 2.)

Table 4: Selectivity coefficient values for modelling Cs sorption on marl (MIN-B). (Selectivity coefficients taken from BRADBURY & BAEYENS 1992).

Type of sites	Site concentration [equiv. kg ⁻¹]	Selectivity coefficients
Frayed-edge sites	2.5 x 10 ⁻⁴	$\frac{C_s}{K} \frac{K_c^{FES}}{K_c} = 3000$
Planar Sites	5 x 10 ⁻²	$\frac{C_s}{Na} \frac{K_C^{PS}}{K_C} = 40$ $\frac{C_s}{B} \frac{K_C^{PS}}{K_C} = 500$ $\frac{K}{Na} \frac{K_C^{PS}}{K_C} = 5$

B = (Mg + Ca + Sr).

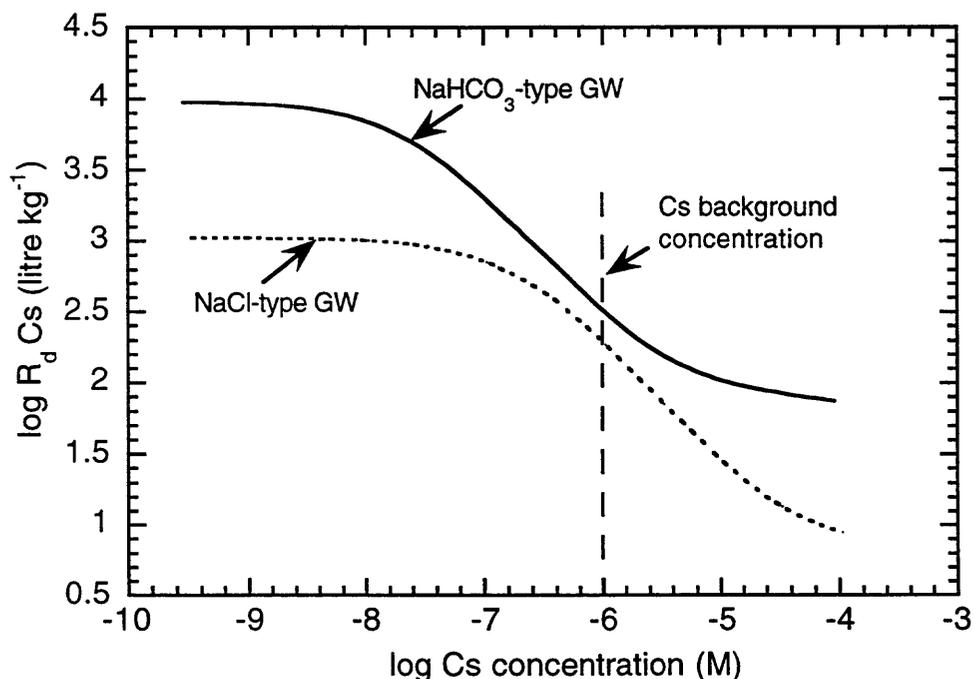


Figure 11. Cs sorption isotherms on marl (MIN-B system, CEC: 0.05 equiv. kg⁻¹) calculated with the selectivity coefficients given in Tables 4 and 5 and the water chemistry data from Table 1.

8.2.2 Potassium, Strontium

The physico-chemical characteristics of marl have been determined in connection with experimental work on marl pore water chemistry (BAEYENS & BRADBURY 1991b, 1994). In the more recent study, a low permeability Palfris marl sample from Wellenberg was investigated. Thus site specific data for cation exchange capacities and selectivity coefficients, K_C values, are available and are given in Table 5. The bivalent cations Mg^{2+} , Ca^{2+} and Sr^{2+} do not show any significant differences in their exchange behaviour (BRUGGENWERT & KAMPHORST 1982) and are hence grouped together.

Table 5: Selectivity coefficients for Na^+ - M^{2+} and K^+ - M^{2+} exchange on Palfris marl. (BAEYENS & BRADBURY 1994, Data set A).

Exchange reaction	K_C
$M^{2+}\text{-marl} + 2 Na^+ = 2 Na^+\text{-marl} + M^{2+}$	0.3
$M^{2+}\text{-marl} + 2 K^+ = 2 K^+\text{-marl} + M^{2+}$	14

$M^{2+} = Mg^{2+}$ or Ca^{2+} or Sr^{2+}

From such physico-chemical data it is relatively straightforward to calculate sorption values for radionuclides sorbing by cation exchange for a specific water composition (see Table 1) and mineralogy, Table 2.

The concentrations of radio-isotopes of cations such as Sr, for example, will almost certainly lie below the natural levels of inactive Sr existing at equilibrium in the groundwater. Therefore, under these circumstances, sorption will be determined by the system itself (fixed fractional occupancy of Sr on the clay and fixed equilibrium aqueous Sr concentration) and occurs via isotopic exchange. It also follows that as long as the radio-isotope concentration lies below that of its inactive counterpart, the sorption will be linear.

The incorporation of cation exchange into geochemical codes is described in detail in BRADBURY & BAEYENS (1994). Using MINSORB and the selectivity coefficients of K, Mg, Ca and Sr with respect to Na allows the distribution ratios for K and Sr to be calculated for the three mineralogies (MIN-A, MIN-B

and MIN-C) in NaCl- and the NaHCO₃-type reference groundwaters. The results of these calculations are summarised in Table 6. In a similar manner to Cs (see below) K can sorb on the frayed-edge sites as well as on the planer exchange sites. However, the former are not considered here because the K concentrations are so high in the groundwater, see Table 1, that the sorption of K is taking place on that part of the sorption isotherm governed by exchange on the planer sites.

Table 6: Calculated reference sorption R_d values for K and Sr in the NaCl- and NaHCO₃-type reference groundwaters.

NaCl-type groundwater	R_d (K) (m ³ kg ⁻¹)	R_d (Sr) (m ³ kg ⁻¹)
MIN-A	7×10^{-4}	4×10^{-4}
MIN-B	10^{-3}	6×10^{-4}
MIN-C	4×10^{-4}	2×10^{-4}
NaHCO ₃ -type groundwater	R_d (K) (m ³ kg ⁻¹)	R_d (Sr) (m ³ kg ⁻¹)
MIN-A	7×10^{-3}	6×10^{-2}
MIN-B	10^{-2}	8×10^{-2}
MIN-C	4×10^{-3}	3×10^{-2}

8.2.3 Radium

Literature values for the sorption of Ra on geological materials are often high ($>1 \text{ m}^3 \text{ kg}^{-1}$) and associated with a large scatter (see Appendix B in STENHOUSE 1995). Almost equally often Ra sorption values tend to exhibit trends which are not compatible with sorption processes. For example, AMES et al. (1983) present values for the quantities of Ra taken up by illite as a function of initial and equilibrium concentrations which increase with increasing concentration. These data can clearly not be regarded as being representative of Ra sorption but rather may be indicative of precipitation processes. We consider that the most likely sorption mechanism for Ra is cation exchange and take Sr as a chemical analogue for Ra. Consequently we have selected the same R_d values for Ra as for Sr.

8.3 Transition metals and heavy metals

Although transition/heavy metals such as Cd, Pb and Zn can sorb onto illite by cation exchange, their selectivity coefficients are similar to that of Ca (BRUGGENWERT & KAMPHORST 1982) and consequently would only be taken up weakly on marl by this mechanism.

However, there is evidence in the literature that at pH values above 6 such elements are taken up strongly on illite by surface complexation (WOLD & PICKERING 1981). Their sorption affinities are correlated with their tendency to hydrolyse. A similar behaviour was observed by MOUVET & BOURG (1983) and CZURDA et al. (1989) on the adsorption of trace metals on sediments in the pH range 7.5 to 8.4. The sequence of affinities is $Pb \sim Cu > Zn \sim Ni \sim Cd \gg Mg > Ca$. (These findings are in general agreement with the linear free energy relationships discussed in DZOMBAK & MOREL (1990) for hydrous ferric oxide systems).

8.3.1 Nickel

The primary source for Ni sorption data are the measurements of TITS et al. (1998) on samples of Valanginian marl from Oberbauenstock which had been conditioned to a synthetic marl water composition at $pH = 8.3 (\pm 0.1)$ (defined in BAEYENS & BRADBURY 1991b), prior to the sorption tests. A sorption isotherm for Ni was determined in the equilibrium concentration range $3 \times 10^{-4} M$ to $3 \times 10^{-9} M$ and is illustrated in Figure 12.

In the pH range up to ~ 8.5 , and in systems saturated with calcite, recent measurements by BAEYENS & BRADBURY (Unpubl. results) have shown that the Ni carbonate complexation constants are so weak that hardly any such complexes form i.e. no corrections to sorption values for HCO_3^-/CO_3^{2-} concentrations are required. Also, since Ni is sorbing predominantly by a surface complexation mechanism, pH is the most important parameter and the influence of ionic strength is only a second order effect. For these two reasons it seems to be justified to use the data of TITS et al. (1998) for both reference water chemistries after making the appropriate corrections for pH to the sorption values. This correction is minimal for the $NaHCO_3$ -type groundwater but is a factor of ~ 30 for the $NaCl$ -type groundwater.

In Table 1 the background concentration of Ni in the bicarbonate reference water is given as being $\sim 10^{-7}$ M and the Ni sorption value of $5 \text{ m}^3 \text{ kg}^{-1}$ ($\log R_d = 3.7 \text{ L kg}^{-1}$) is selected for this concentration from the isotherm in Figure 8. The same value is also selected for the NaCl reference water though no background level for Ni is given.

There is a second source of Ni sorption data on Valaginian marl contained in AKSOYOGLU et al. (1992) which comprises of 22 sorption measurements made in a calcite saturated NaCl-type water with a Ni background concentration of $\sim 10^{-7}$ M but at a pH of 7.3. The mean R_d value from this data set is $\sim 0.8 (\pm 0.1) \text{ m}^3 \text{ kg}^{-1}$. Using the conversion method described in Chapter 6 yields a modified R_d value of $8 \text{ m}^3 \text{ kg}^{-1}$ at pH = 8.3 which is only $\sim 50\%$ greater than the value measured by TITS et al. (1998).

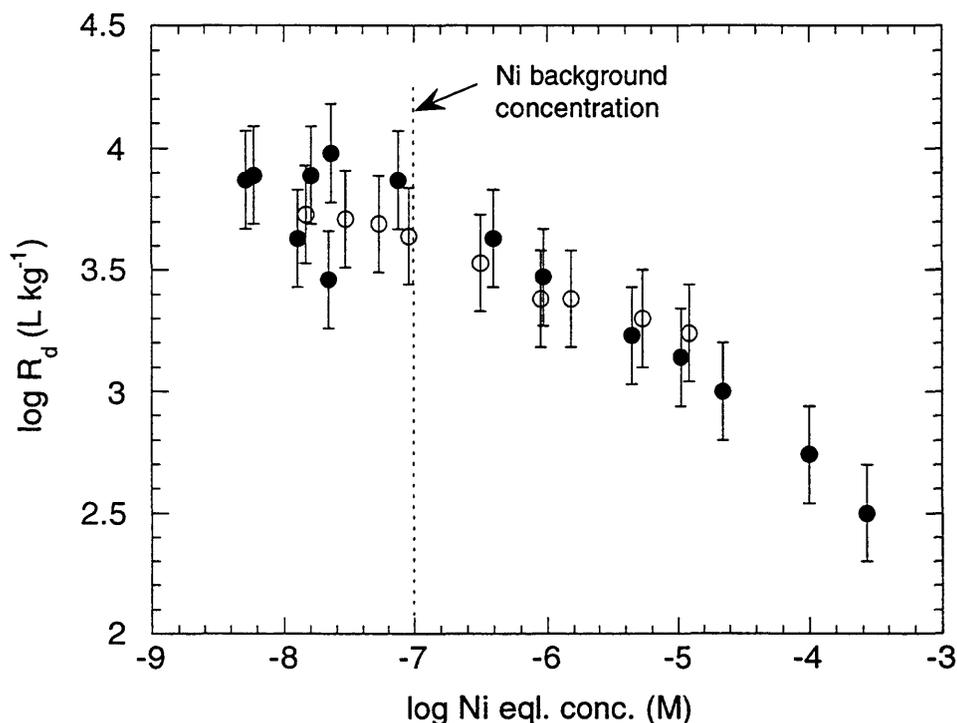


Figure 12: Ni sorption isotherm on Valaginian marl (OBS-PSI-F4) at pH=8.3, S:L = 2.7 g L^{-1} (●); S:L = 23 g L^{-1} (○).

8.3.2 Cobalt

Some clear indications of the pH dependency of Co sorption on illite (surface complexation) at $\text{pH} > 6$ are provided in the work of O'CONNOR & KESTER (1975). In the study presented by BANGASH et al. (1992) on an illitic soil, their sorption measurements when plotted as $\log R_d$ vs pH yielded a slope of ~ 1 in the pH range from 6 to 8. This observation provides some support for the proposed method for estimating the pH conversion factor discussed in section 6.3.2. However, both sets of data contain insufficient information on water chemistry and CEC to make them useful for deducing R_d values in the marl system.

For this purpose the sorption study of Co on illite reported by GRÜTTER et al. (1994) is preferred. This detailed study included the time dependence of sorption and desorption at different concentrations together with a full description of the water chemistry and CEC measurements (GRÜTTER et al. 1992, 1994). From the results given a sorption value of $\sim 5 \text{ m}^3 \text{ kg}^{-1}$, corresponding to trace concentration levels ($< 10^{-8} \text{ M}$), was selected. In contrast to Ni, sorption at trace concentrations for Co was deemed to be appropriate since stable cobalt was not thought to have been present in the groundwaters. Carbonate complexation was treated in the same manner as previously described for Ni.

8.3.3 Palladium

No relevant sorption data could be found for Pd.

Pd forms extremely stable hydroxy species (see Figure 10). This, according to section 6.3.2, is a significant indicator that it can bind strongly with amphoteric $\equiv\text{SOH}$ type surface sites. Consequently high sorption values would be expected. The first hydrolysis constants for Co, Ni and Pb are significantly weaker, and, on the basis that the uptake mechanism is surface complexation, selecting a sorption value for Pd similar to one of the above nuclides must represent a conservative choice. The sorption values chosen for Ni are also used for Pd.

8.3.4 Silver

PLEYSIER (1976) studied the cation exchange behaviour of Ag on homoionic Na-illite in 0.01 M NaNO₃ and determined a selectivity coefficient for Ag-Na exchange of ~5 at low Ag fractional occupancies ($N_{Ag} \sim 0.1$). In a similar manner to K and Sr, see section 8.2.2, the sorption values for Ag can be calculated for the two reference groundwaters and three marl mineralogies. Ag does not form carbonate complexes but does form strong chloro complexes which is automatically taken into account in the calculations. The results are summarised in Table 7 and represent the selected marl reference R_d values of Ag for the three mineralogies.

Table 7. Calculated marl reference sorption values for Ag in the NaCl- and NaHCO₃-type groundwaters for the three marl mineralogies.

	NaCl-type groundwater R_d (m ³ kg ⁻¹)	NaHCO ₃ -type groundwater R_d (m ³ kg ⁻¹)
MIN-A	0	5×10^{-3}
MIN-B	0	8×10^{-3}
MIN-C	0	3×10^{-3}

As can be seen from this table, the Ag sorption values for the NaHCO₃-type water are similar to those calculated for K and are almost unaffected by aqueous complexation reactions (Cl⁻ concentration $\sim 2 \times 10^{-4}$ M). However, in the case of the 0.2 M NaCl-type groundwater there is practically no uptake of Ag due to the formation of neutral and anionic Ag-chloro complexes. It is interesting to note that for the latter groundwater type the calculated solubility of Ag is $\sim 5 \times 10^{-6}$ M.

