

TECHNICAL REPORT 96-06

Far-Field Sorption Data Bases for Performance Assessment of a L/ILW Repository in a Disturbed/ Altered 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

The large quantities of cement/concrete inherent in the current designs for low- and intermediate-level radioactive waste (L/ILW) repositories will interact with the slowly moving deep groundwater and probably give rise to a long pulse of hyper alkaline fluid in the far field. The pH of the plume might remain in excess of 12.5 for tens of thousands of years. Many of the minerals along the flow paths in a sedimentary host rock, with the notable exception of calcite, would be unstable under these conditions leading to dissolution reactions, secondary mineral precipitation and changes in groundwater chemistry. Although it is relatively clear that the most likely types of new mineral phases to form are calcium silicate hydrates (CSH), calcium aluminium silicate hydrates (CASH) and possibly zeolites, the system is very complex and is evolving in time and space. For these reasons the well defined rock mineralogies and water chemistries normally required as a pre-requisite for constructing credible sorption data bases are not available in this case.

The purpose of this report is to attempt to assess the effects of the interactions between a pH plume and Palfris marl on the far-field sorption properties of the formation. Despite the previously mentioned fundamental difficulties, a series of procedures are described in detail whereby it was possible to deduce conservative sorption data bases for altered marl corresponding to the five main mineralogies and two water chemistries characterising the main flow paths in the Palfris marl host rock.

ZUSAMMENFASSUNG

Heutige Endlagerkonzepte für schwach- und mittelaktive Abfälle (SMA) sehen grosse Mengen an Beton/Zement im Endlager vor. Tiefengrundwässer werden den Beton/Zement langsam durchfliessen und zur Bildung einer hochalkalischen "pH-Fahne" in Richtung Fernfeld führen. Der pH-Wert dieser "Fahne" könnte über Zehntausende von Jahren über 12.5 liegen. Mit der Ausnahme von Calcit sind viele der Mineralien, die entlang der Fliesswege in einem sedimentären Wirtgestein vorkommen, unter solchen Bedingungen instabil, was zu Auflösungsreaktionen und sekundärer Mineralausfällung sowie Änderungen der Grundwasserchemie führen könnte. Es gibt viele Hinweise, dass Calcium-Silikat-Hydrate (CSH), Calcium-Aluminium-Silikat-Hydrate (CASH) sowie Zeolithe als mögliche Mineralien neu gebildet werden, das System ist jedoch äusserst komplex und wird sich sowohl zeitlich als auch räumlich entwickeln. Üblicherweise gelten genau definierte Daten als Voraussetzung zur Erstellung von zuverlässigen Sorptions-Datenbasen; aus den obigen Gründen fehlen hier solche Daten.

In diesem Bericht wird der Einfluss der Wechselwirkung zwischen einer pH-Fahne und dem Palfris-Mergel auf die Sorptionseigenschaften der Gesteinsformation im Fernfeld abgeschätzt. Trotz der oben erwähnten Unsicherheiten wird eine Reihe von Verfahren detailliert beschrieben, mit denen konservative Datenbasen für den durch die pH-Fahne veränderten Mergel abgeleitet werden können. Diese Datenbasen berücksichtigen die fünf charakteristischen Mineralzusammensetzungen und die zwei Hauptgrundwassertypen, welche die hauptsächlichen Fliesswege im Mergel charakterisieren.

RESUME

La conception actuelle des dépôts finals pour les déchets de faible et moyenne activité (DFMA) met en jeu de grandes quantités de bétons/ciments. L'interaction à long-terme entre ces stockages et les eaux souterraines conduira à la libération dans le champ lointain d'un fluide hyperalcalin. Le front de pH de ce panache pourrait rester supérieur à 12,5 pendant des dizaines de milliers d'années. Dans une roche d'accueil sédimentaire, la plupart des minéraux présents le long des chemins de circulation hydrodynamique seraient instables dans ces conditions, à l'exception notable de la calcite. Ce panache alcalin entraînerait alors la dissolution d'une partie des minéraux primaires, la précipitation de minéraux secondaires et, par conséquent, des modifications de la chimie des eaux souterraines. Il est relativement clair que les minéraux néoformés les plus probables sont les CSH (gels de silicate de calcium hydraté), les CASH (gels de silicate de calcium et d'aluminium hydraté) et éventuellement des zéolites. Néanmoins, comme ce panache alcalin évolue de manière complexe dans le temps et dans l'espace, il est très difficile de connaître *a priori* avec précision la nature des minéraux et la composition des eaux. Or il s'agit là des données normalement nécessaires pour construire de manière crédible les bases de données de sorption.

L'objectif de ce rapport est d'évaluer les conséquences en terme de sorption dans le champ lointain, de l'interaction entre un panache alcalin et la formation marneuse de Palfris. Malgré les difficultés fondamentales mentionnées précédemment, ce rapport décrit une série de procédures qui ont permis d'estimer de manière pessimiste des bases de données de sorption pour la formation marneuse altérée. Ces bases de données ont été mises en place pour les cinq minéralogies principales et pour les deux compositions des eaux profondes caractérisant les chemins de transport hydrodynamique de la formation marneuse de Palfris.

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1 INTRODUCTION

In common with many other international proposals for the disposal of low- and intermediate-level radioactive waste (L/ILW), the planned repository in the Swiss concepts will be located within a sedimentary rock formation and constructed from and filled with large quantities of cement and concrete ($\sim 1.5 \times 10^6$ tonnes). This cementitious vault is likely to be situated at depth within the Palfris marl at Wellenberg. Interactions between the slowly moving deep groundwater and the large quantities of cement/concrete present in the repository could give rise to a long pulse of hyperalkaline fluid moving into the host rock soon after the caverns re-saturate. For convenience we will refer to this pulse of hyperalkaline fluid as the "pH plume". The pH plume would interact with the marl along the flow paths, dissolving certain minerals and precipitating others, significantly change the groundwater chemistry and also possibly alter the flow characteristics of the major water bearing features. All of these processes would be varying in time and space along the migration pathways.

The purpose of this report is to attempt to assess the effects of such changes and processes on the far-field sorption properties in a marl formation and to construct appropriate sorption data bases.

2 BACKGROUND

2.1 Palfris marl mineralogy

The results from extensive field and laboratory investigations (see for example MAZUREK et al. 1994) have led to the conclusion that the main water conducting features in the Palfris marl formation are cataclastic shear zones and jointed calcareous marl/limestone layers. These features are schematically illustrated in Figures 1 to 3 where the associated mineralogies are also given.

2.2 Palfris marl reference groundwater chemistries

Two main groundwater types have been identified in the Palfris marl at Wellenberg. The first are NaHCO₃-type groundwaters which are predominantly associated with high water yielding regions in the upper part of the marl formation. The second are relatively highly mineralised NaCl-type groundwaters occurring at depth in zones of very low water flow.

Based on water samples from boreholes drilled at Wellenberg (BAEYENS & BRADBURY 1991a, BLASER 1993, PEARSON 1994, PEARSON & SCHOLTIS 1994, SCHOLTIS & DEGUELDRE 1996) and laboratory investigations (BAEYENS & BRADBURY 1991b, 1994) reference water chemistries for these two water types were developed (NAGRA 1997), see Table 1.

2.3 Groundwater/cement interaction

The repository will be sited in the saturated zone of the Palfris marl. Under the regional groundwater conditions the cementitious materials are unstable and will gradually break down through the leaching of the hydrated cement by percolating groundwater. The interaction between leaching solutions and hardened cement paste and the ensuing degradation of the paste has been the topic of many experimental and modelling studies, e.g. ATKINSON et al. (1988), BERNER (1992), NEALL (1994), LAGERBLAD & TRÄGÅRDH (1994).