Literature sorption data for Ag on minerals of interest are scarce. The only sorption values found were on four quartz rich sediments, LEGOUX et al. (1992). In the pH range from ~6.5 to 8, and an initial Ag⁺ concentration of 1.8×10^{-7} M, they measured R_d values between 1.8 and 17 m³ kg⁻¹. These values are very high and should be treated with caution since silver solutions are photosensitive, and Ag⁺ can easily reduce to metallic Ag. In our view, these

values are probably more representative of precipitation processes than sorption reactions. For this reason, the R_d values calculated above assuming a cation exchange mechanism are preferred.

8.3.5 Lead

With the exception of Pb sorption studies in soils (see for example HIGGO 1988) where "organics" in the solid and liquid phases are likely to play an important but unquantified role, almost no reliable sorption data are available in the literature (STENHOUSE 1995, Appendix B).

LIESER & AMENT (1993) present R_d values for Pb in three different groundwater/sediment systems from Gorleben. The water chemistries are available, but no detailed rock mineralogy or CEC values were reported. The values measured by these authors were high (20 to $> 50 \text{ m}^3 \text{ kg}^{-1}$).

RYBICKA et al. (1995) measured heavy metal (Cd, Cu, Pb, Zn and Ni) sorption on illite at pH 5.5. Unfortunately the data cannot be used since no information was given on the water chemistries. The only semi-quantitative conclusion to be drawn from this study is the sequence of adsorption affinities for illite viz. $\text{Pb} > \text{Cd} \sim \text{Cu} > \text{Ni} > \text{Zn}$.

KOSS et al. (1992) experimentally determined Pb sorption values in a groundwater/sediment system for which the water chemistry and rock CEC were given. Unfortunately, the sediment mineralogy was not described. The data were treated in terms of a surface complexation based model. From these measurements an R_d value for Pb of $1.5 \text{ m}^3 \text{ kg}^{-1}$ at pH 6.7 is selected.

In the sorption data conversion process Pb is treated as sorbing by a surface complexation reaction and the "sediment" as having the same Lab->Field conversion factor as marl.

8.3.6 Tin

Reliable sorption data for Sn on relevant geological substrates are extremely rare.

Data exist for soils (see for example the review of MORGAN & BEETHAN 1990) but are not relevant because the sorption of Sn is dominated by the presence of organic matter.

There are a number of studies describing the partition of Sn between suspended particles and seawater (LI et al. 1984; NYFFELER et al. 1984). These authors report very high R_d values ($> 100 \text{ m}^3 \text{ kg}^{-1}$) but no information is given on the possible sorption processes, and in all cases organic matter was present.

BALISTRIERI & MURRAY (1984) studied the adsorption of thirteen trace metals from seawater on a deep sea interfacial sediment at pH 7.8. The adsorption data indicated the following affinity sequence: $\text{Pb} > \text{Fe} > \text{Sn} \sim \text{Co} \sim \text{Mn} > \text{Cu} > \text{Be} > \text{Sc} \sim \text{Zn} > \text{Ni} > \text{Cd} \sim \text{Ba} > \text{Cs}$. The presence of particles of biogenic origin (i.e., organic matter) influenced the binding of these metals, and again, for our purposes, these data cannot be used.

The only measurements found on sedimentary rocks are due to LEGOUX et al. (1992). Batch sorption measurements carried out in the pH range 5.9 to 8, at initial Sn concentrations of $\sim 5.4 \times 10^{-8} \text{ M}$ on "quartz rich rocks containing clay minerals", yielded high R_d values lying between 10 and $45 \text{ m}^3 \text{ kg}^{-1}$. Water chemistries, CEC and surface areas are given in this report which also contains sorption data for a further 18 radionuclides.

One of the major problems in trying to make sense of the sorption behaviour of Sn is that its redox chemistry, aqueous speciation and solubility are poorly known. In laboratory experiments and under the in situ conditions anticipated in marl, Sn is expected to be present in the tetravalent state as SnO_3^{2-} (POURBAIX 1974). This is somewhat difficult to reconcile with a very high distribution ratio of up to $45 \text{ m}^3 \text{ kg}^{-1}$. The lack of knowledge concerning the solubility controlling phase and solubility limit raises the possibility that precipitation effects may be dominating the measurements, even at the low initial Sn concentrations used in the above tests.

Because of these uncertainties we find it difficult to justify the selection of a high distribution ratio for Sn based on just one set of data, although it may well be that Sn does exhibit strong sorption. Instead, we adopt a very conservative

course and choose an R_d value the same as for molybdate (MoO_4^{2-}) on the basis that tin is also existing in solution as a bivalent anion (SnO_3^{2-}).

8.3.7 Zirconium

Reliable sorption data for Zr under well defined conditions are scarce. (HIGGO 1988; STENHOUSE 1995, Appendix B.)

Because of the paucity of sorption values we take Th(IV) as chemical analogue for Zr(IV). (See Figure 10 and also the discussion in BRADBURY & SAROTT 1994).

8.3.8 Niobium

Only two sources of Nb sorption data were found for which both water chemistries and mineralogies were described.

BERRY et al. (1988b) report a single R_d value of $> 6 \text{ m}^3 \text{ kg}^{-1}$ for London clay at $\text{pH} = 8$.

The second source is LEGOUX et al. (1992) who measured Nb sorption values between 1.5 to $2.6 \text{ m}^3 \text{ kg}^{-1}$ on four very similar quartz rich sediments (~ 10 wt% illite+smectite clay minerals) in well defined water chemistries in the pH range from 5.9 to 8. Detailed mineralogies and measured CEC values were also given. Within the uncertainties of the R_d determinations no dependency on pH was discernible.

Although the measurements of both BERRY et al. (1988b) and LEGOUX et al. (1992) on sedimentary rock samples both indicate high Nb sorption, the paucity of the data tended to influence our choice towards conservatism, and we selected a value one order of magnitude lower than the mean value in LEGOUX et al. (1992) i.e. $0.2 \text{ m}^3 \text{ kg}^{-1}$. It is perhaps worth mentioning that niobium is probably predominantly present in the pH/Eh regime existing in these experiments as a neutral hydroxy species, $\text{Nb}(\text{OH})_5^0$ (BAES & MESMER 1976) and not as an anion as might at first be supposed. This might explain the relatively high Nb sorption values measured and the pH independence of sorption in the range 5.9 to 8. At slightly higher pH values, the dominant

aqueous species becomes negatively charged ($\text{Nb}(\text{OH})_6^-$) which may result in a dramatic decrease in sorption.

Finally, since Nb does not form carbonate complexes to any significant extent, and the pH range covered in the experiments corresponds to that of interest for the marl groundwaters, no corrections for water chemistry were made and the same sorption value was taken for both reference waters.

8.3.9 Molybdenum

Mo only exists in the +6 valence state and above pH 4 the dominant aqueous species is the anionic molybdate (MoO_4^{2-}) (BAES & MESMER 1976).

Sorption data for MoO_4^{2-} on geological substrates are scarce. MOTTA & MIRANDA (1989) studied MoO_4^{2-} adsorption on illite under well defined conditions. They modelled the sorption using a constant capacitance surface complexation model and interpreted the data in terms of a ligand exchange mechanism with the reactive hydroxy groups located at the edges of clay mineral particles. The sorption was of the Langmuir type and isotherms at pH 8.9 and 8.2 are presented. Since pH = 8.2 corresponds to that of the NaHCO_3 -type water, a sorption value of $0.016 \text{ m}^3 \text{ kg}^{-1}$ was chosen from the linear region of the isotherm. This R_d value is valid up to Mo equilibrium concentrations of $\sim 5 \times 10^{-4} \text{ M}$.

MOTTA & MIRANDA (1989) do not give sorption edge data and so other sources are required to provide information on the pH dependency. Adsorption of molybdate by soils has been extensively studied within the framework of its mobility and availability to plants (e.g. PARFITT 1978; GONZALEZ et al. 1974; THENG 1971).

From the results presented by THENG (1971), who measured the effects of pH on MoO_4^{2-} retention by soil clays, it is clear that sorption increases as the pH decreases, reaching a maximum at pH = 4. The sorption increases by a factor of approximately 2 for each unit decrease in pH and this is taken as the basis for the pH correction for the NaCl reference water.

MOTTA & MIRANDA (1989) do not give a CEC value for the illite. A typical value of 0.2 equiv. kg⁻¹ is taken and used to calculate conversion factors.

8.3.10 Technetium

Under oxidising conditions where the pertechnetate (TcO_4^-) species is dominant, the sorption of technetium on virtually all geological substrates is very weak, $<10^{-3} \text{ m}^3 \text{ kg}^{-1}$. (See for example WINKLER et al. 1988; LEGOUX et al. 1992; LIESER & BAUSCHER 1987).

Under reducing conditions technetium is present in the +4 valence state and TcO_2 becomes the solubility controlling phase. MEYER et al. (1986) studied the solubility of Tc(IV) oxides and concluded that the solubility limit is constant from pH 4 to 10 and lies between 10^{-8} M and $2 \times 10^{-8} \text{ M}$. The predominant aqueous species is $\text{TcO}(\text{OH})_2^0$.

Tc sorption measurements under reducing conditions at concentrations below the solubility limit are rare. The high value ($1 \text{ m}^3 \text{ kg}^{-1}$) reported by LIESER & BAUSCHER (1987) most probably reflects precipitation and not sorption.

MEYER et al. (1986) observed Tc sorption values of $\sim 0.01 \text{ m}^3 \text{ kg}^{-1}$ at very low initial concentrations on a synthetic groundwater/basalt system at pH ~ 9.7 .

HENRION et al. (1985) measured Tc sorption at Eh $\sim -250 \text{ mV}$ to -300 mV at low Tc concentrations on Boom clay under inert atmosphere conditions. However, complexation with organic matter is certainly important in this system. At the lowest DOC levels R_d values ranged between ~ 0.035 to $0.05 \text{ m}^3 \text{ kg}^{-1}$.

Under "reducing" conditions (0.05 M hydrazine) and at very low initial Tc concentrations ($\sim 4 \times 10^{-11} \text{ M}$) BARNEY (1982) measured sorption values on sandstone (CEC = 0.099 equiv. kg⁻¹), at pH values between 8.7 and 9.4, in the range 0.005 to $0.2 \text{ m}^3 \text{ kg}^{-1}$.

The above represents the extent of the data found on geological systems where the Tc concentrations are well below the solubility limit and the redox conditions are reducing. Because of the general lack of information and mechanistic understanding it is not possible to discuss Tc sorption in terms of

specific water chemistries. Therefore, for Tc we are forced to choose a very conservative sorption value. The data from HENRION et al. (1985) cannot be considered since Tc interacts strongly with natural organics. The mean value calculated from 9 measurements given in BARNEY (1982) yielded $0.01 (\pm 0.006) \text{ m}^3 \text{ kg}^{-1}$ and this value is selected.

8.3.11 Polonium

Po is a radioactive metal which can exist in the +2 and +4 oxidation states and for which no relevant sorption data could be found in the literature. According to FALBE & REGITZ (1992) Po(II) oxidises easily to Po(IV) by self irradiation. Under the Eh/pH conditions envisaged for marl, Po(IV) will probably exist as the polonate anion, PoO_3^{2-} (VAN MUYLDER 1966). Although Bi might be considered the best chemical analogue for Po (FALBE & REGITZ 1992), there is unfortunately no information on this element either. In view of the lack of sorption data, and its anionic form in solution, we set the sorption of polonium to zero.

8.4 Actinides

8.4.1 Trivalent actinides

8.4.1.1 Americium

Sorption of Am on illite has been reported by MUCCIARDI et al. (1978); DEGUELDRE et al. (1994b) and GORGEON (1994). No other sources were found.

GORGEON (1994) thoroughly investigated the sorption behaviour of Am on a purified homo-ionic Na-illite (Puy) at 1 and 0.1 M NaClO_4 as function of pH from 3 to 10. The equilibrium Am concentrations were low ($< 4 \times 10^{-10}$ M from pH 6.5 upwards). The raw data, presented in the form of tables in this study, are reproduced here in Figure 13. The data clearly show that the sorption of Am on illite is pH dependent. Below pH ~ 6, Am sorption is dependent on the NaClO_4 concentration whereas above this pH the ionic strength dependency disappears. This is very reminiscent of the sorption behaviour of Ni and Zn on Na-montmorillonite (BRADBURY & BAEYENS 1995) and can be very

satisfactorily interpreted in terms of two main sorption mechanisms, namely cation exchange and surface complexation. Similar behaviour of Am sorption on other clay minerals has been described in the literature; see for example BEALL & ALLARD (1981) for montmorillonite, GORGEON (1994) for kaolinite and smectite and STAMMOSE & DOLO (1990) for kaolinite/smectite mixed layer.

DEGUELDRE et al. (1994b) measured the sorption of Am on illite as function of S:L ratio in the range of 1 mg and 1 g L⁻¹ at 0.01 M HCO₃⁻/CO₃²⁻ (Data set 1, DEGUELDRE et al. (1994b), Figure 13) and as function of inorganic carbon concentration, between 10⁻⁴ and 0.1 M (Data set 2, DEGUELDRE et al. (1994b), Figure 13) at pH = 8. Because of the relatively large scatter in the data, no clear trends could be seen with respect to the influence of carbonate on Am sorption. The mean R_d value calculated from the data of DEGUELDRE et al. (1994b) is compatible with the measurements of GORGEON (1994) which were carried out in the absence of carbonate. Thus the presence of HCO₃⁻/CO₃²⁻ (up to 0.1 M) does not appear to influence the sorption behaviour of Am on illite to any significant extent. This is also confirmed by data of MUCCIARDI et al. (1978) who measured Am sorption on illite in a 0.03 M NaHCO₃ groundwater at pH 8.5. The R_d value of ~ 50 m³ kg⁻¹ measured after 30 days is also included in Figure 13.

There is substantial evidence in the open literature that Am can form strong carbonate and hydroxy/carbonate complexes (SILVA et al. 1995). Following the approach suggested in section 6.5 a significant decrease in Am sorption would be anticipated for the conditions described by MUCCIARDI et al. (1978) and DEGUELDRE et al. (1994b) which is apparently not confirmed experimentally. Given the relatively good quality of experimental data and the agreement between different authors, the measured values are preferred at the present time and no effect of carbonate complexes on trivalent actinide sorption are included. However, the uptake process leading to continuing high sorption values is not understood.

The Am sorption values for illite are selected from the data of GORGEON (1994) at the appropriate pH values, i.e. R_d = 100 m³ kg⁻¹ (pH = 8.3) and R_d = 25 m³ kg⁻¹ (pH = 6.7).

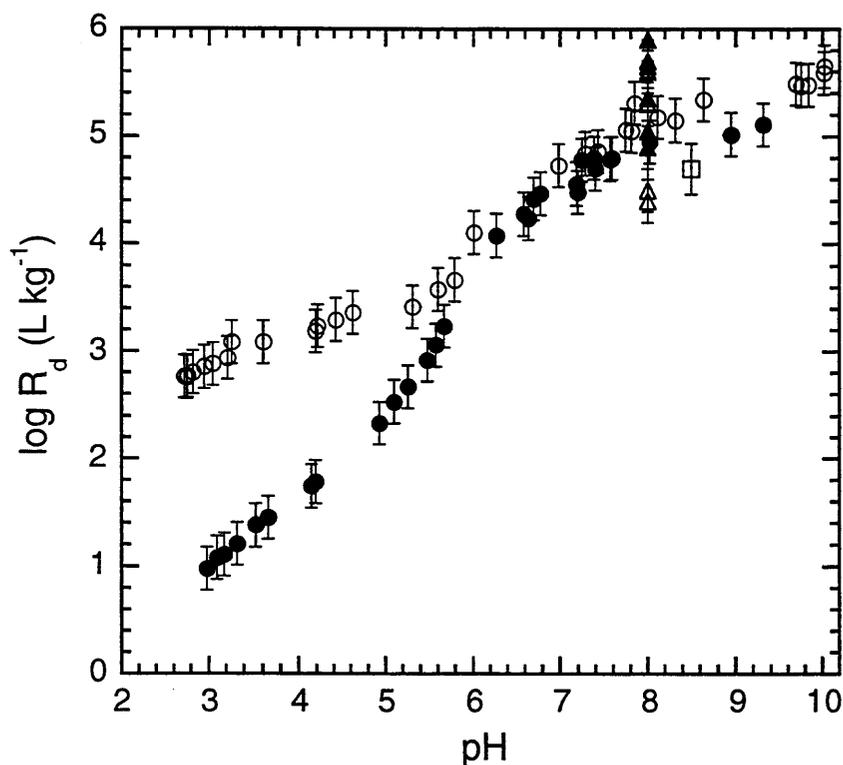


Figure 13: Am sorption on illite as function of pH and ionic strength. (●) Data set 1, $I = 1$ M, GORGEON (1994); (○) Data set 2, $I = 0.1$ M, GORGEON (1994); (▲) Data set 1, DEGUELDRE et al. (1994b); (Δ) Data set 2, DEGUELDRE et al. (1994b); (□) MUCCIARDI et al. (1978).

8.4.1.2 Actinium, Curium

The lack of reliable sorption data for these elements available in the open literature (see for example STENHOUSE 1995, Appendix I) precluded the selection of distribution ratios specific to Ac or Cm. Instead, since both elements are chemically very similar to Am, the same sorption values were selected.

8.4.2 Tetravalent actinides

Under the reducing conditions prevailing in the far-field, the most probable stable oxidation state of Th, U, Np and Pu is +4. The tetravalent actinides have

a strong tendency to hydrolyse, and the neutral tetrahydroxy complexes are, in general, the dominant aqueous species.

The thermodynamic data for hydroxy and carbonate complexes for Th(IV), U(IV), Np(IV) and Pu(IV) in the PSI/NAGRA thermodynamic data base (PEARSON et al. 1992) are inconsistent and incomplete. BERNER (1995) has re-evaluated the thermodynamic data for these tetravalent actinides and proposed a consistent data set. Speciation calculations in both reference waters have been carried out with these updated thermodynamic constants and the results are given in Table 8.

Table 8: Aqueous speciation calculations for the tetravalent actinides in the two marl reference groundwaters using the updated thermodynamic data from BERNER (1995).

	Th(IV)	U(IV)	Np(IV)	Pu(IV)
NaCl-type GW pH=6.7	90% $\text{Th}(\text{OH})_3\text{CO}_3^-$ 10% $\text{Th}(\text{OH})_4^0$	85% $\text{U}(\text{OH})_4^0$ 3% $\text{U}(\text{OH})_3\text{CO}_3^-$ 12% $\text{U}(\text{CO}_3)_4^{4-}$	100% $\text{Np}(\text{OH})_4^0$	100% $\text{Pu}(\text{OH})_4^0$
NaHCO_3 - type GW pH=8.3	94% $\text{Th}(\text{OH})_3\text{CO}_3^-$ 6% $\text{Th}(\text{OH})_4^0$	80% $\text{U}(\text{OH})_4^0$ 5% $\text{U}(\text{OH})_3\text{CO}_3^-$ 15% $\text{U}(\text{CO}_3)_4^{4-}$	100% $\text{Np}(\text{OH})_4^0$	99% $\text{Pu}(\text{OH})_4^0$ 1% $\text{Pu}(\text{CO}_3)_5^{6-}$

This table shows that the calculated aqueous speciation for the tetravalent actinides is very similar in both marl reference groundwaters. The dominant species are the neutral hydroxy complexes. The exception to this is Th(IV) where the $\text{Th}(\text{OH})_3\text{CO}_3^{2-}$ complex is dominant. However, the sorption values for Th selected later were measured at pH ~ 8 under calcite saturation. The carbonate complexation effect is thus already included and as shown in Table 8 speciation at pH = 6.7 and 8.3 is similar.

Also, for the reasons given in section 6.3.2, a pH conversion factor for the tetravalent actinides is not required. Hence no corrections for water chemistry are made and the same sorption values apply to both reference waters.

An important source of sorption data for actinides in the +4 valence state is the

work of BERRY et al. (1989, 1991a) and BASTON et al. (1991, 1992). These authors studied the sorption of Th(IV), U(IV) and Pu(IV) on 3 sediments (London clay, Caithness flagstones and St. Bees sandstone) in the absence and presence of organic degradation products over a range of pH values. The measurements made at approximately pH = 8 in the absence of organics are relevant for the undisturbed far field. The general trend in the distribution ratios determined for these sediments was that $R_d(\text{Th}) < R_d(\text{U}) \sim R_d(\text{Pu})$.

The data for London clay, where illite is the dominant mineral (~ 40 wt.%), are considered to be the most relevant for marl. The water compositions and mineralogies used in these tests were reported. A CEC value for the London clay was not given but, by using CEC data for the pure mineral components (ALLARD et al. 1983b) a value of 0.14 equiv. kg⁻¹ was estimated. This value is used in the calculation of the mineralogy conversion factors.

8.4.2.1 Thorium

BASTON et al. (1991, 1992) studied the sorption of Th(IV) on London clay at pH ~ 8 at S:L ratios of 1:50 and 1:5 in the absence and presence of "authentic" cellulose degradation products. The initial Th(IV) concentration was 2×10^{-11} M in all cases. The measured R_d values were approximately constant, lying in the range 1 - 2 m³ kg⁻¹. There was no influence of organics on the sorption behaviour of Th on London clay. On the Caithness flagstone and St. Bees sandstone sediments the R_d values for Th(IV), in the absence of organics, were within 20% of the London clay values. The mean value of these measurements was 1 m³ kg⁻¹ and this distribution ratio was selected.

8.4.2.2 Uranium

BASTON et al. (1992) compared the sorption of U(IV) and U(VI) on St. Bees sandstone in a CaCO₃ saturated groundwater at a pH of ~8. A direct comparison showed that the sorption of U(IV) was 2 to 3 orders of magnitude larger than that of U(VI). A similar observation had been made previously for the sorption on the Caithness flagstones (BASTON et al. 1991). These authors attributed this effect to the formation of uranium(VI) carbonate complexes which are less sorbing. The U(IV) speciation at pH ~ 8 was predicted to be almost totally dominated by the hydroxide species, U(OH)₄ (BOND et al.

1991). Because of the reducing conditions in the far field, sorption data under oxidised conditions are not considered further. The U(IV) sorption on London clay was measured at an Eh of ~ -230 mV, a pH of 8 and at U equilibrium concentrations below 10^{-9} M. The lowest measured sorption value of $5 \text{ m}^3 \text{ kg}^{-1}$ is selected.

8.4.2.3 Neptunium

Various authors including HIGGO (1988); LIESER et al. (1991) and ALLARD (1985) have stated that at Eh values below +200 mV Np(IV) is the dominant aqueous species. LIESER et al. (1991) investigated the effect of Eh on the sorption of Np in various groundwater sediments systems and demonstrated a clear increase in the uptake of Np at Eh values below +200 mV. Therefore, at the Eh conditions in the unaltered marl (~ -320 mV, see section 3.3) Np is most likely to be in the tetravalent oxidation state.

HENRION et al. (1985) studied Np sorption on Boom clay under reducing conditions. However, because strong complexation with humic substances essentially determined the Np sorption, the results from this work are not relevant for the marl system.

The only other potentially relevant data found were those from BARNEY (1982) where Np was measured under reducing conditions (0.05 M hydrazine) on a sandstone ($\text{CEC} = 0.099 \text{ equiv. kg}^{-1}$) in a synthetic groundwater at pH values between 8.7 to 9.4. The R_d values determined in this study for Np ranged from 0.1 to $0.7 \text{ m}^3 \text{ kg}^{-1}$. The Np equilibrium concentration was $\sim 3 \times 10^{-7}$ M. The mean R_d value of 10 independent measurements was $0.4 (\pm 0.3) \text{ m}^3 \text{ kg}^{-1}$. Because of the uncertainties with respect to the influence of hydrazine and the scatter in the data we do not consider this data further.

On the basis of chemical analogy with tetravalent actinides we assign the same R_d values for Np(IV) as for Th(IV). In Figure 10 the position of Np(IV) lies between Th(IV) and the other actinides, U(IV) and Pu(IV).

8.4.2.4 Plutonium

The results from Pu(IV) sorption measurements on London clay ($> 10 \text{ m}^3 \text{ kg}^{-1}$), St. Bees sandstone ($3 - 10 \text{ m}^3 \text{ kg}^{-1}$) and Caithness flagstones ($3.5 - 7.5 \text{ m}^3 \text{ kg}^{-1}$) (BASTON et al. 1992; BERRY et al. 1989, 1991a) are comparable with the U(IV) sorption data measured on these sediments. Even though the Pu(IV) sorption value for London clay is given as being $> 10 \text{ m}^3 \text{ kg}^{-1}$, a value of $5 \text{ m}^3 \text{ kg}^{-1}$ is selected to be consistent with the distribution ratio chosen for U(IV) on the basis of the general observation that $R_d(\text{Th}) < R_d(\text{U}) \sim R_d(\text{Pu})$.

In most other Pu sorption studies reported in the open literature, the valence state is not given and often different oxidation states are present. For example, Pu sorption on illite was measured by TICKNOR (1993) with Pu(IV) as the dominant species but Pu(V) and Pu(VI) species were also present. MUCCIARDI et al. (1978) also measured Pu sorption on illite in the presence and absence of carbonate but did not specify the valence state. Within the large scatter of the experimental data (R_d values ranging from 1 to $17 \text{ m}^3 \text{ kg}^{-1}$) no effects of carbonate were observed.

8.4.3 Protactinium

Under the anticipated in situ redox and pH conditions, Pa probably exists predominantly in the pentavalent oxidation state. BERRY et al. (1988a) measured the sorption of Pa(V) under reducing conditions. They investigated the sorption of Pa on six geological media* in the pH range 6 to 9.5 and measured R_d values between 1 - $>1000 \text{ m}^3 \text{ kg}^{-1}$. The values for London clay, selected as being the most similar of the six materials to marl, lay between ~ 3 and $>1000 \text{ m}^3 \text{ kg}^{-1}$ (pH = 8.8 to 9.1, initial Pa concentration $\sim 5 \times 10^{-11} \text{ M}$). The sorption values for Pa(V) are (significantly) greater than the values determined for Th(IV), which is surprising. This, coupled with the large spread in the data, makes the choice of a sorption value for Pa(V) based on just these results somewhat uncertain.

MEYER et al. (1985) conducted a series of measurements on the sorption of Np(V) on illite at trace concentrations in an 0.1 M NaCl solution as a function

*Permian anhydrite, New red sandstone, Hebridean granite, London clay, Lower lias clay, Permian triassic shale.

of pH (range 5.5 to 10) in the absence and presence of carbonate. We have taken Np(V) as a chemical analogue for Pa(V) and selected sorption values on illite of 0.1 and 0.2 m³ kg⁻¹ for the NaCl- and NaHCO₃-type waters at their corresponding pH values respectively. Compared even with the lowest R_d values determined by BERRY et al. (1988a), the selections are clearly conservative.

8.5 Anions

8.5.1 Iodine, Chloride

LIU & VON GUNTEN (1988) have carried out an extensive review of the sorption behaviour of I on geological substrates. They state: "Even if it seems reasonable to adopt an R_d value of 0.0003 m³ kg⁻¹ for sorption of I by the Valanginian marl, for safety assessment a conservative value of zero should still be used". We accept their conclusion and select R_d = 0 m³ kg⁻¹ for I⁻.

The sorption of Cl on soils and clays is low, and occurs only under acidic conditions (PARFITT 1978). In the NaHCO₃-type water no Cl sorption is expected because of the high pH. Due to the very high chloride concentration in the NaCl-type reference water, no Cl sorption is expected here as well.

8.5.2 Selenium

Under the reducing conditions prevailing in situ (-310 mV), Se is most probably present as Se⁰/HSe⁻ over the pH range from 7 to 8.5 (see for example NEAL et al. 1987a; BROOKINS 1988).

Sorption values for Se in the range 0.001 to 0.01 m³ kg⁻¹ were reported by BARNEY (1982) on sandstone and tuff for initial concentrations of 4 x 10⁻⁵ to 5 x 10⁻⁸ M selenite under oxidising and reducing (0.05 M hydrazine) conditions. Similar values were measured for both materials irrespective of whether the reducing agent was present or not. The explanation suggested for this behaviour was that the selenite was not reduced.

In view of the lack of relevant sorption data, and considering that the species HSe⁻ is anticipated to be dominant in the marl reference groundwater

chemistries, the sorption of Se is taken to be zero.

8.5.3 Organic Carbon

About 25% of the total ^{14}C activity in the SMA waste streams is likely to be in the form of organic molecules arising principally from research, industry and medicine sources (McGINNES 1993).

It is generally well known that dissolved organic ligands interact with mineral surfaces (see for example THENG 1974; RAUSSELL-COLOM & SERRATOSA 1987). In particular cases, such as the complexes formed between polyamines and transition metals, it has been shown that they sorb extremely strongly on clay minerals (PLEYSIER & CREMERS 1975; MAES et al. 1976, 1978 and PEIGNEUR et al. 1979). However, since no quantitative information could be found for the organics of interest, it was assumed (conservatively) that they do not undergo sorption.

8.5.4 Inorganic Carbon

The main sorption mechanism for $\text{H}^{14}\text{CO}_3^- / ^{14}\text{CO}_3^{2-}$ is isotope exchange on calcite surfaces and this is treated in the next chapter.

9 SELECTED SORPTION VALUES FOR CALCITE (MIN-D)

The rock types grouped together under the heading "MIN-D" are all very rich in calcite and contain no significant quantities of clay minerals. As stated in section 5.4, only sorption data on calcite are relevant in this case.

Because of the uncertainties associated with the sorption mechanisms on calcite, no corrections for water chemistries were attempted. Wherever possible sorption values were selected at the appropriate pH. The mineralogical conversion factor (0.95) and the Lab->Field transfer factor (0.05) are the same for all radionuclides and are applied to the selected laboratory sorption data in the following sections. Hence, separate data sheets for MIN-D were not produced.

The exception to the above is ^{14}C ($\text{HCO}_3^-/\text{CO}_3^{2-}$). Calcite was chosen as the main sorbing phase for this radionuclide and sorption data sheets for the four mineral groupings MIN-A to MIN-D and the two reference groundwater chemistries are given in Appendix C.

9.1 Alkaline and alkaline-earth metals

9.1.1 Caesium

Cs sorption on calcite has been reported to lie in the region of $0.001 \text{ m}^3 \text{ kg}^{-1}$ by ANDERSON et al. (1983) and TORSTENFELT et al. (1982). However, BERRY et al. (1991b) concluded from their batch sorption experiments that Cs is not taken up by calcite at all. Adopting a conservative position, we assume that Cs is not sorbed by calcite in both reference waters.

9.1.2 Potassium, Strontium

For K no sorption data on calcite could be found. A conservative R_d value of zero is taken for this element.

Various authors have reported Sr sorption on calcite (LORENS 1981; MIYAKE et al. 1988; ZACHARA et al. 1991) which is characterised by low, pH dependent values. Below pH 8 no sorption seems to take place at all. For this

reason we have selected $R_d(\text{Sr})=0$ for the NaCl-type groundwater where the pH = 6.7. At higher pH values the sorption increases, and at pH ~ 8.3 a value of $0.001 \text{ m}^3 \text{ kg}^{-1}$ could be extracted from the sorption edge data given in the above studies. This sorption value was selected for the NaHCO_3 -type reference water.

9.1.3 Radium

On the basis of chemical analogy, the same sorption values were taken for Ra as for Sr.