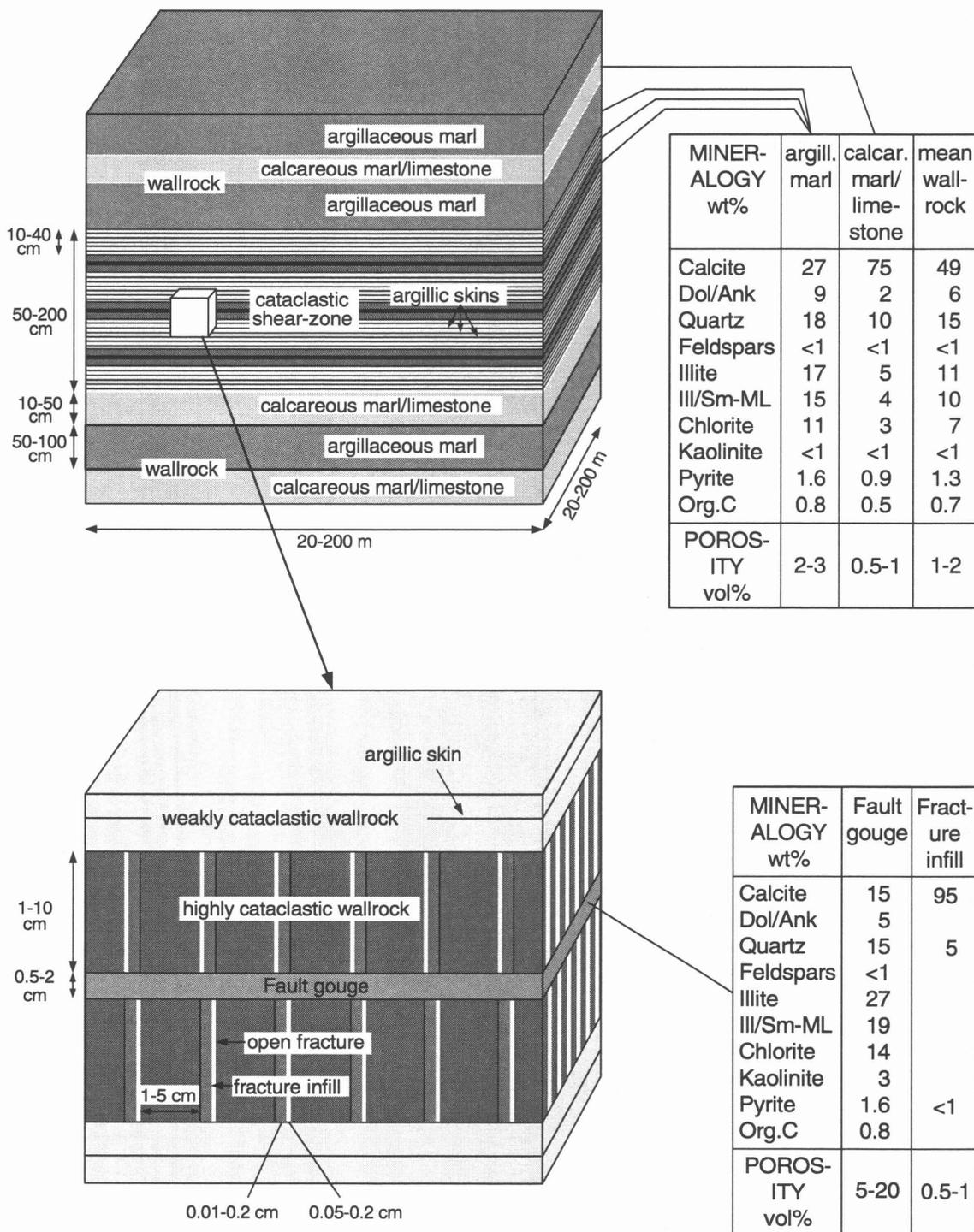


Figure 1: Conceptual model of cataclastic zones (water-conducting feature type 1), comprising geometric, mineralogic and porosimetric parameters. (Taken from MAZUREK 1994.)

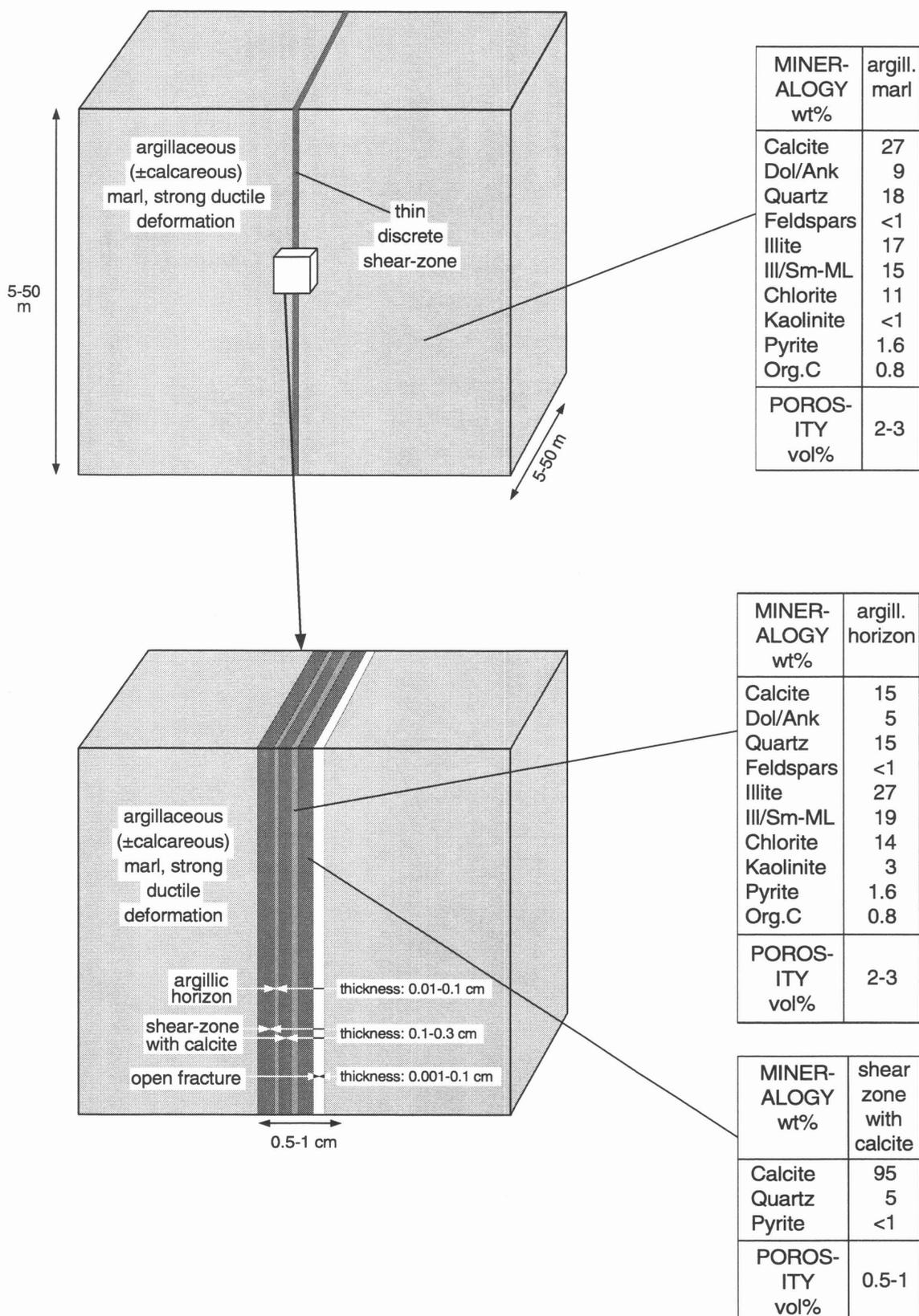


Figure 2: Conceptual model of thin discrete shear-zones (water-conducting feature type 2), comprising geometric, mineralogic and porosimetric parameters. (Taken from MAZUREK 1994.)