9.2 Transition Metals and Heavy Metals

9.2.1 Nickel, Cobalt

ZACHARA et al. (1991) studied the sorption of seven divalent metals on calcite over a large initial metal concentration range (10^{-4} to 10^{-8} M) at constant ionic strength ($I = 0.1\text{M}$) and variable pH. These authors observed the following selectivity sequence: $\text{Cd} > \text{Zn} \geq \text{Mn} > \text{Co} > \text{Ni} \gg \text{Ba} \sim \text{Sr}$. Increase in sorption as a function of pH occurred for Ni and Co but only began at pH values of 7.5 and 8 respectively. (See Figure 2a in ZACHARA et al. 1991.) At pH 8.3 sorption values for Co of $0.04 \text{ m}^3 \text{ kg}^{-1}$ and for Ni of $0.01 \text{ m}^3 \text{ kg}^{-1}$ could be extracted from the sorption edges and these values are selected for the NaHCO_3 -type groundwater. (Co equilibrium conc. = 5×10^{-8} M; Ni equilibrium conc. = 8×10^{-8} M.) From the linear part of the Langmuir isotherms also presented in this study, similar R_d values could be calculated. The uptake of these elements by calcite was interpreted in terms of a surface-exchange reaction with Ca. In general, for those radionuclides having an ionic radius greater than Ca (e.g. Sr) the sorption is weak, whereas those with smaller ionic radii tended to sorb more strongly.

At pH values of ~7, the uptake of Co and Ni is very small. ZACHARA et al. (1991) presented their measurements graphically as % sorbed versus pH which made the calculation of R_d values from their data under these conditions rather uncertain. AKSOYOGLU et al. (1992) measured the sorption of Ni on calcite in a NaCl-type marl water at pH 7.2 at an equilibrium concentration of $\sim 10^{-7}$ M. A low value of $0.006 \text{ m}^3 \text{ kg}^{-1}$ was measured and this value is taken for

the NaCl-type reference groundwater. On the basis of chemical analogy the same value is taken for Co.

COMANS & MIDDELBURG (1987); KORNICKER et al. (1985) and LORENS (1981) have all determined the sorption of Co on calcite and these measurements are in accord with the above selected values.

9.2.2 Palladium

Sorption data for Pd on calcite could not be found. We consider Ni as a chemical analogue and take the same R_d value.

9.2.3 Silver, Technetium, Niobium and Polonium

Since no measurements on the uptake of these elements on calcite could be found in the open literature, they were assumed to be non sorbing.

9.2.4 Lead

Although there are numerous studies describing the immobilisation of Pb by calcite and aragonite (MIYAKE et al. 1988; GAMSJÄGER et al. 1984), they tend to deal with the surface precipitation of $PbCO_3$ and not the sorption behaviour of Pb. Because no relevant sorption data for Pb on calcite were found, the same sorption value as for Ni was taken.

9.2.5 Tin and Molybdenum

Sorption data for Sn and Mo on calcite could not be found. Under the relevant pH/Eh conditions they are predominant present in solution as stannate (SnO_3^{2-}) and molybdate (MoO_4^{2-}). In the following we have chosen to use selenite (SeO_3^{2-}) as a chemical analogue.

The sorption behaviour of the SeO_4^{2-}/SeO_3^{2-} has been investigated extensively in the open literature. Data on selenite (SeO_3^{2-}) sorption on soils (SPOSITO et al. 1988; SINGH et al. 1981) and mineral components of soils and sediments (FROST & GRIFFIN 1977; GOLDBERG & GLAUBIG 1988; NEAL et al. 1987a,b; BAR-YOSEF & MEEK 1987) are available and surface complexation models

have been applied to describe $\text{SeO}_4^{2-}/\text{SeO}_3^{2-}$ adsorption on these sorbents (see for example DAVIS & KENT 1990).

COWAN et al. (1990) studied the sorption of SeO_3^{2-} on calcite and sorption edges and isotherms are presented together with "solution effects" (phosphate competition). The general trend observed was that sorption increased with decreasing pH. The authors were able to model their results using a surface complexation model.

The presence of 10^{-4} M PO_4^{3-} only reduced the SeO_3^{2-} sorption by about 10%. Since the PO_4^{3-} levels in both reference waters are much lower (Table 1) this effect can be neglected.

The selected R_d values for SeO_3^{2-} , $8 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ at pH 8.3 and $0.01 \text{ m}^3 \text{ kg}^{-1}$ at pH 6.7, were taken from the sorption edges at the appropriate pH values and these values were consequently used for Sn and Mo.

9.2.6 Zirconium

No sorption data could be found for Zr and in common with previous practice, Th was taken as the chemical analogue.

9.3 Actinides

9.3.1 Americium

ALLARD measured the sorption of Am on calcite and dolomite (ALLARD 1982; ALLARD & BEALL 1979) in a synthetic groundwater in a pH range between 7 and 8.5. The R_d values ranged from ~ 5 to $50 \text{ m}^3 \text{ kg}^{-1}$. The data did not show any pH dependency.

There are several reports on studies of Am interactions with calcite under neutral to slight alkaline conditions. SHANBHAG & MORSE (1982) give a minimum value of $200 \text{ m}^3 \text{ kg}^{-1}$ for Am sorption on calcite in the pH range 7 to 8. This value agrees with the very high Am-calcite affinity determined by SANCHEZ et al. (1981). HIGGO et al. (1983) investigated the sorption of Am

onto calcareous rich deep sea sediments (up to 90% CaCO_3 with trace amounts of illite/kaolinite) at $\text{pH} = 8.2$ in a saline NaCl-type water. Sorption values of 50 to $100 \text{ m}^3 \text{ kg}^{-1}$ were recorded after 7 days and increased gradually up to 100 to $200 \text{ m}^3 \text{ kg}^{-1}$ after 56 day equilibrium times.

The mechanism of Am uptake by calcite is poorly understood. The high values recorded by SHANBHAG & MORSE (1982) and HIGGO et al. (1983) may be due to a two step sorption process in which the second step is some sort of incorporation/precipitation into the calcite surface layer. CARROLL (1993) has proposed a mechanistic description for the uptake of Nd (used as analogue for Am) onto calcite and concluded that a Nd-Ca carbonate solid solution is formed. This author compared the Nd results with the Am uptake studies from SHANBHAG & MORSE (1982) and state that the uptake of Am is most likely due to the precipitation of a pure Am-carbonate or a mixed Am-Ca carbonate phase. (The initial Am concentrations in the above mentioned studies were always low, and, according to the authors, undersaturated with respect to common Am phases.)

From the above data sources, the sorption data sets measured by ALLARD (1982) and ALLARD & BEALL (1979) are preferred and are selected for both types of reference groundwaters. The value of $20 \text{ m}^3 \text{ kg}^{-1}$ is representative of distribution ratios in the lower range of the measured data.

9.3.2 Thorium, Uranium, Neptunium and Plutonium

For Th in a synthetic brine ($\text{pH} = 7$) single R_d determinations of $15 \text{ m}^3 \text{ kg}^{-1}$ are given by MAITE et al. (1989) for calcite and dolomite. CARROLL et al. (1992) have studied the interaction of Th at the calcite solution interface and conclude that a Th-Ca- CO_3 solid solution is formed. However, they were not able to quantify their data sufficiently well for the model to be used with confidence to predict Th uptake by calcite. Since no additional data could be found the value of MAITE et al. (1989) is selected.

Because no data could be found for the sorption of U, Pu, and Np in the tetravalent state on calcite, the same value as for Th was taken.

9.3.3 Protactinium

No sorption data for Pa on calcite were found. However, if as before, Np(V) may be taken as an analogue for Pa(V), ALLARD (1982) measured the sorption of the former on calcite in a NaHCO₃-type groundwater over the pH range from ~ 7.5 to ~ 8.5. From these data we select R_d values for Pa(V) of 0.5 and 2 m³ kg⁻¹ for the NaCl- and NaHCO₃-type reference groundwaters respectively.

9.4 Anions

9.4.1 Iodine, Chloride, Selenium

No sorption data on calcite could be found for these elements and we assign a conservative value of zero for the MIN-D mineralogy. (Under the prevailing Eh/pH conditions is selenium present as Se⁰/HSe⁻.)

9.4.2 ¹⁴C as H¹⁴CO₃⁻/¹⁴CO₃²⁻

COWAN et al. (1990) carried out isotopic exchange measurements of H¹⁴CO₃⁻ on calcite (particle size ~ 10 μm) at pH = 7.5 over time scales of up to 48 hours. H¹⁴CO₃⁻ exchanged with the hydrated CaCO₃ surface layer at a linear rate of ~ 2 x 10⁻⁸ mol H¹⁴CO₃⁻/g/hour and there were no indications of saturation within the experimental time scale.

DAVIS et al. (1987) determined isotopic exchange for Ca on calcite over time periods of up to ~ 150 hours at different pH values in an artificial groundwater. At pH values of 6.5, 7.6 and 8.3 the rates of Ca isotopic exchange were 8.8 x 10⁻⁸, 3.2 x 10⁻⁸ and 1.6 x 10⁻⁸ moles Ca/g/hour respectively. Again, these rates showed no signs of decreasing with time. The data of COWAN et al. (1990) for H¹⁴CO₃⁻ are compatible with these measurements.

Given that the most likely removal mechanism for H¹⁴CO₃⁻/¹⁴CO₃²⁻ from solution is isotopic exchange with the surface layers of CaCO₃, the most critical (and difficult) question to answer is then how much of the intact calcite present is available to take part in this exchange.

An estimate can be made on the basis of the work of STIPP et al. (1994, 1996) who showed that the calcium in the first approximately 30 monolayers i.e. to a depth of $\sim 10^{-8}$ m, is readily accessible on time scales of the order of a few months. If we take this value of 10^{-8} m and the accessible surface area in intact calcite (~ 0.1 m² g⁻¹, Table 3a) then the volume of calcite available for exchange is $\sim 10^{-6}$ m³ kg⁻¹. For a calcite density of 2700 kg m⁻³, this converts to $\sim 2.7 \times 10^{-3}$ kg kg⁻¹, or ~ 0.3 % of the total calcite. This estimate is almost certainly conservative, since more calcite is likely to become available over longer times. Note also that the above value is an in situ estimate since the surface area for intact calcite was used.

If 0.3 wt.% of the bulk calcite is taken to be available for exchange with $\text{H}^{14}\text{CO}_3^- / {}^{14}\text{CO}_3^{2-}$, then the total moles of exchangeable CO_3^{2-} in the solid phase is 2.7×10^{-2} mol kg⁻¹. Thus, the $\text{H}^{14}\text{CO}_3^- / {}^{14}\text{CO}_3^{2-}$ sorption values in the two reference groundwaters can be readily obtained using their respective aqueous concentrations given in Table 1. At equilibrium the R_d values are estimated to be 2.1×10^{-3} m³ kg⁻¹ and 1.6×10^{-3} m³ kg⁻¹ for the NaCl-type and NaHCO₃-type waters respectively i.e. practically the same. The above values need only to be scaled by the weight fractions of calcite in the different mineral groupings to yield the corresponding in situ distribution ratios (see Appendix C).

10 **SELECTED R_d VALUES CORRESPONDING TO IN SITU CONDITIONS IN PALFRIS MARL: SUMMARY TABLES**

The selected in situ* distribution ratios for the mineral classes defined in Chapter 2 and the two reference water chemistries, NaCl-type groundwater and NaHCO₃-type groundwater (Chapter 3) are summarised in Tables 9 and 10 respectively.

Fault gouge (MIN-B, Chapter 2) is treated separately since a Lab -> Field conversion factor of unity was used. The "marl reference sorption values" for MIN-B (Appendix A) were taken directly for each reference groundwater chemistry. The selected distribution ratios for both water chemistries are given in Table 11.

*The term "in situ" is used here to describe the R_d values given in the SDB which result from modifying the selected laboratory sorption data in the manner described in Chapters 5, 6 and 7.

Table 9: In situ R_d values ($m^3 kg^{-1}$) for the NaCl-type groundwater.

RADIONUCLIDE	MIN-A	MIN-B	MIN-C	MIN-D
C(inorg.)	10^{-3}	9×10^{-4}	1.5×10^{-3}	2×10^{-3}
C(org.)	0	0	0	0
Cl	0	0	0	0
K	3×10^{-4}	4×10^{-4}	1.5×10^{-4}	0
Co	1.5×10^{-2}	2×10^{-2}	6×10^{-3}	3×10^{-4}
Ni	2×10^{-2}	3×10^{-2}	10^{-2}	3×10^{-4}
Se	0	0	0	0
Sr	1.5×10^{-4}	2.5×10^{-4}	8×10^{-5}	0
Zr	10^{-1}	1.5×10^{-1}	5×10^{-2}	7×10^{-1}
Nb	8×10^{-2}	10^{-1}	4×10^{-2}	0
Mo	3×10^{-3}	5×10^{-3}	2×10^{-3}	5×10^{-4}
Tc	1.5×10^{-3}	2×10^{-3}	7×10^{-4}	0
Pd	2×10^{-2}	3×10^{-2}	10^{-2}	3×10^{-4}
Ag	0	0	0	0
Sn	3×10^{-3}	5×10^{-3}	2×10^{-3}	5×10^{-4}
I	0	0	0	0
Cs	5×10^{-2}	8×10^{-2}	3×10^{-2}	0
Pb	3×10^{-1}	5×10^{-1}	1.5×10^{-1}	3×10^{-4}
Po	0	0	0	0
Ra	1.5×10^{-4}	2.5×10^{-4}	8×10^{-5}	0
Ac	1.5	2	8×10^{-1}	1
Th	10^{-1}	1.5×10^{-1}	5×10^{-2}	7×10^{-1}
Pa	7×10^{-3}	10^{-2}	4×10^{-3}	3×10^{-2}
U	5×10^{-1}	7×10^{-1}	3×10^{-1}	7×10^{-1}
Np	10^{-1}	1.5×10^{-1}	5×10^{-2}	7×10^{-1}
Pu	5×10^{-1}	7×10^{-1}	3×10^{-1}	7×10^{-1}
Am	1.5	2	8×10^{-1}	1
Cm	1.5	2	8×10^{-1}	1

Table 10: In situ R_d values ($\text{m}^3 \text{kg}^{-1}$) for the NaHCO_3 -type groundwater.

RADIONUCLIDE	MIN-A	MIN-B	MIN-C	MIN-D
C(inorg.)	9×10^{-4}	7×10^{-4}	10^{-3}	1.5×10^{-3}
C(org.)	0	0	0	0
Cl	0	0	0	0
K	3×10^{-3}	4×10^{-3}	1.5×10^{-3}	0
Co	5×10^{-1}	7×10^{-1}	3×10^{-1}	2×10^{-3}
Ni	9×10^{-1}	1.5	5×10^{-1}	5×10^{-4}
Se	0	0	0	0
Sr	2.5×10^{-2}	3×10^{-2}	10^{-2}	5×10^{-5}
Zr	10^{-1}	1.5×10^{-1}	5×10^{-2}	7×10^{-1}
Nb	8×10^{-2}	10^{-1}	4×10^{-2}	0
Mo	10^{-3}	1.5×10^{-3}	6×10^{-4}	4×10^{-5}
Tc	1.5×10^{-3}	2×10^{-3}	7×10^{-4}	0
Pd	9×10^{-1}	1.5	5×10^{-1}	5×10^{-4}
Ag	2×10^{-3}	3×10^{-3}	10^{-3}	0
Sn	10^{-3}	1.5×10^{-3}	6×10^{-4}	4×10^{-5}
I	0	0	0	0
Cs	10^{-1}	1.5×10^{-1}	5×10^{-2}	0
Pb	7×10^{-2}	10^{-1}	4×10^{-2}	5×10^{-4}
Po	0	0	0	0
Ra	2.5×10^{-2}	3×10^{-2}	10^{-2}	5×10^{-5}
Ac	7	10	4	1
Th	10^{-1}	1.5×10^{-1}	5×10^{-2}	7×10^{-1}
Pa	1.5×10^{-2}	2×10^{-2}	7×10^{-3}	10^{-1}
U	5×10^{-1}	7×10^{-1}	3×10^{-1}	7×10^{-1}
Np	10^{-1}	1.5×10^{-1}	5×10^{-2}	7×10^{-1}
Pu	5×10^{-1}	7×10^{-1}	3×10^{-1}	7×10^{-1}
Am	7	10	4	1
Cm	7	10	4	1

Table 11: In situ R_d values ($m^3 kg^{-1}$) for fault gouge.