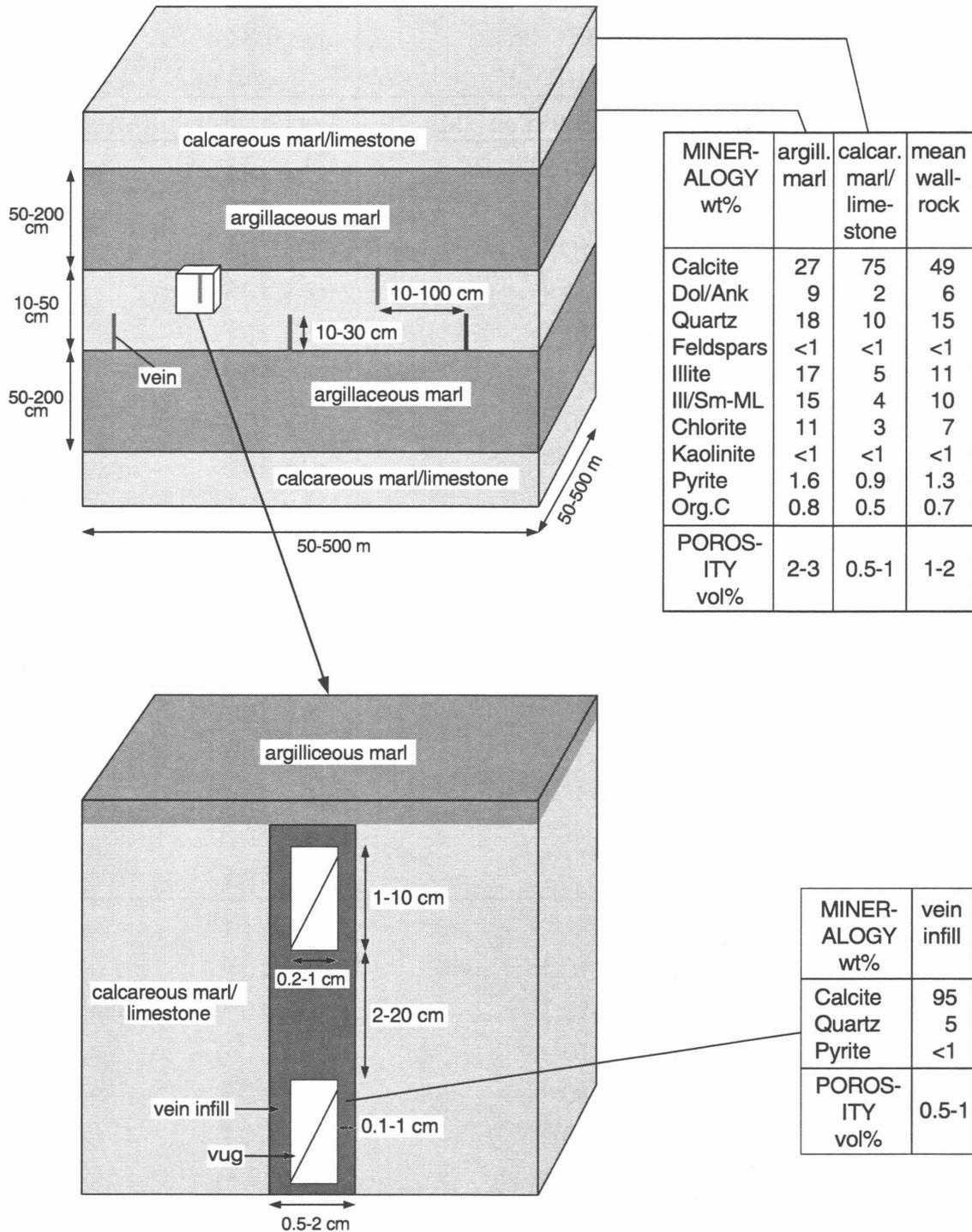


Figure 3: Conceptual model of joined calcareous marl/limestone layers (water-conducting feature type 3), comprising geometric, mineralogical and porosimetric parameters. (Taken from MAZUREK 1994.)

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

From a chemical point of view it is probably fair to say that the major processes are sufficiently well understood to be able to model the cement degradation and cement porewater with a fairly high degree of confidence. These chemical degradation models indicate that the differences in composition between the two groundwater types in the Palfris marl have only second order effects on the degradation processes, see Figure 4.

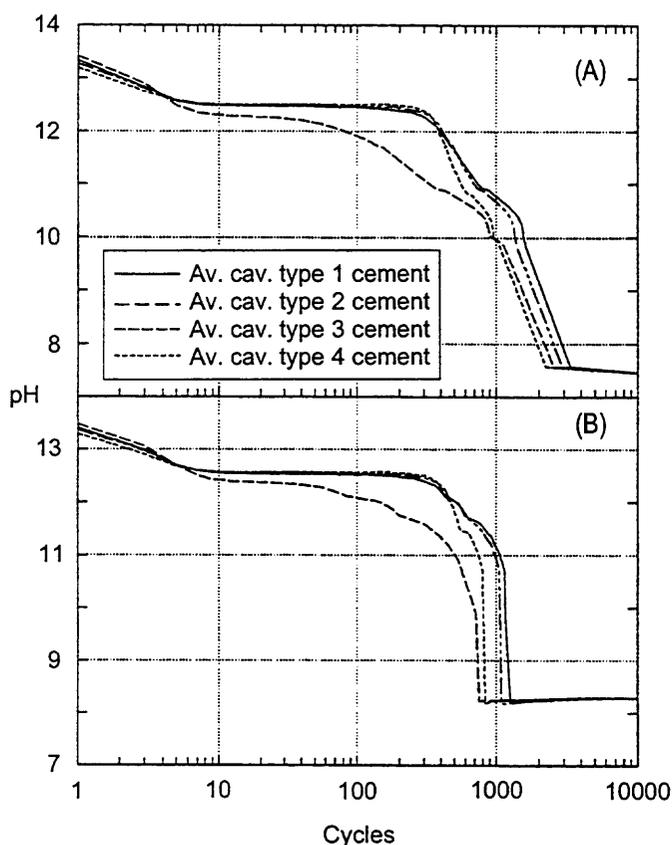


Figure 4: Evolution of cement pore fluid pH with increasing cycles of pore water exchange during degradation for the four averaged cavern type cements in: (A) Wellenberg NaHCO_3 water and (B) Wellenberg NaCl water. (Taken from NEALL 1994, Figure 5.)

However, the temporal and spatial evolution of the repository is another matter. The repository will not degrade homogeneously and dissolution/precipitation reactions will have a dynamic feedback effect on the processes occurring. Models based on treating the near-field as a mixing tank are over simplifications of reality and can only yield global estimates. Calculations with

fully coupled codes indicate that under certain circumstances the repository could "seal" through precipitation of calcite (PFINGSTEN, pers. comm.).

2.4 The pH plume

Under the high pH conditions predicted, sheet silicate and quartz minerals within and adjacent to the water conducting features in the marl host rock will be unstable. (See for example SAVAGE et al. 1990, 1991.) The extent to which they dissolve depends on many factors; the magnitude of the pH and its variation in time are but two of them. In general such mineral dissolution reactions generate an excess of protons so that the tendency is for the pH to be buffered towards that of the natural groundwater the further the plume migrates away from the repository.

At some point down stream from the repository the conditions will favour the precipitation of secondary minerals. The most likely types of new mineral phases to form are calcium silicate hydrates (CSH), calcium aluminium silicate hydrates (CASH) including tobermorite, jennite and hydrogarnet; chlorite, brucite ($\text{Mg}(\text{OH})_2$) and zeolites such as mordenite (CRAWFORD & SAVAGE 1994). Laboratory studies (BATEMAN et al. 1995) and the Maqarin natural analogue investigations (ALEXANDER & MAZUREK 1996, MILODOWSKI et al. 1997) have confirmed the formation of minerals of the types listed above. It is interesting to note that many of the secondary minerals formed (e.g. CSH, CASH, tobermorite, jennite) are similar to major mineral components found in hydrated cements. The sorption properties of the altered marl in which such secondary minerals are present, should, in principle, be similar to those in hardened cement paste (HCP).

2.5 Colloids

Colloids, and the quantification of their effects, nearly always presents a problem, predominantly because of the uncertainties surrounding their generation, concentrations and sorption characteristics. The potential for the generation of colloids as a result of the interaction between the pH plume and marl has been recognised but little information exists on this topic. CRAWFORD & SAVAGE (1994) have ventured an opinion based largely on

the increased solubility of quartz at high pH, and we quote directly from their work.

"The solubility of quartz increases dramatically at pH values greater than 7 (EIKENBERG 1990) such that it is 103 times more soluble at pH 12 than at pH 7. The nucleation and growth of quartz is an extremely slow process at temperatures less than 200 °C. Since migration of the alkaline plume may produce sharp fronts of alteration, and by analogy, large gradients in concentration of components such as pH and Si in the fluid, it is likely that large supersaturations with respect to certain solids may develop. Large supersaturations of fluids with respect to stable silica polymorphs would lead to the homogeneous nucleation of amorphous silica and the development of floc-like precipitates or gels (WERES et al. 1982). Thus there may be considerable potential for the generation of colloidal silica at the extreme leading edge of the alkaline plume."

Thus, according to CRAWFORD & SAVAGE (1994) the most significant region for the formation of colloids is likely to be at the interface between the hyperalkaline fluid and the groundwater after the pH plume has become "loaded" with dissolved silica. Although we are not in a position to quantitatively assess the impact of silica colloid generation at the present time, we will return to this topic in Chapter 4 and attempt to make some qualitative comments on its likely effect.

The formation of floc-like precipitates or gels could well have an overall positive effect on radionuclide migration. Silica in this highly divided amorphous form will have very large surface area to mass ratios and under high pH conditions behave as an additional important sink for radionuclides. (See, for example, DUGGER et al. 1964)

2.6 Redox

In a long term down hole groundwater monitoring programme in boreholes SB1 and SB6 at Wellenberg, DEGUELDRE et al. (1994) showed that the redox potential reached a stable value of -300 ± 30 mV. This value was used for both NaHCO₃ and NaCl reference waters, (see Table 1), and implies that the conditions are relatively strongly reducing. If it is assumed that the same redox couple maintains equilibrium and continues to control the in situ

potential, then the tendency would be for the Eh to become more negative as the pH increased.

2.7 Organic ligands

There are likely to be two major sources of organic ligands in the aqueous phase.

The first is the soluble component of the solid organic matter in the marl itself which is released into solution during interaction with the hyperalkaline fluid. This process will be most significant during the period of highest pH where the solution chemistry is dominated by the (K,Na)OH concentrations i.e. during the first stage in cement degradation. TITS et al. (1993) performed organic extraction on marl samples at high pH. These authors concluded that the solid organic matter was not composed of humic substances. Further, the complexation constants and capacities determined by the Schubert method (see for example VAN LOON & KOPAJTIC, 1991) for UO_2^+ indicated that the DOC comprised predominantly of small organic molecules similar to phthalic acid. Such types of organic ligands would not be expected to have any significant consequences for sorption. Further, no humic substances have been found in the groundwaters at the Maqarin site (ALEXANDER & MAZUREK 1996).

The second source of organic ligands is the degradation products from the organic substances in the radioactive waste and additives from the cement such as Na-Gluconate (GLU). Of the degradation products, isosaccharinic acid (ISA) from cellulose is by far the most important. (See BRADBURY & VAN LOON 1998) These organic ligands will migrate from the near-field and be present in the high pH solutions in contact with the altered marl.

Since organic ligands, particularly ISA and GLU under alkaline conditions, can form strong complexes with radionuclides (GREENFIELD et al. 1992, 1993, 1995) and thereby potentially alter their sorption characteristics significantly, this aspect of the influence of the pH plume on the performance of the geological barrier has to be assessed together with all of the other factors, see Chapter 9.

3 MODELS AND MODELLING

3.1 Secondary mineral formation

As can be appreciated from the very brief overview given before, the interaction of a hyperalkaline plume with marl is extremely complex. The major processes which are likely to occur are known in general, but not in detail. This implies, for example, that there is a relatively high degree of confidence in the types of secondary minerals which will form but large uncertainties in the spatial and temporal evolution of the mineralogy, water chemistry, matrix accessibility and flow porosity along the migration pathway. Investigations on natural analogues such as the Maqarin study (MILODOWSKI 1994, THOENEN 1996, MILODOWSKI et al. 1997) may increase our understanding of the important processes but, by their very nature, can only at most provide partial answers to the above problems.

Thermodynamic modelling approaches are also likely to be of limited help at the moment. For example, after attempting the difficult task of trying to model the secondary mineral evolution sequence, THOENEN (1995) concluded,

1. There is a general lack of relevant thermodynamic data for the classes of solids likely to form as a result of the alteration of marl by hyperalkaline fluids. It is not clear that the thermodynamically most stable secondary minerals are the ones which form. Metastable phases may precipitate out which will remain, even on geological time scales. One of the major difficulties with modelling is predicting exactly which metastable phases form.
2. At the low temperatures expected for the repository, kinetic factors (dissolution, nucleation, growth) will play a significant role, and currently only a rudimentary knowledge concerning these kinetic processes exists.
3. Uncertain thermodynamic data and critical gaps in our knowledge concerning kinetics make it impossible to make detailed and robust predictions for the alteration phases and the associated water chemistries.

4. The further application of 1-D coupled codes such as MPATH (LICHTNER 1992, LICHTNER & EIKENBERG 1993) should not be continued, see THOENEN (1994). The modelling of temporal and spatial evolution of the alteration zone requires at least 2-D coupled codes.

3.2 Sorption mechanisms

Cation exchange and surface complexation mechanisms have been applied to a wide range of mineral/radionuclide systems to explain their sorption characteristics. For the specific case of marl, many such mechanistic studies on the major mineral components can be readily found in the open literature e.g. quartz (SCHINDLER & KAMBER 1968; SCHINDLER et al. 1976), clay minerals (BRUGGENWERT & KAMPHORST 1982, SCHINDLER et al. 1987, BRADBURY & BAEYENS 1995), calcite (DAVIS et al. 1987; ZACHARA et al. 1991; STIPP et al. 1992; CARROLL et al. 1992, TITS et al. 1997, 1998b).

However, two points need to be mentioned here. The first is that the investigations have not generally extended to the highest pH values expected for the hyperalkaline plume ($\text{pH} > 12.5$) and there is some uncertainty as to whether such sorption models are valid in this pH range. Secondly, even at $\text{pH} < 11$ it is seldom the case that the thermodynamic sorption parameters associated with the models are sufficiently well known to be able to reliably calculate radionuclide uptake. Once more the situation is that the major processes are known in general (at least up to $\text{pH} \sim 11$) but not in detail and hence mechanistic arguments can, in the main, only be used to indicate trends in sorption values under changing conditions.

Although sorption under hyperalkaline conditions has been studied extensively in certain systems e.g. hardened cement paste (see for example the cement sorption data base compilation of BRADBURY & SAROTT (1994) and references therein) and calcite (TITS et al. 1997, 1998b), there is as yet little or no mechanistic understanding. There are some preliminary indications that cation exchange and surface complexation may not be the main sorption mechanisms but that the uptake of radionuclides may be more akin to surface precipitation (TITS et al. 1997) and/or coprecipitation effects (CURTI 1997). If this is so, then even predicting trends becomes somewhat difficult because the main parameters influencing the processes are not known. However, this

may be not be of critical importance in a first assessment of the uptake of radionuclides at these very high pH values since most of the experimental evidence currently available indicates exceedingly high "sorption" values on many different types of solid phase, see Chapters 6 to 8.

4 pH PLUME: LEAD TIME AND CONSEQUENCES

An important point which has not yet been sufficiently considered in detail is that the hyperalkaline plume will move out into the marl well in advance of the majority of radionuclides. Immediately after re-saturation of the disturbed zone around the repository and the repository itself, the pH front will begin to migrate into the host rock. For the radionuclide on the other hand, the canisters must first corrode and the radionuclides must diffuse through various cement/concrete barriers. Different radionuclides will be retarded to different degrees, but for most the apparent diffusion coefficients through these low permeability cements are exceedingly small, probably $<10^{-15} \text{ m}^2 \text{ s}^{-1}$. Once in the backfill, the very slow flow rates and effective retardation through sorption onto the monokorn cement[#] will further delay the emergence of radionuclides. (If diffusive processes only are occurring in the back-fill, then transit times to the far field will be even longer.)

Even radionuclides such as I, Cl, Nb and Mo, which do not significantly sorb onto cement/concrete, will enter the far field at a much later stage than the pH plume depending on how long the canister lasts, diffusion rates and path lengths and the transit times through the monokorn. For such non- or weakly-sorbing radionuclides, the lead time of the pH plume may be many hundreds or even thousands of years whereas for the more strongly sorbing radionuclides the lead times may be tens of thousands of years. (See NAGRA 1994, Figure 4.1-7.) The consequences of this may be far reaching since many processes involving the interaction between the pH plume and the marl may be over before certain radionuclides arrive and different radionuclides may "see" different far field mineralogies and water chemistries. In this specific context we would like to return to and consider further two of the points listed in Chapter 2, namely silica colloid formation and the high pH dissolution of the organic matter in the marl.

The formation of (silica) colloids will be most intense during the initial phase of the pH plume (high (K,Na)OH concentrations, pH >12.5) and will be occurring predominantly at the leading edge of the plume where the concentrations and concentration gradients of components are greatest. The dissolution rates and

[#] A highly porous cement backfill consisting of mm sized quartz particles which are coated with and held together by hardened cement paste.

solubility of quartz at these pH values are high (EIKENBERG 1990). If the lead time of the pH front is many hundred or even thousands of years, as suggested above, then the quartz hyperalkaline fluid reactions producing Si colloids are either occurring at such an early stage in the alteration of the far-field that they are over before the radionuclides arrive or, alternatively, so far spatially ahead that the radionuclides do not "see" the colloids. In both cases it would appear to be unlikely that Si and other types of colloid produced at the leading edge of the alkaline plume will have any adverse effect on radionuclide transport. On the contrary, the influence of quartz dissolution and precipitation of amorphous flocs and gels (WERES et al. 1982) may have a positive effect by providing highly active surfaces in the altered host rock on which the trailing radionuclides could sorb (DUGGER et al. 1964).

A similar argument can also be constructed for the dissolution of the solid organic matter in the marl i.e. the pH plume is so far temporally and/or spatially in front of the radionuclides that they never see the dissolved organics. For this reason, and in the light of the results from complexation studies with organic ligands leached from marl at high pH (TITS et al. 1993) we conclude that the solid organic matter content in marl will have no significant influence on sorption processes in the pH altered system.

5 pH-PLUME/MARL: APPROACH FOR GENERATING SORPTION DATA BASES

5.1 General

Normally, in order to construct a credible sorption data base for any given system, a pre-requisite is a relatively well defined rock mineralogy and water chemistry. In the case of the pH-plume/marl system these are areas of uncertainty. The consequence of this is that we are not in a position to use similar methodologies to devise a SDB for altered marl as were used for marl (BRADBURY & BAEYENS 1997) and cement (BRADBURY & SAROTT 1994; BRADBURY & VAN LOON 1998), for example. Although this more rigorous and detailed approach may be possible at some later stage, a different and more general procedure, taking into account the uncertainties and gaps in our knowledge, is required here.