RADIONUCLIDE	NaCl-type groundwater	NaHCO ₃ -type groundwater
C(inorg.)	9×10^{-4}	7×10^{-4}
C(org.)	0	0
Cl	0	0
K	10^{-3}	10^{-2}
Co	4×10^{-2}	2
Ni	8×10^{-2}	3
Se	0	0
Sr	6×10^{-4}	8×10^{-2}
Zr	4×10^{-1}	4×10^{-1}
Nb	3×10^{-1}	3×10^{-1}
Mo	10^{-2}	4×10^{-3}
Tc	5×10^{-3}	5×10^{-3}
Pd	8×10^{-2}	3
Ag	0	8×10^{-3}
Sn	10^{-2}	4×10^{-3}
I	0	0
Cs	2×10^{-1}	4×10^{-1}
Pb	1	3×10^{-1}
Po	0	0
Ra	6×10^{-4}	8×10^{-2}
Ac	5	25
Th	4×10^{-1}	4×10^{-1}
Pa	3×10^{-2}	5×10^{-2}
U	2	2
Np	4×10^{-1}	4×10^{-1}
Pu	2	2
Am	5	25
Cm	5	25

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REFERENCES

- AKSOYOGLU, S., MANTOVANI, M., HASELBECK, S. & DIERCKX, A. (1992): Sorption of nickel on marl and its components. Paul Scherrer Institut, Internal Report TM-43-92-28.
- ANDERSSON, K., TORSTENFELT, B. & ALLARD, B. (1983): Sorption of radionuclides in geologic systems. KBS Technical Report 83-63, KBS, Stockholm, Sweden.
- ALLARD, B. & BEALL, G.W. (1979): Sorption of americium on geologic media. J. Environ. Sci. Health A1 (6), pp. 507-518.
- ALLARD, B. (1982): Sorption of actinides in granitic rock. SKB/KBS Technical Report KBS-TR 82-21, SKB, Stockholm, Sweden.
- ALLARD, B., OLOFSSON, U., TORSTENFELT, B. & KIPATSI, H. (1983a): Sorption behaviour of well-defined oxidation states. KBS Report 83-61. SKBF/KBS, Stockholm, Sweden.
- ALLARD, B., KARLSSON, M., TULLBORY, E.L. & LARSON, S.A. (1983b): Ion exchange capacities and surface areas of some major components and common fracture filling materials of igneous rocks. SKBF/KBS Technical Report 83-64.
- ALLARD, B. (1985): Radionuclide sorption on carbonate-clayish rocks. Nagra Technical Report NTB 85-20, Nagra, Wettingen, Switzerland.
- AMES, L.L., MCGARRAH, J.E. & WALKER, B.A. (1983): Sorption of trace constituents from aqueous solutions onto secondary minerals.II. Radium. Clays Clay Minerals 31, pp. 335-342.
- BAEYENS, B. & BRADBURY, M.H. (1991a): Characterisation of downhole water samples taken during pumping tests from borehole SB4, Wellenberg: "Can the groundwater chemistry be deduced from such measurements?" Nagra Unpublished Internal Report.

- BAEYENS, B. & BRADBURY, M.H. (1991b): A physico-chemical characterisation technique for determining the pore-water chemistry in argillaceous rocks. PSI Bericht Nr. 103, Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 90-40, Nagra, Wettingen, Switzerland.
- BAEYENS, B. & BRADBURY, M.H. (1994): Physico-chemical characterisation and calculated in situ porewater chemistries for a low permeability Palfris marl sample from Wellenberg. PSI Bericht Nr. 94-19, Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 94-22, Nagra, Wettingen, Switzerland.
- BAEYENS, B. & BRADBURY, M.H. (1995a): A quantitative mechanistic description of Ni, Zn and Ca sorption on Na-montmorillonite. Part I: Physico-chemical characterisation and titration measurements. PSI Bericht Nr. 95-10. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 95-04, Nagra, Wettingen, Switzerland.
- BAEYENS, B. & BRADBURY, M.H. (1995b): A quantitative mechanistic description of Ni, Zn and Ca sorption on Na-montmorillonite. Part II: Sorption measurements. PSI Bericht Nr. 95-11. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 95-05, Nagra, Wettingen, Switzerland.
- BAES, C. & MESMER, R. (1976): The hydrolysis of cations. John Wiley & Sons, New York.
- BALISTRIERI, L.S. & MURRAY, J.W. (1984): Marine scavenging: Trace metal adsorption by interfacial sediment from MANOP site H¹. *Geochim. Cosmochim. Acta* 48, pp. 921-929.
- BANGASH, M.A., HANIF, J. & ALI KHAN, M. (1992): Sorption behaviour of cobalt on illitic soil. *Waste Management* 12, pp. 29-38.
- BARNEY, G.S. (1982): Radionuclide sorption on basalt-interbed materials. RHO-BW-35P. Rockwell International.

- BAR-YOSEF, B. & MEEK, D. (1987): Selenium sorption by kaolinite and montmorillonite. *Soil Sci.* 144, pp. 11-19.
- BASTON, G.M.N., BERRY, J.A., BOND, K.A., BROWNSWORD, M. & LINKLATER, C.M. (1991): Studies of the effects of organic materials on the sorption of uranium(IV) and thorium(IV) on London clay and Caithness flagstones. *Safety Studies Nirex Radioactive Waste Disposal*, NSS/R258, AEA-D&R-0210.
- BASTON, G.M.N., BERRY, J.A., BOND, K.A., BROWNSWORD, M. & LINKLATER, C.M. (1992): Effects of organic degradation products on the sorption of actinides. *Radiochimica Acta* 58/59, pp. 349-356.
- BEALL, G.W. & ALLARD, B. (1981): Sorption of actinides from aqueous solutions under environmental conditions. In: *Adsorption from aqueous solutions* (P.H. TEWARI, ed.), pp. 193-212, Plenum Press, New York.
- BERNER, U. (1995): KRISTALLIN-I: Estimates of solubility limits for safety relevant radionuclides. PSI Bericht Nr. 95-07, Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 94-08, Nagra, Wettingen, Switzerland.
- BERRY, J.A., HOBLEY, J., LANE, S.A., LITTLEBOY, A.K., NASH, M.J., OLIVER, P., SMITH-BRIGGS, J.L. & WILLIAMS, S.J. (1988a): The solubility and sorption of protactinium in the near-field and far-field environments of a radioactive waste repository. *Safety Studies Nirex Radioactive Waste Disposal*, NSS/R122.
- BERRY, J.A., BOURKE, P.J., COATES, H.A., GREEN, A., JEFFERIES, N.L. & LITTLEBOY, A.K. (1988b): Sorption of radionuclides on sandstones and mudstones. *Radiochimica Acta* 44/45, pp. 135-141.
- BERRY, J.A., BOND, K.A., FERGUSON, D.R. & PILKINGTON, N.J. (1989): Studies of the effects of organic materials on the sorption of uranium and plutonium. *Safety Studies Nirex Radioactive Waste Disposal*, NSS/R183.
- BERRY, J.A., BOND, K.A., FERGUSON, D.R. & PILKINGTON, N.J. (1991a):

Experimental studies of the effects of organic materials on the sorption of uranium and plutonium. *Radiochimica Acta* 52/53, pp. 201-209.

BERRY, J.A., COWPER, M.M., GREEN, A., JEFFERIES, N.L. & LINKLATER, C.M. (1991b): Sorption of radionuclides on mineral surfaces. Proc. Intern. Conf. on Nuclear Fuel Reprocessing and Waste Management, Sendai, Japan, pp. 988-993.

BLASER, P. (1993): WLB: Dokumentation der Wasser- und Gasprobenentnahmen und der hydrochemischen und isotopenhydrologischen Rohdaten in den Sondierbohrungen SB4, SB3, SB1, SB6 und SB2. Nagra Unpublished Internal Report.

BOND, K.A., CROSS, J.E. & EWART, F.T. (1991): Thermodynamic modelling of the effect of organic complexants on sorption behaviour. *Radiochimica Acta* 52/53, pp. 433-437.

BRADBURY, M.H., BAEYENS, B. & ALEXANDER, W.R. (1990): Experimental proposals for procedures to investigate the water chemistry, sorption and transport properties of marl. PSI Bericht Nr 82. Paul Scherrer Institut, Villigen, Switzerland. November 1990. Nagra Technical Report NTB 90-16. Nagra, Wettingen, Switzerland.

BRADBURY, M.H. & BAEYENS, B. (1992): Modelling the sorption of Cs: Application to the Grimsel experiment. PSI Nuclear Energy Research, Progress Report 1992, Annex IV, pp 59-64. Paul Scherrer Institut, Villigen, Switzerland.

BRADBURY, M.H. & BAEYENS, B. (1993): A general application of surface complexation to modeling radionuclide sorption in natural systems. *J. Colloid Interface Sci.* 158, pp. 364-371.

BRADBURY, M.H. & BAEYENS, B. (1994): Sorption by cation exchange. Incorporation of a cation exchange model into geochemical computer codes. PSI Bericht Nr. 94-07. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 94-11, Nagra, Wettingen, Switzerland. 1994.

- BRADBURY, M.H. & BAEYENS, B. (1995): A quantitative mechanistic description of Zn, Ca and Ni sorption on Na-montmorillonite. Part III: Modelling. PSI Bericht Nr. 95-12. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 95-06, Nagra, Wettingen, Switzerland.
- BRADBURY, M.H. & BAEYENS, B. (1997): Far-field sorption data bases for performance assessment of a L/ILW repository in a disturbed/altered Palfris marl host rock. PSI Bericht Nr 95-xx Paul Scherrer Institut, Villigen, Switzerland. Nagra Technical Report NTB 96-06, Nagra, Wettingen, Switzerland (in preparation).
- BRADBURY, M.H. & SAROTT, F-A. (1994): Sorption data bases for the cementitious near-field of a L/ILW repository for performance assessment. PSI Bericht Nr 95-06 Paul Scherrer Institut, Villigen, Switzerland. Nagra Technical Report NTB 93-08, Nagra, Wettingen, Switzerland.
- BROOKINS, D.G. (1988): Eh-pH diagrams for geochemistry. Springer Verlag, Berlin.
- BROUWER, E., BAEYENS, B., MAES, A. & CREMERS, A. (1983): Cesium and rubidium ion equilibria in illite clay. *J. Phys. Chem.* 87, pp. 1213-1219.
- BRUGGENWERT, M.G.M. & KAMPHORST, A. (1982): Survey of experimental information on cation exchange in soil systems. In *Soil Chemistry: B. Physico-chemical Models* (Ed. G.H. Bolt) Chap. 5, pp. 141-203. Elsevier, Amsterdam.
- BURGER, H. (1982): Tonmineralische und sedimentpetrolographische Untersuchungen in der untersten Kreide des oestlichen Helviticums. *Schweiz. Mineral. Petrog. Mitt.* 62, pp. 369-414.
- BURGER, H. (1985): PALFRIS-Formation, OHRLI-Formation und VIZNAU-Mergel (Basale Kreide des Helviticums) zwischen Reuss und Rhein; Stratigrafische, fazielle, mineralogische und palaeogeographische Untersuchungen. *Mitteilungen aus dem Geologischen Institut der Eidg.*

Technischen Hochschule und der Universität Zürich.

- CARROLL, S.A., BRUNO, J., PETIT, J.C. & DRAN, J.C. (1992): Interactions of U(VI), Nd(III) and Th(IV) at the calcite-solution interface. *Radiochimica Acta* 58/59, pp. 245-252.
- CARROLL, S.A. (1993): Precipitation of Nd-Ca carbonate solid solution at 25 °C. *Geochim. Cosmochim. Acta* 57, pp. 3383-3393.
- COLEMAN, N.T., CRAIG, DORIS & LEWIS, R.J. (1963): Ion-exchange reactions of cesium. *Soil Sci. Soc. Am. Proc.* 27, pp. 287-289.
- COMANS, R.N.J. & MIDDELBURG, J.J. (1987): Sorption of trace metals on calcite: Applicability of the surface precipitation model. *Geochim. Cosmochim. Acta* 51, pp. 2587-2591.
- COMANS, R.N.J., HALLER, M. & DE PRETER, P. (1991): Sorption of cesium on illite: Non-equilibrium behaviour and reversibility. *Geochim. Cosmochim. Acta* 55, pp. 433-440.
- COWAN, C.E., ZACHARA, J.M. & RESCH, C.T. (1990): Solution ion effects on the surface exchange of selenite on calcite. *Geochimica Cosmochimica Acta* 54, pp. 2223-2234.
- CREMERS, A., ELSEN, A., DE PRETER, P. & MAES, A. (1988): Quantitative analysis of radiocesium retention in soils. *Nature* 335, pp. 247-249.
- CZURDA, K.A., BÖHLER, U. & WAGNER, J.-F. (1989): Clay Basins as Especially Suitable Areas for Hazardous Waste Repositories. *Proc. Int. Symp. on Intermontane Basins: Geology & Resources* (Eds. T. Thanasuthipitak & P. Ounchanum). Chiang Mai, Thailand (30 January - 2 February 1989), pp. 146-160.
- DAVIS, J.A., FULLER, C.C. & COOK, A.D. (1987): A model for trace metal sorption processes at the calcite surface: Adsorption of Cd²⁺ and subsequent solid solution formation. *Geochimica Cosmochimica Acta*, 51, pp. 1477-1490.

- DAVIS, J.A. & KENT, D.B. (1990): Surface complexation modelling in aqueous geochemistry. In: Mineral-water interface geochemistry (M.F. HOCELLA, Jr. & WHITE, A.F., eds.) Reviews in Mineralogy 23, pp. 177-260.
- DEGUELDRE, C.A. (1994): Colloid properties in groundwaters from crystalline formations. PSI Bericht Nr 94-21 Paul Scherrer Institut, Villigen, Switzerland. Nagra Technical Report NTB 92-05 Nagra, Wetingen, Switzerland.
- DEGUELDRE, C.A., LAUBE, A. & SCHOLTIS, A: (1994a): A study of colloids: Groundwaters at the Wellenberg site. Status Report. Nagra Unpublished Internal Report.
- DEGUELDRE, C., ULRICH, H.J. & SILBY, H. (1994b): Sorption of ^{241}Am onto montmorillonite, illite and hematite colloids. Radiochimica Acta 65, pp. 173-179.
- DE PRETER, P. (1990): Radiocesium retention in the aquatic, terrestrial and urban environment: A quantitative and unifying analysis. Unpubl. PhD Thesis. Katholieke Universiteit Leuven, Belgium.
- DUGGER, D.L., STANTON, J.H., IRBY, B.N., McCONNEL, B.L., CUMMINGS, W.W. & MAATMAN, R.W. (1964): The exchange of twenty metal ions with the weakly acidic silanol group of silica gel. J. Phys. Chem. 68, pp. 757-760.
- DZOMBAK, D.A. & MOREL, F.M.M. (1990): Surface complexation modelling. John Wiley & Sons, New York.
- FALBE, J. & REGITZ, M. (1992): Römpp Chemie Lexikon. Georg Thieme Verlag Stuttgart.
- FROST, R.R. & GRIFFIN, R.A. (1977): Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Am. J. 41, pp. 53-57.