Our intention is to show that despite all the uncertainties it is still possible to devise an approach to the problem which allows us to make defensible statements concerning the effect of the pH plume on sorption. In general the procedures rely on a comparison between estimated sorption values for an altered marl system with the values for marl to produce conservative SDBs. The essential question here is whether the influence of the pH plume is likely to lead to better or worse far-field sorption characteristics for the safety relevant radionuclides. At the moment, a more detailed approach is, in our opinion, not justified (or possible) because of the lack of understanding and data.

Although many consequences of the interaction between marl and the high pH plume are uncertain, two simple facts can be used as a basis upon which to develop robust arguments.

The first is that the fluid emerging from the cementitious near field will tend to increase the pH of the groundwater in the far-field. How great this increase is depends on many factors such as the starting pH of the emerging cement porewater (NEALL 1996), dilution by the marl groundwater, the mineral phases which the fluid "sees" and how rapidly and to what extent reactions can take place etc.

The second is that the large calcite component in the marl will not be significantly affected by the pH plume. The hyperalkaline fluid is already saturated with respect to calcite, calcite solubilities are low at the high pH values expected, and although Ca is consumed during the formation of CSH type phases, the quantities involved are minute compared with the massive amounts present.

5.2 Clay minerals and pH

In a sedimentary rock such as marl, clay minerals are the most important class of minerals governing the sorption properties of many of the safety relevant radionuclides (see BRADBURY & BAEYENS 1997). As a starting point we would propose to consider two cases, depending on whether the clay minerals are in a pH regime where they are stable or whether the pH conditions are such that they are unstable and tend to dissolve. It should be remembered that the pH of the plume depends on many factors and its magnitude cannot be determined uniquely and will, anyway, vary in time and space. For the following discussions we have chosen a pH of 11 as a stability boundary for clay minerals. The stability, solubilities and weathering of clay minerals under alkaline conditions are complex. They depend strongly on the water chemistry, in particular on the silica and aluminium concentrations, and reaction kinetics are also an important consideration here. (See for example BRINKMAN, 1982; TARDY et al., 1987.) Hence, in many ways this is a rather arbitrary choice and it could be argued that a lower, or higher, value is more appropriate. At the moment a pH of 11 merely provides a reasonable dividing point for the two different types of approach to the problem outlined below. It will become apparent that the exact value of the pH chosen does not significantly influence the validity of the arguments presented. However, the importance of this assumption, and its consequences, may have to be reconsidered in future updated sorption data bases.

5.2.1 pH < 11

In the first case when the pH is rising from its natural level up to pH values less than 11, we can view the system as being essentially the same as for marl but at a higher pH. In general terms, cationic species which sorb predominantly by surface complexation tend to exhibit an increasing affinity

for solid surfaces with increasing pH. For anionic species, the reverse is the case. Where cation exchange is the main uptake mechanism, pH does not have a significant effect except possibly via aqueous speciation. Hence, in a regime where the mineral surfaces remain stable, a rise in solution pH is likely to have an overall positive (or at least neutral) influence on the uptake of positively charged and neutral species and a negative effect on anionic species. A more detailed discussion together with the procedure for the selection of sorption data is given in Chapter 6.

5.2.2 pH > 11

At pH values greater than 11 we must assume that most of the minerals making up the marl, in particular the clay minerals and quartz, are unstable and will tend to dissolve. Also, at some stage depending on the local conditions, secondary minerals will precipitate out. The most important parameters in this respect are the pH and time. The best information currently available is that the precipitates will be "hydrated cement like minerals" such as ettringite, calcium silicate hydrates (CSH), calcium aluminium silicate hydrates (CASH); and possibly zeolites (mordenite) as the pH falls, see section 2.4.

In the higher pH regions where the main sorbing phases are most likely to be "hydrated cement like minerals", we make the assumption that the clay minerals are "converted" to CSH phases. (For a pH plume migrating in advance of the radionuclides, CSH and CASH phases will be the dominant sorbing solids.) In this context THOENEN (1996, pers. comm.) carried out some simple mass balance calculations on the transformation of the clay minerals in fault gouge (see Figure 1) to the crystalline CSH phase tobermorite. To a first approximation he found that the conversion was one to one i.e. 1 gram of "clay mineral" converted to an equivalent mass of tobermorite.

In the estimations of sorption values for altered marl made in Chapter 7, the cement sorption data base from BRADBURY & VAN LOON (1998) will be used together with direct measurements on CSH phases. The CSH phase content of HCP is ~70% whereas the maximum CSH phase content of a fully altered marl would be between ~20 and ~40%, corresponding to the initial clay

mineral contents. Thus, when estimating sorption values for altered marl using data for cement this should be taken into account. For the comparison exercise described in chapter 7 we have reduced the sorption values for HCP by a factor of 5. (It should not be forgotten that there is already a high degree of conservatism built into the sorption values in the cement SDBs.)

5.3 Calcite and pH

Calcite is the most abundant mineral in the Palfris marl, with levels between 20 and 90 wt.%, and is effectively stable under the hyperalkaline conditions expected around a cementitious repository. In addition, the calcite lined open fractures of the jointed calcareous marl/limestone layers, Figure 2, constitute one of the main water conducting features in the Palfris marl host rock formation. Principally for these reasons sorption on calcite at elevated pH values is treated separately in Chapter 8.

5.4 Terminology

In order to clearly distinguish between the various "marl states" existing in the different pH regions, it is useful at this point to define a terminology.

The term "marl" will be reserved for the undisturbed host rock in its natural state.

"Disturbed marl" will be used to refer to the rock in a system where the pH has risen above its ambient level to values less than 11 and where the mineralogy has not changed in any significant way.

At pH values greater than 11, where minerals can dissolve and new secondary minerals form, the term "altered marl" will be used.

6 **SORPTION DATA FOR DISTURBED MARL (pH<11)**

The aim in this chapter is to provide a selection of data which either illustrates or supports conclusions to be drawn regarding the general trends in sorption values in the pH region less than 11. In this pH range clay minerals are considered to be stable. Since in the Palfris marl formation the clay minerals are the principle sorbents (BRADBURY & BAEYENS 1997), any differences here between the sorption characteristics of disturbed marl and marl are predominantly a pH effect.

6.1 **Alkaline and alkaline earth metals**

The sorption mechanism for these elements on clay minerals is predominantly cation exchange which exhibits virtually no dependency on pH. Hence, any rise in pH will not significantly influence the sorption behaviour of these non- or weakly-hydrolysable cations.

Cs and K

Caesium is known to interact strongly and non-linearly with illite and micaceous clay minerals in natural solids (SAWHNEY 1970; FRANCIS & BRINKLEY 1976; CREMERS et al. 1988; DE PRETER 1990). The sorption mechanism for the uptake of Cs on illite is generally described by cation exchange occurring on different types of sites exhibiting different sorption affinities (TAMURA & JACOBS 1960; BOLT et al. 1963; BROUWER et al. 1983; COMANS et al. 1992; BRADBURY & BAEYENS 1992).

Although the bulk of Cs sorption data available in the open literature was measured at pH<11, pH is not expected to significantly influence sorption since the uptake mechanism for Cs is cation exchange and Cs does not hydrolyse at pH<11 (BAES & MESMER 1976). This is illustrated by GORGEON (1994) who measured the sorption of Cs on illite in the pH range 2 to 11 in a 1 M NaClO₄ background electrolyte and observed, if anything, a slight increase in sorption with increasing pH.

General comment

Cs sorption on illite is a somewhat special case since at trace concentrations sorption is likely to be mainly on the so called frayed edge sites (SAWHNEY

1972; EBERL 1980). If the increase in pH up to 11 is caused predominantly by increased concentrations of (K,Na)OH, then the higher K levels may well have a significant influence on Cs sorption since K is competitive with Cs for these frayed edge sites. Because of this competition, Cs sorption in this case may become restricted to the normal planar cation exchange sites for which the sorption is much lower. If $\text{Ca}(\text{OH})_2$ is the cause of the pH rise then any detrimental effect on Cs sorption will be negligible.

In order to account quantitatively for the above considerations, similar Cs sorption calculations to those presented in the SDB for marl (BRADBURY & BAEYENS 1997) were carried out for disturbed marl. If we assume conservatively that the rise in pH is due to alkali-hydroxide, then the concentration of (K,Na)OH required to raise the pH to 11 is $\sim 10^{-3}$ M. (The K concentrations (most important for Cs sorption) change from 6.6×10^{-4} to 1.3×10^{-3} M for an NaCl type water and for the NaHCO_3 case from 8×10^{-5} to 4.9×10^{-4} .) The results of the calculations for both groundwater types show that a decrease in sorption by a factor of ~ 1.2 might be expected. This factor can be neglected in comparison with other uncertainties.