- GAMSJÄGER, H., FLUCH, A. & SWINEHART, J.H. (1984): The effect of potential aqueous pollutants on the solubility of Pb^{2+} in cerussite-calcite phases. *Monatshefte für Chemie* 115, pp. 251-259.
- GARRELS, R.G. & CHRIST, C.L. (1975): *Solution, minerals and equilibria*. Harper and Row, NY.
- GOLDBERG, S. & GLAUBIG, R.A. (1988): Anion sorption on a calcareous, montmorillonite soil-selenium. *Soil Sci. Soc. Amer. J.* 49, pp. 954-958.
- GONZALEZ, B.R., APPELT, H., SCHALSCHA, E.B. & BINGHAM, F.T. (1974): Molybdate adsorption characteristics of volcanic-ash-derived soils in Chile. *Soil Sci. Soc. Am. Proc.* 38, pp. 903-906.
- GORGEON, L. (1994): Contribution à la modélisation physico-chimique de la rétention de radioéléments à vie longue par des matériaux argileux. Unpublished PhD Thesis. Université Paris 6.
- GRIM, R.E. (1953): *Clay mineralogy*. McGraw Hill, New York.
- GRÜTTER, A., VON GUNTEN, H.R. & RÖSSLER, E. (1992): Sorption of barium on unconsolidated glaciofluvial deposits and clay minerals. *Radiochimica Acta* 58/59, pp. 259-265.
- GRÜTTER, A., VON GUNTEN, H.R., RÖSSLER, E. & KEIL, R. (1994): Sorption of nickel and cobalt on a size-fraction of unconsolidated glaciofluvial deposits and on clay minerals. *Radiochimica Acta* 65, pp. 181-187.
- HADERMANN, J. & JAKOB, A. (1987): Modelling small case infiltration experiments into bore cores of crystalline rock and break-through curves. EIR Bericht Nr. 622. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 87-07, Nagra, Wettingen, Switzerland.
- HEER, W. & HADERMANN, J. (1994): Grimsel Test Site. Modelling radionuclide migration field experiments. PSI Bericht Nr. 94-13. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 94-18, Nagra, Wettingen, Switzerland.

- HENRION, P.N., MONSECOUR, M., FONTEYNE, A., PUT, M. & DE REGGE, P. (1985): Migration of radionuclides in Boom clay. *Radioactive Waste Management and the Nuclear Fuel Cycle* 6(3-4), pp. 313-359.
- HIGGO, J.J.W., REES, L.V.C. & CRONAN, D.S. (1983): Sorption of americium and neptunium by deep-sea sediments. *Radioactive Waste Management and the Nuclear Fuel Cycle* 4 (I), pp. 73-102.
- HIGGO J.J.W. (1988): Review of sorption data applicable to the geological environments of interest for the deep disposal of ILW and LLW in the UK. *Safety Studies Nirex Radioactive Waste Disposal, NSS/R162*.
- HUNTER, A., HAWKE, D.J. & CHOO, L.K. (1988): Equilibrium adsorption of thorium by metal oxides in marine electrolytes. *Geochimica Cosmochimica Acta* 52, pp. 627-636.
- JAKOB, A. & HADERMANN, J. (1991): INTRAVAL Test case 1B: Modelling results. PSI Bericht Nr. 105. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 91-27, Nagra, Wettingen, Switzerland.
- JAKOB, A. & HADERMANN, J. (1994): INTRAVAL Finnsjön Test: Modelling results for some tracer experiments. PSI Bericht Nr. 94-12. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 94-21, Nagra, Wettingen, Switzerland.
- JENNE A.E. (1977): Trace element sorption by sediments and soils: Sites and processes. In: *Molybdenum in the environment* (W. Chappel and K. Peterson Eds.) Dekker, New York.
- KORNICKER, W.A., MORSE, J.W. & DAMASCENO, R.N. (1985): *Chemical Geology* 53, pp. 229-236.
- KOSS, V., WINKLER, A. & BÜTOW, E. (1992): Experimental investigation and modelling of the migration of radionuclides from the Ellweiler uranium mill tails. *Radiochimica Acta* 58/59, pp. 447-451.
- LEGOUX Y., BLAIN G., GUILLAUMONT R., OUZOUNIZIAN G., BRILLARD L. &

- HUSSONNOIS M. (1992): Kd measurements of activation, fission and heavy elements in water/solid phase systems. *Radiochimica Acta* 58/59, pp. 211-218.
- LI, Y.-H., BURKHARDT, L., BUCHHOLTZ, M., O'HARA, P. & SANTSCHI, P.H. (1984): Partition of radiotracers between suspended particles and seawater. *Geochim. Cosmochim. Acta* 48, pp. 2011-2019.
- LIESER, K.H. & BAUSCHER, CH. (1987): Technetium in the Hydrosphere and in the Geosphere I. Chemistry of Technetium and Iron in Natural Waters and Influence of the Redox Potential on the Sorption of Technetium. *Radiochimica Acta* 42, pp. 205-213.
- LIESER, K.H., HILL, R., MÜHLENWEG, U., SINGH, R.N., TU SHU-DE, STEINKOPFF, Th. (1991): Actinides in the Environment. *J. Radioanalyt. Nucl. Chem., Articles* 147, pp. 117-131.
- LIESER, K.H. & AMENT, A. (1993): Radiochemical investigation of the partition and sorption of lead in groundwater/sediment systems. *Radiochimica Acta* 60, pp. 153-158.
- LIU, Y. & VON GUNTEN, H. (1988): Migration chemistry and behaviour of iodine relevant to geological disposal of radioactive wastes. A literature review with a compilation of sorption data. PSI Bericht Nr. 16, PSI, Villigen, Switzerland.
- LORENS, R.B. (1981): Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. *Geochimica Cosmochimica Acta* 45, pp. 553-561.
- MAES, A., PEIGNEUR, P. & CREMERS, A. (1976): Thermodynamics of transition metal ion exchange in montmorillonite. *Proc. Int. Clay Conf.* 1975. Mexico. pp. 319-329.
- MAES, A., PEIGNEUR, P. & CREMERS, A. (1978): Stability of metal-uncharged ligand complexes in ion exchangers. II. The copper ethylenediamine complex in montmorillonite and sulphonic resin. *J. Chem. Soc.*

Faraday Transactions I 74, pp. 182-189.

- MAES, A. & CREMERS, A. (1986): High selective ion exchange in clay minerals and zeolites. In: DAVIS J.A. & HAYES, K.F. (eds.): Geochemical processes at mineral surfaces.- ACS Symposium Series 323, pp 254-295.
- MAITE, T.C., SMITH, M.R. & LAUL, J.C. (1989): Sorption of uranium, thorium, and radium on matrices under oxic environments. Radioactive Waste Management and the Nuclear Fuel Cycle, Vol. 11(3), pp. 269-278.
- MAZUREK, M. (1994): Geological input for safety assessment calculations of the proposed repository at Wellenberg. In: MAZUREK, M., WABER, N. & BLAESI, H.-R.: WLB: Geology, mineralogy and geochemistry of Wellenberg. Nagra Unpublished Internal Report.
- MAZUREK, M., WABER, N. & BLAESI, H.-R. (1994): WLB: Geology, mineralogy and geochemistry of Wellenberg. Nagra Unpublished Internal Report.
- McGINNES, D.F. (1993): Chemical form of C-14 in SMA waste streams. Nagra Unpublished Internal Report.
- McKINLEY, J.P. & JENNE, E.A. (1991): Experimental investigation and review of the "solids concentration" effect in adsorption studies. Environ. Sci. Technol. 25, pp. 2082-2087.
- MECHERRI, O.M., BUDIMAN-SASTROWARDOYO, P., ROUCHAUD, J.-C & FEDOROFF, M. (1990): Study of neodymium sorption on orthoclase and calcite for radionuclide migration modelling in groundwater. Radiochimica Acta 50, pp. 169-175.
- MEYER, R.E., ARNOLD, W.D. & CASE, F.I. (1985): Valence Effects on the Sorption of Nuclides on Rocks and Minerals. II. NUREG/CR-4114, ORNL-6137.
- MEYER, R.E., ARNOLD, W.D. & CASE, F.I. (1986): The Solubility of Electrodeposited Tc(IV) Oxides. II. NUREG/CR-4865, ORNL-6374.

- MIYAKE, M., KOMARNENI, S. & ROY, R. (1988): Immobilization of Pb^{2+} , Cd^{2+} , Sr^{2+} and Ba^{2+} ions using calcite and aragonite. *Cement and Concrete Research* 18, pp. 485-490.
- MORGAN, J.E. & BEETHAM, C.J. (1990): Review of literature for radium, protactinium, tin and carbon. Nirex Safety Series Report NSS/R220.
- MOTTA, M. M. & MIRANDA, C.F. (1989): Molybdate adsorption on kaolinite, montmorillonite and illite: Constant capacitance modelling. *Soil Sci. Soc. Am. J.* 53, pp. 380-385.
- MOUVET, C. & BOURG, A.C.M. (1983): Speciation (including adsorbed species) of copper, lead, nickel and zinc in the Meuse river. *Water Res.* 17, pp. 641-649.
- MUCCIARDI, A.N., BOOKER, I.J., ORR, E.C. & CLEVELAND, D. (1978): Statistical investigation of the mechanics controlling radionuclide sorption. WISAP Task 4. Second Contractor Meeting Proceedings. PNL-SA-7352.
- NAGRA (1994): Bericht zur Langzeitsicherheit des Endlagers SMA am Standort Wellenberg (Gemeinde Wolfenscheissen, NW). Nagra Technical Report NTB 94-06, Nagra, Wettingen, Switzerland.
- NAGRA (1997): Geosynthese Wellenberg 1996. Ergebnisse der Untersuchungsphasen I und II. Nagra Technical Report NTB 96-01, Nagra, Wettingen, Switzerland.
- NEAL, R.H., SPOSITO, G., HOLTZCLAW, K.M. & TRAINA, S.J. (1987a): Selenite adsorption on alluvial soils: I. Soil composition and pH effects. *Soil Sci. Soc. Am. J.* 51, pp. 1161-1165.
- NEAL, R.H., SPOSITO, G., HOLTZCLAW, K.M. & TRAINA, S.J. (1987b): Selenite adsorption on alluvial soils: II. Solution composition effects. *Soil Sci. Soc. Am. J.* 51, pp. 1165-1169.
- NYFFELER, U.P., LI, Y.-H. & SANTOSCHI, P.H. (1984): A kinetic approach to

describe trace-element distribution between particles and solution in natural aquatic systems. *Geochim. Cosmochim. Acta* 48, pp. 1513-1522.

O'CONNOR, T.P. & KESTER, D.R. (1975): Adsorption of copper and cobalt from fresh and marine systems. *Geochimica Cosmochimica Acta* 39, pp. 1531-1543.

PARFITT, R.L. (1978): Anion adsorption by soils and soil materials. *Advances in Agronomy* 30, pp. 1-50.

PEARSON, Jr. F.J. (1994): Quality of groundwater samples from Wellenberg, Switzerland: Estimation of contamination by drilling fluid using tracers and stable and radioactive isotopes. Nagra Unpublished Internal Report.

PEARSON, Jr. F.J., & BERNER, U. (1991): Nagra thermochemical data base I. Core data. Nagra Technical Report NTB 91-17, Nagra, Wettingen, Switzerland.

PEARSON, Jr. F.J., BERNER, U. & HUMMEL, W. (1992): Nagra thermochemical data base II. Supplemental Data 05/92. Nagra Technical Report NTB 91-18, Nagra, Wettingen, Switzerland.

PEARSON, Jr. F.J. and SCHOLTIS A. (1994): WLB: Hydrochemical characterisation and geochemical modelling of groundwater from Wellenberg. Nagra Unpublished Internal Report.

PEIGNEUR, P., MAES, A. & CREMERS, A. (1979): Ion exchange of the polyamine complexes of some transition metal ions in montmorillonite. *Proc. Int. Clay Conf. 1978, Oxford*, pp. 207-216. Elsevier Sci. Publ. Co., Amsterdam.

PLEYSIER, J. & CREMERS, A. (1975): Stability of silver-thiourea complexes in montmorillonite clay. *J. Chem. Soc., Faraday I* 71, pp. 256-264.

PLEYSIER, J. (1976): Silver uncharged ligand complexes in aluminosilicates adsorption and stability. Unpublished Ph.D. Thesis. Katholieke Universiteit Leuven, Belgium.

- POURBAIX, M. (1974): Atlas of electrochemical equilibria in aqueous solutions. NACE/CEBELCOR, Brussels.
- RAUSSELL-COLOM, J.A. & SERRATOSA, J.M. (1987): Reactions of clays with organic substances. In: Chemistry of clays and clay minerals (A.C.D. Newman (ed.) Longman Scientific & Technical, Mineralogical Society.
- RYBICKA, E.H., CALMANO, W. & BREEGER, A. (1995): Heavy metal sorption/desorption on competing clay minerals: an experimental study. Applied Clay Science 9, pp. 369-381.
- SANCHEZ, A.L., SCHELL, W.R. & SIBLEY, T.H. (1981): Distribution coefficients for radionuclides in aquatic environments: Adsorption and desorption studies of plutonium and americium. NUREG/CR-1852 Vo.. 5, College of Fisheries, University of Washington, Seattle.
- SAWHNEY, B.L. (1972): Selective sorption and fixation of cations by clay minerals: A review. Clays Clay Minerals 20, pp. 93-100.
- SCHINDLER, P. W., FURST, B., DICK, R. & WOLF, P.U. (1976): Ligand properties of surface silanol groups. I. Surface complex formation with Fe^{3+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} . J. Colloid Interface Sci. 55, pp. 469-475.
- SCHUBERT, J. & LINDENBAUM, A. (1952): Stability of Alkaline Earth-Organic Acid Complexes Measured by Ion-Exchange. J. Am. Chem. Soc. 74, pp. 3529-3532.
- SHANBHAG, P.M. & MORSE, J.W. (1982): Americium interaction with calcite and aragonite surfaces in seawater. Geochim. Cosmochim. Acta 46, pp. 241-246.
- SIGG, L. & STUMM, W. (1981): The interaction of anions and weak acids with the hydrous goethite surface ($\alpha\text{-FeOOH}$) surface. Colloids and Surfaces 2, pp. 101-117.
- SILVA, R.J., BIDOGLIO, G., RAND, M.H., ROBOUCH, P.B., WANNER, H. & PUIGDOMENECH, I. (1995): Chemical Thermodynamics of Americium.

Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Elsevier, Amsterdam.

SINGH, M., SINGH, N. & RELAN, P.S. (1981): Adsorption and desorption of selenate and selenite on different soils. *Soil Sci.* 132, pp. 134-141.

SMITH, P.A. (1992): Modelling of laboratory high-pressure infiltration experiments. PSI Bericht Nr. 116. Paul Scherrer Institut, Villigen, Switzerland and Nagra Technical Report NTB 91-33, Nagra, Wettingen, Switzerland.

STAMMOSE, D. & DOLO, J.-M. (1990): Sorption of americium at trace level on a clay mineral. *Radiochimica Acta* 51, pp. 189-193.

STEEFEL, C.I. & VAN CAPPELLEN, P. (1990): A new kinetic approach to modeling water-rock interaction: The rôle of nucleation, precursors and Ostwald ripening. *Geochim. Cosmochim. Acta* 54, pp. 2657-2677.

STENHOUSE, M. (1995): Sorption databases for crystalline, marl and bentonite for performance assessment. Nagra Technical Report NTB 93-06, Nagra, Wettingen, Switzerland.

STIPP, S.L.S., HOHELLA Jr., M.F., PARKS, G.A. & LECKIE, J.O. (1992): Cd²⁺ uptake by calcite, solid-state diffusion, and the formation of solid-solutions: Interface processes observed with near-surface sensitive techniques (XPS, LEED, and AES). *Geochimica Cosmochimica Acta* 56, pp. 1941-1954.

STIPP, S.L.S., EGGLESTON, C.M. & NIELSEN, B.S. (1994): Calcite surface structure observed at microtopographic and molecular scales with atomic force microscopy (AFM). *Geochimica Cosmochimica Acta* 58, pp. 3023-3033.

STIPP, S.L.S., GUTMANNSSBAUER, W. & LEHMANN, T. (1996): The dynamic nature of calcite surfaces in air. *American Mineralogist* 81, pp. 1-8.

SPOSITO, G., DE WIT, J.C.M. & NEAL, R.H. (1988): Selenite adsorption on alluvial soils III. Chemical modelling. *Soil Sci. Soc. Am. J.* 52, pp. 947-

950.

STUMM, W., KUMMERT, R. & SIGG, L. (1980): A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croat Chem. Acta* 53, pp. 291-312.