A similar procedure applied to K sorption gave the same result, i.e. a decrease in sorption by $\sim 10\%$ for the $\text{pH} < 11$ case.

Recommendation

For increases in pH up to 11 the Cs and K sorption values for disturbed marl are taken to be the same as those for marl for the two groundwater types.

Mg, Ca, Sr

In the case of alkaline earth metals such as Mg, Ca and Sr there is some evidence to suggest that sorption on clay minerals via surface complexation may become as, or even more important than cation exchange at higher pH values. For example, a noticeable increase in Mg and Ca sorption on Na-montmorillonite from $\text{pH} \sim 8$ upwards was observed by BAEYENS & BRADBURY (1995), Figure 5.

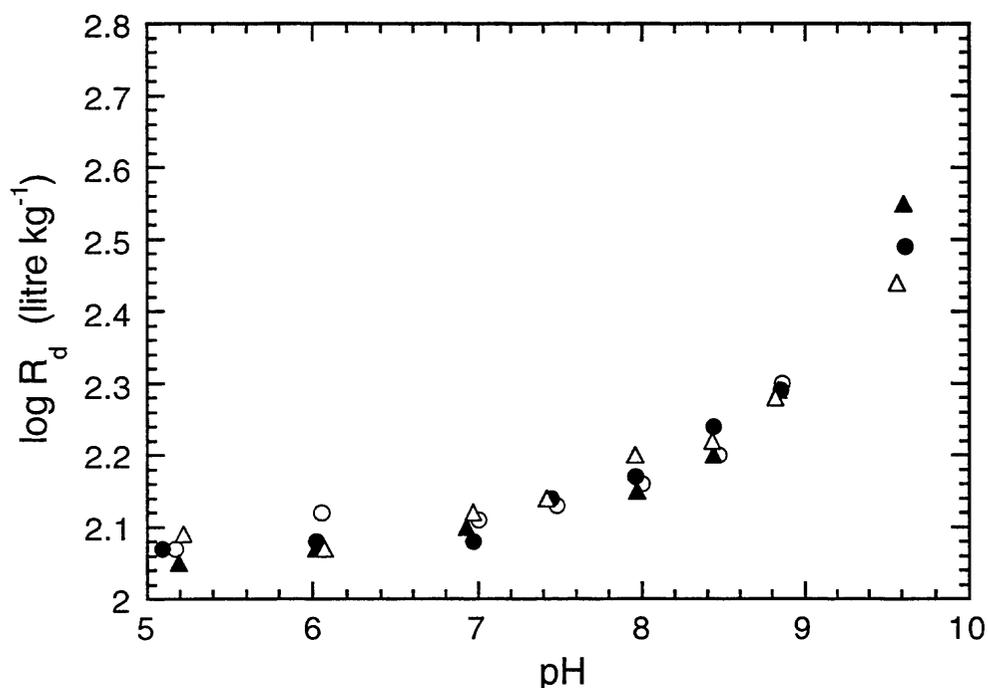


Figure 5: Ca sorption edges on conditioned Na-montmorillonite in 0.1 M NaClO₄ measured after 1 (○), 3 (●), 7 (△) and 21 (▲) days. (Taken from BAEYENS & BRADBURY 1995, Figure 8)

Increases in Sr sorption on clay minerals (kaolinite and illite) with increasing pH have been reported by RAFFERTY et al. (1981) and MAHONEY & LANGMUIR (1991). Figure 6, taken from RAFFERTY et al. (1981), illustrates the effect for a Na-illite. Superimposed on the increases in sorption with decreasing ionic strength (a cation exchange effect) is a clear increase in sorption with increasing pH. The pH dependent sorption of Sr on Na-kaolinite was measured up to pH~10.5, and was even more pronounced than for Na-illite.

Ra

No relevant sorption data could be found for Ra, and Sr has been taken throughout as its chemical analogue.

General comment

Although the main sorption mechanism for alkaline earth metals is cation exchange, there is a tendency for sorption to increase as a function of pH,

possibly due to an additional contribution from surface complexation reactions. This is a clear but not particularly strong effect.

Recommendation

The Sr and Ra sorption data for marl represent conservative values for disturbed marl.

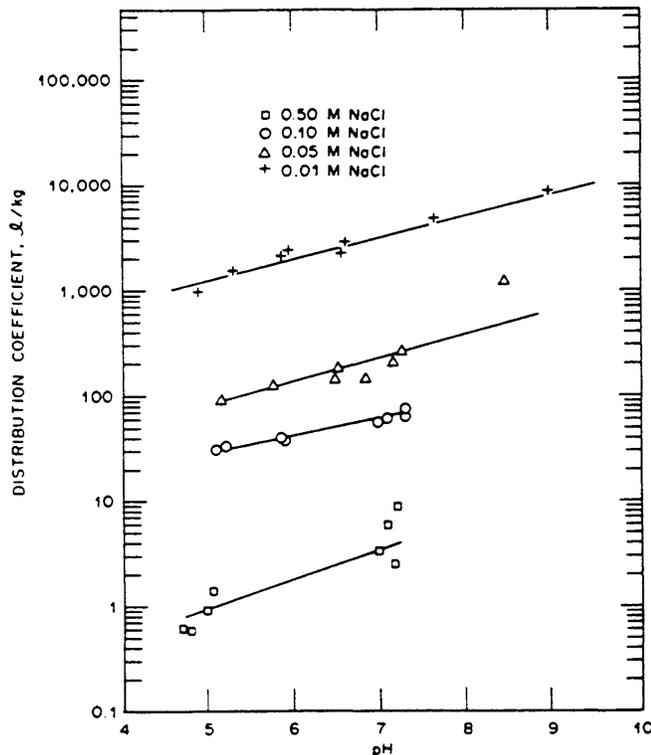


Figure 6: Sorption of Sr on Na-illite as function of ionic strength and pH. (Taken from RAFFERTY et al. 1981, Figure 7.)

6.2 Transition metals and heavy metals

Co, Ni, Cu, Zn, Cd, Pb

There is a large body of information in the open literature which indicates clear increases in sorption with increasing pH (so-called "sorption edges") for transition and heavy metals at trace concentrations on a variety of solid phases.

WOLD & PICKERING (1981) studied the sorption behaviour of Cu, Zn, Cd and Pb on illite, kaolinite and montmorillonite as a function of pH in the range from 5 to 7. In all cases the sorption increased as function of pH. Although data at

pH values higher than 7 were not measured, this study illustrates the very close similarity in the pH dependent sorption behaviour of this group of metals on different clay minerals.

BAEYENS & BRADBURY (1995) have measured Zn and Ni sorption edges on Na-montmorillonite. In Figure 7 the pH dependent sorption of Ni is illustrated in the pH range 2 to 11. The figure shows that the distribution ratios increase rapidly in the pH range 5 to 9, remain approximately constant and then decrease at pH values above 10. (The decrease in sorption at high pH is most likely due to the formation of negatively charged hydroxy complexes.) Despite this decrease, the distribution coefficient at pH~11 is greater than at ~8, the highest pH in the reference groundwaters.

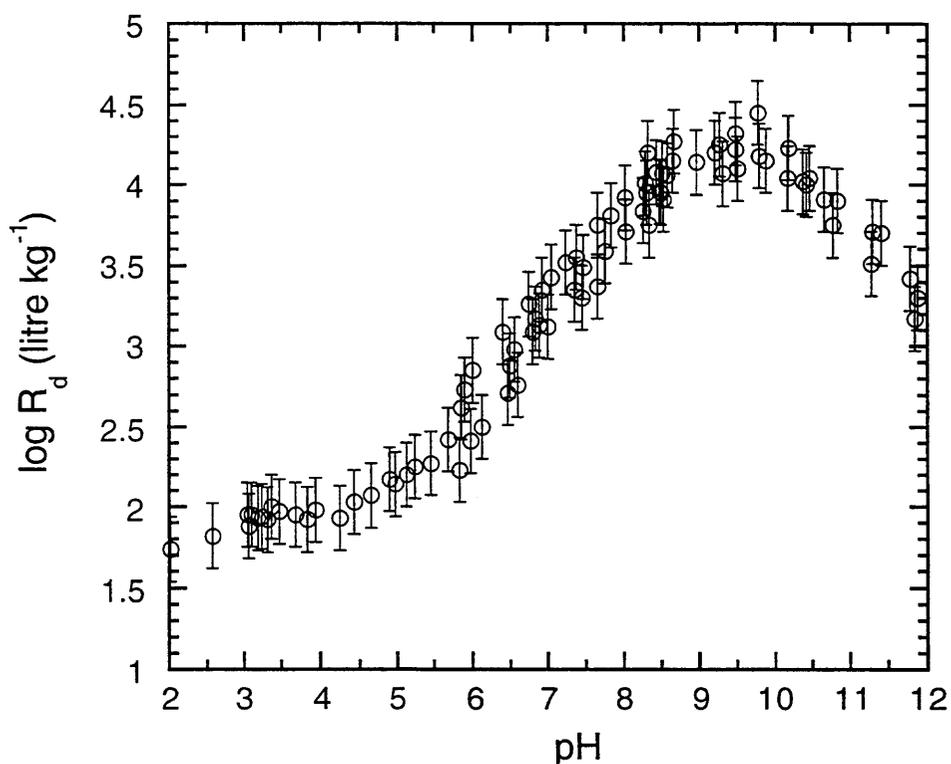


Figure 7: Ni sorption edge on conditioned Na-montmorillonite in 0.1 M NaClO₄. (Taken from BAEYENS & BRADBURY 1995, Figure 10.)