TICKNOR, K.V. (1993): Actinide sorption by fracture-infilling minerals. *Radiochimica Acta* 60, pp. 33-42.

THENG, B.K.G. (1971): Adsorption of molybdate by some crystalline and amorphous soil clays. *New Zealand J. Sci.* 14, pp. 1040-1056.

THENG, B.K.G. (1974): *The chemistry of clay organic reactions*. Adam Hilger, London.

TITS J., BRADBURY M.H., HASELBECK S. & VAN LOON L. (1993): Preliminary investigations on the complexation behaviour of marl organic matter. Paul Scherrer Institut, Internal report TM-43-93-17.

TITS J., BAEYENS B. & BRADBURY M.H. (1998): Physico-chemical characterisation and Ni sorption isotherms on Valanginian marl and illite in NaCl-type groundwaters. Paul Scherrer Institut, Technical Report (In preparation).

TORSTENFELT, B., ANDERSON, K. & ALLARD, B. (1982): Sorption of strontium and cesium on rocks and minerals. *Chemical Geology* 36, pp. 123-138.

VAN CAPPELLEN, P., CHARLET, L., STUMM, W. & WERSIN, P. (1993): A surface complexation model of the carbonate mineral aqueous solution interface. *Geochimica Cosmochimica Acta* 57, pp. 3503-3518.

VAN MUYLDER, J. (1966): Polonium. In: *Atlas of electrochemical equilibria in aqueous solutions*. (M. POURBAIX) Section 19.5, pp. 572-576, Pergamon Press, Oxford.

WABER, N.H., MAZUREK, M. & GAUTSCHI, A. (1994): Cation exchange capacities and anion leaching studies on rock samples from the

Wellenberg. In: MAZUREK, M., WABER, N. & BLAESI, H.-R.: WLB: Geology, mineralogy and geochemistry of Wellenberg. Nagra Unpublished Internal Report.

WERSIN, P., CHARLET, L., KARTHEIN, R. & STUMM, W. (1989): From adsorption to precipitation: Sorption of Mn^{2+} on $FeCO_3(s)$. *Geochim. Cosmochim. Acta* 53, pp. 2787-2796.

WINKLER, A, BRÜHL, H., TRAPP, CH. & BOCK, W.-D. (1988): Mobility of technetium in various rocks and defined combinations of natural minerals. *Radiochimica Acta* 44/45, pp.183-186.

WOLD, J. & PICKERING, W.F. (1981): Influence of electrolytes on metal ion sorption by clays. *Chemical Geology* 33, pp. 91-99.

YARIV, S. & CROSS, H. (1979): *Geochemistry of Colloid Systems*, Springer-Verlag New-York.

ZACHARA, J.M., COWAN, C.E. & RESCH, C.T. (1991): Sorption of divalent metals on calcite. *Geochim. Cosmochim. Acta* 55, pp. 1549-1562.

APPENDIX A

FLOW DIAGRAM OF SCALING PROCEDURE

The general procedure whereby laboratory/literature sorption data are modified to apply to the two groundwater types (Table 1) and the simplified mineralogies (section 2.1) is presented in the form of a flow diagram in Figure 14.

After the initial laboratory sorption data have been modified according to the flow diagram in Figure 14, we have for each radionuclide, marl mineralogy and reference water chemistry a series of "in situ" corrected sorption values from original measurements on marl and/or illite and/or calcite. Should the situation ever arise that more than one "in situ" sorption value for the same radionuclide has been selected, deduced for example from literature sorption values on marl and, say, illite, then the question arises as to which of the values should be taken. Clearly, in cases where the origin of the source data are measurements on marl or sediments with similar mineralogies, then these values should be preferred.

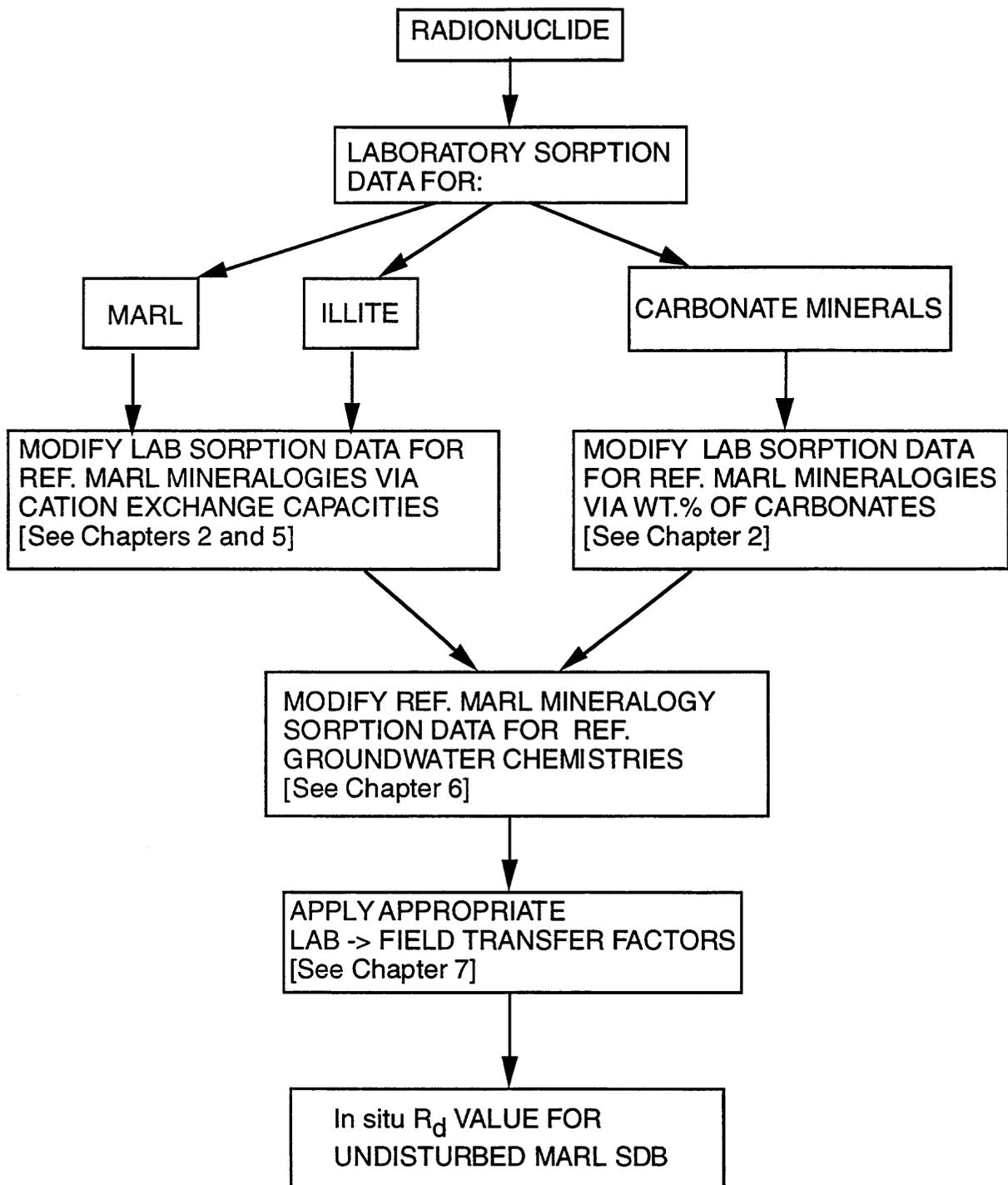


Figure 14: Flow diagram for the general procedure for the conversion of selected literature/laboratory sorption values to R_d values for the in situ undisturbed marl SDB.

APPENDIX B

RADIONUCLIDE DATA SHEETS

Appendix B consists of a compendium of data sheets for each safety relevant radionuclide illustrating how the values selected from the literature (Chapter 8) were converted to distribution ratios appropriate to the in situ conditions existing in the various water conducting features in Palfris marl (Chapter 2). Factors taken into consideration in modifying the selected laboratory data were mineralogy (Chapters 2 and 5), water chemistry (Chapter 6) and a crushed rock to intact rock conversion parameter (Chapter 7).

Separate data sheets are provided for each of the two reference groundwater chemistries (Chapter 3). For the following radionuclides Zr, Nb, Tc, Th, Pa, U, Np and Pu only one data sheet is given for both NaCl- and NaHCO₃-type reference groundwater since no corrections for pH and complexation were applied (see Chapter 8).

For silver (NaCl-type groundwater), chloride, iodine and organic carbon no data sheets are provided since the arguments given in Chapter 8 led to the conclusion that they were either non sorbing or that there was insufficient information available to select a defensible value.

The data sheets are ordered according to increasing atomic number.

K data sheet for NaCl-type reference water**Literature data summary:** This work, see section 8.2.2

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	$pH_{lit.}$	$CEC_{lit.}$ (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

Marl reference sorption values are calculated.

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
7×10^{-4}	10^{-3}	4×10^{-4}

K equilibrium conc. = 6×10^{-4} M**In situ sorption values:**

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

 R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
2.8×10^{-4}	4×10^{-4}	1.6×10^{-4}	10^{-3}

K data sheet for NaHCO₃-type reference water**Literature data summary:** This work, see section 8.2.2

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
-	-	-

Marl reference sorption values:

Marl reference sorption values are calculated.

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
7 x 10 ⁻³	10 ⁻²	4 x 10 ⁻³

K equilibrium conc. = 4.6 x 10⁻⁵ M**In situ sorption values:**

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
2.8 x 10 ⁻³	4 x 10 ⁻³	1.6 x 10 ⁻³	10 ⁻²

Co data sheet for NaCl-type reference water**Literature data summary:** GRÜTTER et al. (1994)

See section 8.3.2

Solid	*Selected R_d lit. ($m^3 kg^{-1}$)	pH _{lit.}	CEC _{lit.} (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	F _{lit. carb.}
Illite	5.0	7.9	0.36	4.2×10^{-4}	-

*Co equilibrium conc. $< 10^{-8}$ M**Conversion factor (c.f.) for NaCl-type water:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	0.063

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
0.1	0.14	0.05

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
3.2×10^{-2}	4.4×10^{-2}	1.6×10^{-2}

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
1.3×10^{-2}	1.8×10^{-2}	6.4×10^{-3}	4.4×10^{-2}

Co data sheet for NaHCO₃-type reference water**Literature data summary:** GRÜTTER et al. (1994)

See section 8.3.2

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Illite	5.0	7.9	0.36	4.2 x 10 ⁻⁴	-

*Co equilibrium conc. < 10⁻⁸ M**Conversion factor (c.f.) for NaHCO₃-type water:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	2.5

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
0.1	0.14	0.05

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
1.2	1.7	0.7

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.5	0.7	0.3	1.7

Ni data sheet for NaCl-type reference water**Literature data summary:** TITS et al. (1998)

See section 8.3.1

Solid	*Selected R_d lit. ($m^3 kg^{-1}$)	$pH_{lit.}$	$CEC_{lit.}$ (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
Marl	5	8.3	0.08	3.2×10^{-3}	-

*Ni equilibrium concentration: 10^{-7} M**Conversion factor (c.f.) for NaCl-type water:**

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	0.025

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
0.44	0.63	0.23

Marl reference sorption values:

$$R_d ref. = (R_d lit.) \times (Carb. c. f.) \times (pH c. f.) \times (Min c. f.)$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
5.5×10^{-2}	7.9×10^{-2}	2.9×10^{-2}

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d in situ = (R_d ref.) \times (Lab->Field T.F.)$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
2.2×10^{-2}	3.2×10^{-2}	1.2×10^{-2}	7.9×10^{-2}

Ni data sheet for NaHCO₃-type reference water**Literature data summary:** TITS et al. (1998)

See section 8.3.1

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Marl	5	8.3	0.08	3.2 x 10 ⁻³	-

*Ni equilibrium concentration: 10⁻⁷ M**Conversion factor (c.f.) for NaHCO₃-type water:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	1

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
0.44	0.63	0.23

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
2.2	3.2	1.2

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.9	1.3	0.5	3.2

Sr data sheet for NaCl-type reference water**Literature data summary:** This work, see section 8.2.2

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	pH _{lit.}	CEC _{lit.} (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

Marl reference sorption values are calculated.

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
4×10^{-4}	6×10^{-4}	2×10^{-4}

Sr equilibrium conc.: 5.8×10^{-4} M**In situ sorption values:**

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

 R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
1.6×10^{-4}	2.4×10^{-4}	8×10^{-5}	6×10^{-4}

Sr data sheet for NaHCO₃-type reference water**Literature data summary:** This work, see section 8.2.2

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

Marl reference sorption values are calculated.

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
6 x 10 ⁻²	8 x 10 ⁻²	3 x 10 ⁻²

Sr equilibrium conc.: 5.7 x 10⁻⁶ M**In situ sorption values:**

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
2.4 x 10 ⁻²	3.2 x 10 ⁻²	1.2 x 10 ⁻²	8 x 10 ⁻²

Zr data sheet for NaCl/NaHCO₃-type reference waters

Literature data summary: Th is taken as chemical analogue.
Th sorption values are used.
See section 8.4.2.1

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl/NaHCO₃-type waters:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
-	-	-

Marl reference sorption values:

R_d ref. = (R_d lit.) x (Carb. c. f.) x (pH c. f.) x (Min c. f.)

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.1	0.14	0.05	0.36

Nb data sheet for NaCl/NaHCO₃-type reference waters**Literature data summary:** LEGOUX et al. (1992)

See section 8.3.8

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Sediment	0.2	5.9 - 8	0.034	-	-

*Nb equilibrium concentration: 5 x 10⁻¹³ M**Conversion factor (c.f.) for NaCl/NaHCO₃-type waters:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
1	1.5	0.5

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
0.2	0.3	0.1

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.08	0.12	0.04	0.3

Mo data sheet for NaCl-type reference water**Literature data summary:** MOTTA & MIRANDA (1989)

See section 8.3.9

Solid	*Selected R_d lit. ($m^3 kg^{-1}$)	$pH_{lit.}$	$CEC_{lit.}$ (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
Illite	0.016	8.2	0.2	-	-

*Mo equilibrium conc.: $< 5 \times 10^{-4}$ M**Conversion factor (c.f.) for NaCl-type water:**

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	3

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
0.18	0.25	0.09

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
8.6×10^{-3}	1.2×10^{-2}	4.3×10^{-3}

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
3.4×10^{-3}	4.8×10^{-3}	1.7×10^{-3}	1.2×10^{-2}

Mo data sheet for NaHCO₃-type reference water**Literature data summary:** MOTTA & MIRANDA (1989)

See section 8.3.9

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Illite	0.016	8.2	0.2	-	-

*Mo equilibrium conc.: < 5 x 10⁻⁴ M**Conversion factor (c.f.) for NaHCO₃-type water:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	1

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
0.18	0.25	0.09

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
2.9 x 10 ⁻³	4 x 10 ⁻³	1.4 x 10 ⁻³

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
1.2 x 10 ⁻³	1.6 x 10 ⁻³	5.6 x 10 ⁻⁴	4 x 10 ⁻³

Tc data sheet for NaCl/NaHCO₃-type reference waters

Literature data summary: BARNEY (1982)

See section 8.3.10

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Sandstone	0.01	8.7-9.4	0.099	calcite sat.	-

*Tc equilibrium conc.: ~ 3 x 10⁻¹¹ M

Conversion factor (c.f.) for NaCl/NaHCO₃-type waters:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
0.35	0.5	0.18

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
3.5 x 10 ⁻³	5 x 10 ⁻³	1.8 x 10 ⁻³

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
1.4 x 10 ⁻³	2 x 10 ⁻³	7.2 x 10 ⁻⁴	5 x 10 ⁻³

Pd data sheet for NaCl-type reference water

Literature data summary: Ni taken as chemical analogue
 Ni sorption values used
 See section 8.3.3

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	$pH_{lit.}$	$CEC_{lit.}$ (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
2.2×10^{-2}	3.2×10^{-2}	1.2×10^{-2}	7.9×10^{-2}

Pd data sheet for NaHCO₃-type reference water

Literature data summary: Ni taken as chemical analogue
 Ni sorption values used
 See section 8.3.3

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
-	-	-

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.9	1.3	0.5	3.2

Ag data sheet for NaHCO₃-type reference water**Literature data summary:** This work, see section 8.3.4

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
-	-	-

Marl reference sorption values:

Marl reference sorption values are calculated.

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
5 x 10 ⁻³	8 x 10 ⁻³	3 x 10 ⁻³

Ag equilibrium conc. calculated at 10⁻⁸ M**In situ sorption values:**

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
2 x 10 ⁻³	3.2 x 10 ⁻³	1.2 x 10 ⁻³	8 x 10 ⁻³

Sn data sheet for NaCl-type reference water

Literature data summary: Mo taken as chemical analogue.
 Mo sorption values used.
 See section 8.3.6

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	pH _{lit.}	CEC _{lit.} (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
3.4×10^{-3}	4.8×10^{-3}	1.7×10^{-3}	1.2×10^{-2}

Sn data sheet for NaHCO₃-type reference water

Literature data summary: Mo taken as chemical analogue.
 Mo sorption values used.
 See section 8.3.6

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
1.2 x 10 ⁻³	1.6 x 10 ⁻³	5.6 x 10 ⁻⁴	4 x 10 ⁻³

Cs data sheet for NaCl-type reference water**Literature data summary:** This work, see section 8.2.1

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	pH _{lit.}	CEC _{lit.} (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

Marl reference sorption values are calculated.

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
1.3×10^{-1}	1.9×10^{-1}	7×10^{-2}

Cs equilibrium conc.: 10^{-6} M**In situ sorption values:**

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

 R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
5.2×10^{-2}	7.6×10^{-2}	2.8×10^{-2}	1.9×10^{-1}

Cs data sheet for NaHCO₃-type reference water**Literature data summary:** This work, see section 8.2.1

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
-	-	-

Marl reference sorption values:

Marl reference sorption values are calculated.

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
2.4 x 10 ⁻¹	3.5 x 10 ⁻¹	1.2 x 10 ⁻¹

Cs equilibrium conc.: 10⁻⁶ M**In situ sorption values:**

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

R_d in situ = (R_d ref.) x (Lab->Field T.F.)

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
9.6 x 10 ⁻²	1.4 x 10 ⁻¹	4.8 x 10 ⁻²	3.5 x 10 ⁻¹

Pb data sheet for NaCl-type reference water**Literature data summary:** KOSS et al. (1992)

See section 8.3.5

Solid	*Selected R_d lit. ($m^3 kg^{-1}$)	pH _{lit.}	CEC _{lit.} (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
Sediment	1.5	6.7	0.036	10^{-3} M	0.32

*Pb equilibrium conc.: $\sim 1.5 \times 10^{-8}$ M**Conversion factor (c.f.) for NaCl-type water:**

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
0.61	0.57	1

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
1.0	1.4	0.5

Marl reference sorption values:

$$R_d ref. = (R_d lit.) \times (Carb. c. f.) \times (pH c. f.) \times (Min c. f.)$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
0.8	1.2	0.4

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d in situ = (R_d ref.) \times (Lab->Field T.F.)$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
0.3	0.5	0.16	1.2

Pb data sheet for NaHCO₃-type reference water**Literature data summary:** KOSS et al. (1992)

See section 8.3.5

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Sediment	1.5	6.7	0.036	10 ⁻³ M	0.32

*Pb equilibrium conc.: ~ 1.5 x 10⁻⁸ M**Conversion factor (c.f.) for NaHCO₃-type water:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
0.998	0.003	40

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
1.0	1.4	0.5

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
1.8 x 10 ⁻¹	2.5 x 10 ⁻¹	9 x 10 ⁻²

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
7.2 x 10 ⁻²	10 ⁻¹	3.6 x 10 ⁻²	2.5 x 10 ⁻¹

Ra data sheet for NaCl-type reference water

Literature data summary: Sr taken as chemical analogue.
Sr sorption values used.
See section 8.2.3

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	$pH_{lit.}$	$CEC_{lit.}$ (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
1.6×10^{-4}	2.4×10^{-4}	8×10^{-5}	6×10^{-4}

Ra data sheet for NaHCO₃-type reference water

Literature data summary: Sr taken as chemical analogue.
 Sr sorption values used.
 See section 8.2.3

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

R_{d ref.} = (R_{d lit.}) x (Carb. c. f.) x (pH c. f.) x (Min c. f.)

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

R_{d in situ} = (R_{d ref.}) x (Lab->Field T.F.)

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
2.4 x 10 ⁻²	3.2 x 10 ⁻²	1.2 x 10 ⁻²	8 x 10 ⁻²

Ac data sheet for NaCl-type reference water

Literature data summary: Am taken as chemical analogue.
Am sorption values used.
See section 8.4.1.2

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	$pH_{lit.}$	$CEC_{lit.}$ (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

$$R_{d ref.} = (R_d lit.) \times (Carb. c. f.) \times (pH c. f.) \times (Min c. f.)$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d in situ = (R_d ref.) \times (Lab->Field T.F.)$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
1.6	2	0.8	5

Ac data sheet for NaHCO₃-type reference water**Literature data summary:** Am taken as chemical analogue.

Am sorption values used.

See section 8.4.1.2

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
-	-	-

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
7	10	4	24

Th data sheet for NaCl/NaHCO₃-type reference waters

Literature data summary: BASTON et al. (1991)

See section 8.4.2.1

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
London clay	1	8	0.14	Calcite sat.	-

*Th equilibrium conc. < 10⁻¹² M

Conversion factor (c.f.) for NaCl/NaHCO₃-type waters:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
0.25	0.36	0.13

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
2.5 x 10 ⁻¹	3.6 x 10 ⁻¹	1.3 x 10 ⁻¹

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.1	0.14	0.05	0.36

Pa data sheet for NaCl-type reference water

Literature data summary: Np(V) taken as chemical analogue
 MEYER et al. (1985), Fig. 1, See section 8.4.3

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Illite	0.1	6.7	0.2*	present	-

*CEC assumed

Conversion factor (c.f.) for NaCl-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
0.18	0.25	0.09

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
1.8 x 10 ⁻²	2.5 x 10 ⁻²	9 x 10 ⁻³

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
7 x 10 ⁻³	10 ⁻²	4 x 10 ⁻³	2.5 x 10 ⁻²

Pa data sheet for NaHCO₃-type reference water

Literature data summary: Np(V) taken as chemical analogue
MEYER et al. (1985), Fig. 1, See section 8.4.3

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Illite	0.2	8.2	0.2*	present	-

*CEC assumed

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
0.18	0.25	0.09

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
3.5 x 10 ⁻²	5 x 10 ⁻²	1.8 x 10 ⁻²

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
1.4 x 10 ⁻²	2 x 10 ⁻²	7 x 10 ⁻³	5 x 10 ⁻²

U data sheet for NaCl/NaHCO₃-type reference waters**Literature data summary:** BASTON et al. (1992)

See section 8.4.2.2

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
London clay	5	8	0.14	calcite sat.	-

*U equilibrium conc.: ~ 10⁻⁹ M**Conversion factor (c.f.) for NaCl/NaHCO₃-type waters:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
0.25	0.36	0.13

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
1.3	1.8	0.65

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.5	0.7	0.26	1.8

Np data sheet for NaCl/NaHCO₃-type reference waters

Literature data summary: Th taken as chemical analogue.
 Th sorption values used.
 See section 8.4.2.3

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}

Conversion factor (c.f.) for NaCl/NaHCO₃-type waters:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.1	0.14	0.05	0.36

Pu data sheet for NaCl/NaHCO₃-type reference waters**Literature data summary:** BASTON et al. (1992)

See section 8.4.2.4

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
London clay	5	8	0.14	calcite sat.	-

*Pu equilibrium conc.: < 10⁻¹² M**Conversion factor (c.f.) for NaCl/NaHCO₃-type waters:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
0.25	0.36	0.13

Marl reference sorption values:R_{d ref.} = (R_{d lit.}) x (Carb. c. f.) x (pH c. f.) x (Min c. f.)

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
1.3	1.8	0.65

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

R_{d in situ} = (R_{d ref.}) x (Lab->Field T.F.)

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
0.5	0.7	0.26	1.8

Am data sheet for NaCl-type reference water**Literature data summary:** GORGEON (1994)

See section 8.4.1.1

Solid	*Selected R_d lit. ($m^3 kg^{-1}$)	pH _{lit.}	CEC _{lit.} (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	F _{lit. carb.}
Illite	25	6.7	0.21	air P-CO ₂	-

*Am equilibrium conc.: $\sim 4 \times 10^{-10}$ M**Conversion factor (c.f.) for NaCl-type water:**

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	1

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
0.17	0.24	0.09

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
4	5	2

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
1.6	2	0.8	5

Am data sheet for NaHCO₃-type reference water

Literature data summary: GORGEON (1994)

See section 8.4.1.1

Solid	*Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
Illite	100	8.3	0.21	air P-CO ₂	-

*Am equilibrium conc. ~ 7 x 10⁻¹¹ M

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	1

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
0.17	0.24	0.09

Marl reference sorption values:

$$R_{d \text{ ref.}} = (R_{d \text{ lit.}}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
17	24	9

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_{d \text{ in situ}} = (R_{d \text{ ref.}}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
7	10	4	24

Cm data sheet for NaCl-type reference water**Literature data summary:** Am taken as chemical analogue.

Am sorption values used.

See section 8.4.1.2

Solid	Selected R_d lit. ($m^3 kg^{-1}$)	$pH_{lit.}$	$CEC_{lit.}$ (equiv. kg^{-1})	Total $C_{inorg.}$ (M)	$F_{lit. carb.}$
-	-	-	-	-	-

Conversion factor (c.f.) for NaCl-type water:

$F_{ref. carb.}$	Carbonate c.f.: $\frac{1 - F_{ref. carb.}}{1 - F_{lit. carb.}}$	pH c.f.: $\frac{1}{10^{-(pH_{ref.} - pH_{lit.})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{CEC_{Min-A}}{CEC_{lit.}}$	Min-B: $\frac{CEC_{Min-B}}{CEC_{lit.}}$	Min-C: $\frac{CEC_{Min-C}}{CEC_{lit.}}$
-	-	-

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R_d ref. ($m^3 kg^{-1}$)	MIN-B R_d ref. ($m^3 kg^{-1}$)	MIN-C R_d ref. ($m^3 kg^{-1}$)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R_d in situ ($m^3 kg^{-1}$)	Min-B R_d in situ ($m^3 kg^{-1}$)	Min-C R_d in situ ($m^3 kg^{-1}$)	Fault gouge R_d in situ ($m^3 kg^{-1}$)
1.6	2	0.8	5

Cm data sheet for NaHCO₃-type reference water

Literature data summary: Am taken as chemical analogue.
Am sorption values used.
See section 8.4.1.2

Solid	Selected R _d lit. (m ³ kg ⁻¹)	pH _{lit.}	CEC _{lit.} (equiv. kg ⁻¹)	Total C _{inorg.} (M)	F _{lit. carb.}
-	-	-	-	-	-

Conversion factor (c.f.) for NaHCO₃-type water:

F _{ref. carb.}	Carbonate c.f.: $\frac{1 - F_{\text{ref. carb.}}}{1 - F_{\text{lit. carb.}}}$	pH c.f.: $\frac{1}{10^{-(\text{pH}_{\text{ref.}} - \text{pH}_{\text{lit.}})}}$
-	-	-

Mineralogy conversion factors:

Min-A: $\frac{\text{CEC}_{\text{Min-A}}}{\text{CEC}_{\text{lit.}}}$	Min-B: $\frac{\text{CEC}_{\text{Min-B}}}{\text{CEC}_{\text{lit.}}}$	Min-C: $\frac{\text{CEC}_{\text{Min-C}}}{\text{CEC}_{\text{lit.}}}$
-	-	-

Marl reference sorption values:

$$R_d \text{ ref.} = (R_d \text{ lit.}) \times (\text{Carb. c. f.}) \times (\text{pH c. f.}) \times (\text{Min c. f.})$$

MIN-A R _d ref. (m ³ kg ⁻¹)	MIN-B R _d ref. (m ³ kg ⁻¹)	MIN-C R _d ref. (m ³ kg ⁻¹)
-	-	-

In situ sorption values:

Lab->Field transfer factor (T.F.) for intact marl: 0.4

Lab->Field T.F. for fault gouge: 1.0

$$R_d \text{ in situ} = (R_d \text{ ref.}) \times (\text{Lab->Field T.F.})$$

Min-A R _d in situ (m ³ kg ⁻¹)	Min-B R _d in situ (m ³ kg ⁻¹)	Min-C R _d in situ (m ³ kg ⁻¹)	Fault gouge R _d in situ (m ³ kg ⁻¹)
7	10	4	24

APPENDIX C

Appendix C contains the data sheets for ^{14}C (as $\text{HCO}_3^-/\text{CO}_3^{2-}$) for each of the two reference groundwater chemistries (Chapter 3).

Since calcite is taken as the major mineral responsible for the uptake of this radionuclide the mineral conversion factors are made using the calcite wt.% for the four groupings of mineralogies, MIN-A to MIN-D (Chapter 2).

Inorg. C DATA SHEET FOR NaCl-TYPE REFERENCE WATER**LITERATURE DATA SUMMARY:** This work (see section 9.4.2)

Rock/ Mineral	pHLit.	Total C _{inorg.} (M)
calcite	6.7	1.28 x 10 ⁻²

The sorption value for ¹⁴C as HCO₃⁻/CO₃²⁻ in the NaCl-type groundwater for bulk calcite was calculated as shown in section 9.4.2.

Distribution ratio ¹⁴C R_d (inorg. C) = 2.1 x 10⁻³ m³ kg⁻¹

MINERALOGY CONVERSION FACTORS:

MIN-A 53 wt.% calcite	MIN-B 42 wt.% calcite	MIN-C 71 wt.% calcite	MIN-D 95 wt.% calcite
0.53	0.42	0.71	0.95

IN SITU SORPTION VALUES:

R_d In Situ = R_d (inorg. C) x MIN conv. factor.

MIN-A R _d In Situ (m ³ kg ⁻¹)	MIN-B R _d In Situ (incl. fault gouge) (m ³ kg ⁻¹)	MIN-C R _d In Situ (m ³ kg ⁻¹)	MIN-D R _d In Situ (m ³ kg ⁻¹)
1.1 x 10 ⁻³	8.8 x 10 ⁻⁴	1.5 x 10 ⁻³	2.0 x 10 ⁻³

Inorg. C DATA SHEET FOR NaHCO₃-TYPE REFERENCE WATER**LITERATURE DATA SUMMARY:** This work (section 9.4.2)

Rock/ Mineral	pHLit.	Total C _{inorg.} (M)
calcite	8.3	1.64 x 10 ⁻²

The sorption value for ¹⁴C as HCO₃⁻/CO₃²⁻ in the NaHCO₃-type groundwater for bulk calcite was calculated as shown in section 9.4.2.

Distribution ratio ¹⁴C R_d (inorg. C) = 1.6 x 10⁻³ m³ kg⁻¹

MINERALOGY CONVERSION FACTORS:

MIN-A 53 wt.% calcite	MIN-B 42 wt.% calcite	MIN-C 71 wt.% calcite	MIN-D 95 wt.% calcite
0.53	0.42	0.71	0.95

IN SITU SORPTION VALUES:

R_d In Situ = R_d (inorg. C) x MIN conv. factor.

MIN-A R _d In Situ (m ³ kg ⁻¹)	MIN-B R _d In Situ (incl. fault gouge) (m ³ kg ⁻¹)	MIN-C R _d In Situ (m ³ kg ⁻¹)	MIN-D R _d In Situ (m ³ kg ⁻¹)
8.5 x 10 ⁻⁴	6.7 x 10 ⁻⁴	1.1 x 10 ⁻³	1.5 x 10 ⁻³