O'CONNOR & KESTER (1975) measured the sorption of Cu and Co on illite in two different water compositions, a low ionic strength artificial river water (ARW, I~10⁻³ M) and a high ionic strength saline water (I~0.7 M). The fraction of metal adsorbed increased sharply between pH~4 and ~7, remained

constant and high ($R_d \sim 20 \text{ m}^3 \text{ kg}^{-1}$) between 7 and 12 and only decreased at $\text{pH} > 12$. The results of these measurements are plotted in Figures 8 and 9 as fraction sorbed against pH. An important point to note is that at low pH sorption is dependent on the ionic strength whereas at higher pH this dependency disappears.

Such behaviour is characteristic of sorption by a combination of cation exchange and surface complexation, see BRADBURY & BAEYENS (1995). Clearly, when surface complexation is the main sorption mechanism, high ionic strength waters, such as the NaCl-type groundwater, will not negatively influence the uptake of radionuclides on clay minerals.

BANGASH et al. (1992) measured the sorption of Co on an illitic soil and observed a similar behaviour to that reported above. This data set is reproduced here in Figure 10.

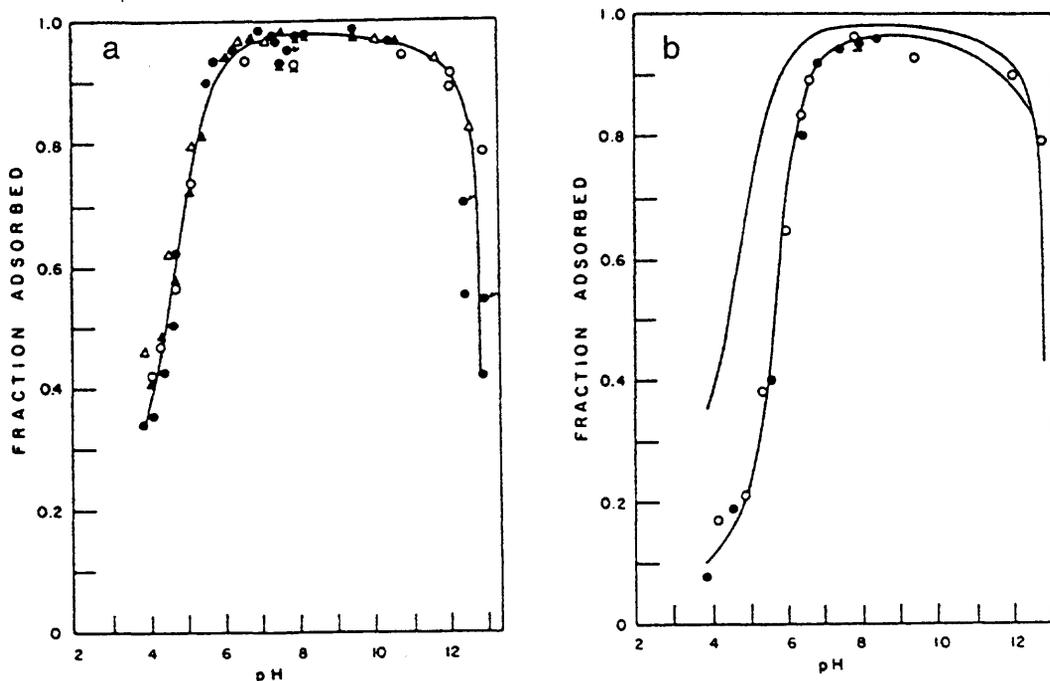


Figure 8: Copper adsorption from (a) an artificial river water (ARW) and (b) from sea water on illite as function of pH. Circles and triangles indicate total Cu concentrations of $8 \times 10^{-7} \text{ M}$ and $1.6 \times 10^{-6} \text{ M}$, respectively. (Taken from O'CONNOR & KESTER (1975), Figures 1 and 2.)

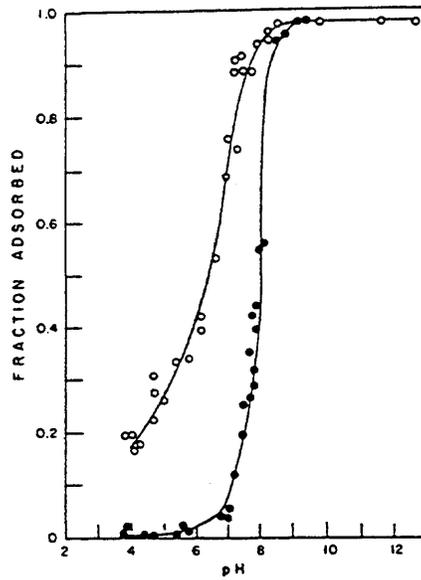


Figure 9: Cobalt adsorption from ARW (open circles) and sea water (closed circles) on illite as function of pH. Total Co concentrations in the sea water systems were 8×10^{-7} M. The total concentrations in ARW systems varied from 8.5×10^{-7} to 3.4×10^{-6} M. (Taken from O'CONNOR & KESTER (1975), Figure 4.)

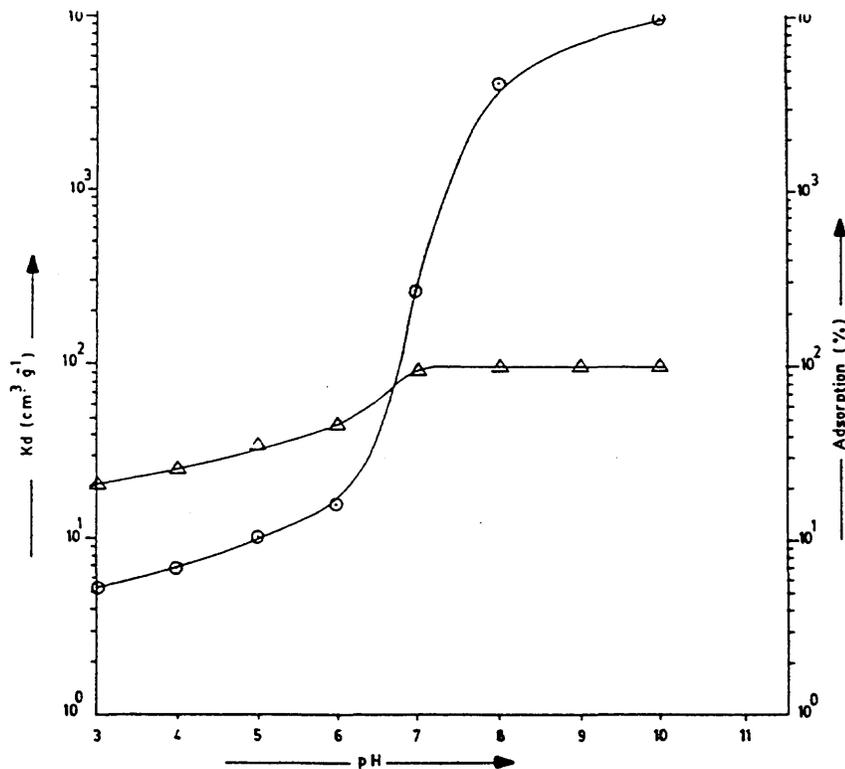


Figure 10: Variation of R_d (O) and % sorbed (Δ) of cobalt as function of pH on an illitic soil. (Taken from BANGASH et al. 1992, Figure 1.)

General comment

As a general observation on the sorption behaviour of transition and heavy metals (Ni, Co, Pd, Pb) on clay minerals it may be stated that rises in pH up to ~11 are likely to lead to an increase in the uptake of such radionuclides by the solid phase. This group of metals exhibit clear and strong sorption edges with rapidly increasing R_d values generally occurring in the pH range from ~5 to ~10. In general terms, above pH~9 sorption values tend to plateau and then decrease at higher pH values, most probably due to the formation of hydrolysed species. The exact pH at which this decrease occurs is radionuclide dependent but up to pH~11 the sorption values are greater than or equal to those in the pH range 6.5 to 8.5. In addition, changes in the ionic strength of the groundwaters are unlikely to have any significant adverse influence since the predominant sorption mechanism is surface complexation.

Recommendation

Increases in pH up to ~11 are likely to promote the uptake of radionuclides such as Co, Ni, Pd and Pb by clay minerals. Consequently, the sorption values given for marl most probably represent conservative values for a disturbed marl.

Pd

No relevant sorption data could be found for Pd, and Ni has been taken throughout as its chemical analogue.

Ag

No sorption data for Ag at high pH values could be found in the open literature.

General comment

In an NaCl-type groundwater Ag probably does not sorb on marl because of the formation of Ag-chloro complexes (BRADBURY & BAEYENS 1997). An increase in pH will not change this situation.

In the case of a NaHCO₃-type groundwater, BRADBURY & BAEYENS (1997) treated Ag sorption on marl in terms of a cation exchange mechanism. Calculations carried out under similar conditions to those described previously for Cs showed that the addition of ~10⁻³ M (Na,K)OH did not have

any significant effect on Ag sorption values. (Ag does not hydrolyse to any significant extent at pH values less than 11, see BAES & MESMER, 1976)

Recommendation

The sorption values selected for Ag on marl can also be applied to the disturbed marl.

Tc

The quantity and quality of the sorption data available in the open literature for Tc(IV) is poor. For marl (BRADBURY & BAEYENS 1997) a conservative value of $0.01 \text{ m}^3 \text{ kg}^{-1}$ was chosen, pH range 8.7 to 9.4. No sorption data could be found at elevated pH and the sorption mechanism of tetravalent Tc is unknown.

General comment

According to the interpretations of solubility data for TcO_2 at low carbonate levels (MEYER et al. 1987; ERIKSEN et al. 1993), the overwhelmingly dominant aqueous species from pH~3 to ~11 is the neutral oxyhydroxy species $\text{TcO}(\text{OH})_2$ and on the basis that the speciation remains constant it is plausible to suggest that the sorption also remains constant in this pH range. At higher pH values solubilities appear to increase through the formation of negatively charged oxyhydroxy species (ERIKSEN et al. 1993).

Recommendation

The values selected for Tc in the marl can be used for the disturbed marl.

Po

No sorption data for Po could be found in the open literature.

General comment

Under the Eh/pH conditions prevailing in the disturbed marl/groundwater system, the dominant aqueous species is the polonate anion, PoO_3^{2-} , (VAN MUYLDER, 1966). Although bismuth is considered to be chemically most similar to Po (FALBE & REGITZ 1992) this is not a useful analogue since no information on this element is available either.

Recommendation

We recommend that the sorption for Po in the disturbed marl sorption data bases is set at zero.

6.3 Actinides

6.3.1 Trivalent actinides

Am

ALLARD (1982) studied the pH dependent sorption behaviour of Am on approximately 40 minerals and rocks in a synthetic groundwater. In all cases where measurements were extended to pH values above 9, there were no indications of decreases in Am sorption.

GORGEON (1994) measured the sorption of Am as function of pH on three clay minerals (illite, montmorillonite and kaolinite). Depending on pH, the Am equilibrium concentrations ranged between 4×10^{-8} M and 3×10^{-11} M. The results are illustrated in Figures 11 to 13. In all three cases increasing sorption values with increasing pH were measured up to pH~12.

Eu

The lanthanide Eu is often considered to be a chemical analogue for trivalent actinides and appears here for this reason. Some recent detailed studies of Eu sorption on Na- and Ca-montmorillonites at concentrations of $<10^{-8}$ M (BRADBURY & BAEYENS 1998a) have shown similar sorption edges to those in Figure 11-13 for Am. Likewise, some earlier data of BAEYENS (1982) for Eu sorption on Boom Clay (a similar sedimentary rock to marl) exhibit strongly increasing sorption with increasing pH, Figure 14.

These data clearly illustrate that there is a strong tendency for the sorption of trivalent lanthanides and actinides to increase with increasing pH up to values of at least 11.

Ac, Cm

No relevant sorption measurements could be found for Ac and Cm, and Am and/or Eu have been taken throughout as their chemical analogues.

General comment

Am, and by inference also other trivalent actinides, sorb extremely strongly on almost all mineral surfaces, particularly clay minerals, at pH values above ~5. As illustrated in Figures 11 to 13 for montmorillonite, illite and kaolinite respectively, sorption tends to increase strongly up to pH~8 where after the rate of increase decreases or plateaus up to pH~12. In the pH range 8 to 12 the measured sorption values are extremely high, reaching in some cases values of $10^3 \text{ m}^3 \text{ kg}^{-1}$. Because the main sorption mechanism in this pH range is most likely to be surface complexation, the values are practically independent of ionic strength.

Recommendation

The Am, Ac and Cm sorption value selected for marl are considered to be conservative for pH values up to and including 11.

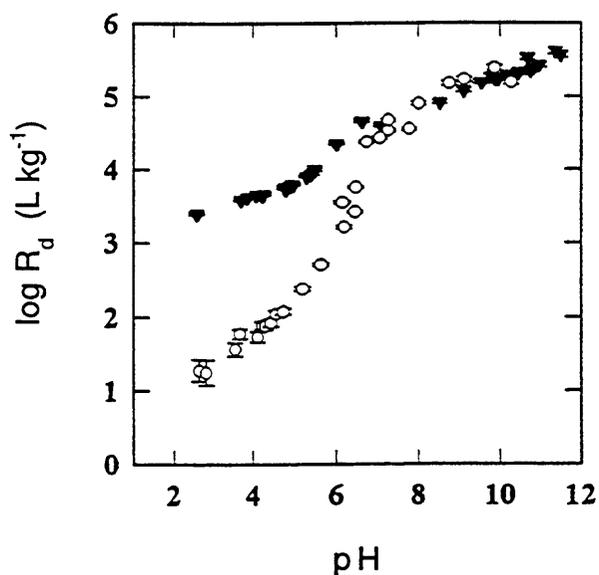


Figure 11: Sorption (L kg^{-1}) of Am on Na-montmorillonite in 0.1 M (filled symbols) and 1 M (open symbols) NaClO_4 . (Taken from GORGEON 1994, Figure III-7.)

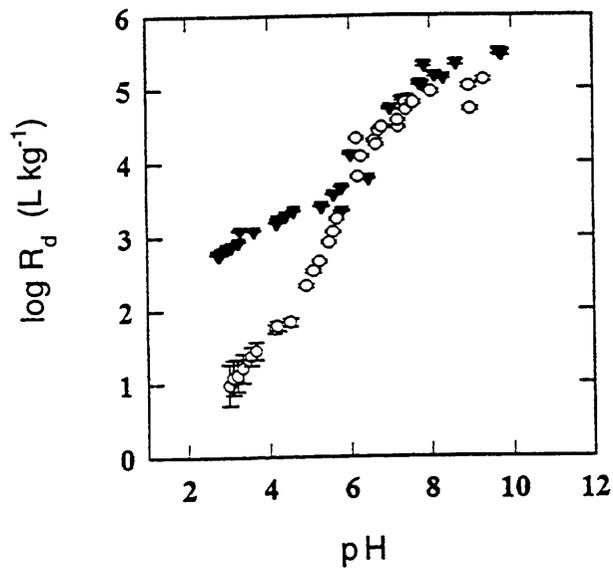


Figure 12: Sorption (L kg^{-1}) of Am on Na-illite in 0.1 M (filled symbols) and 1 M (open symbols) NaClO_4 . (Taken from GORGEON 1994, Figure III-8.)

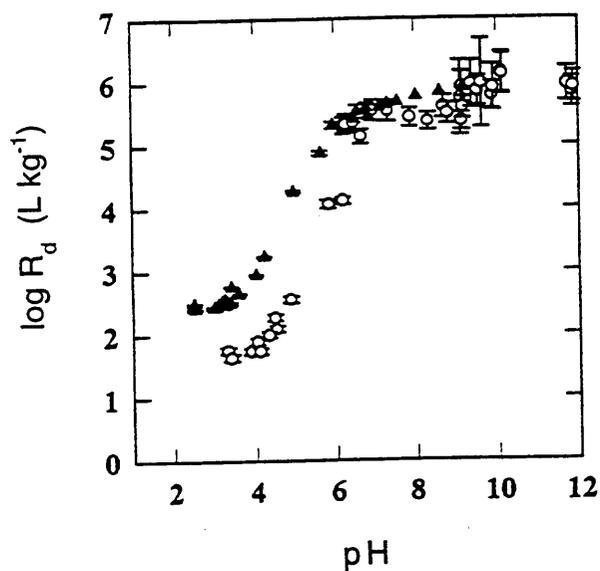


Figure 13: Sorption (L kg^{-1}) of Am on Na-kaolinite in 0.1 M (filled symbols) and 1 M (open symbols) NaClO_4 . (Taken from GORGEON 1994, Figure III-9.)

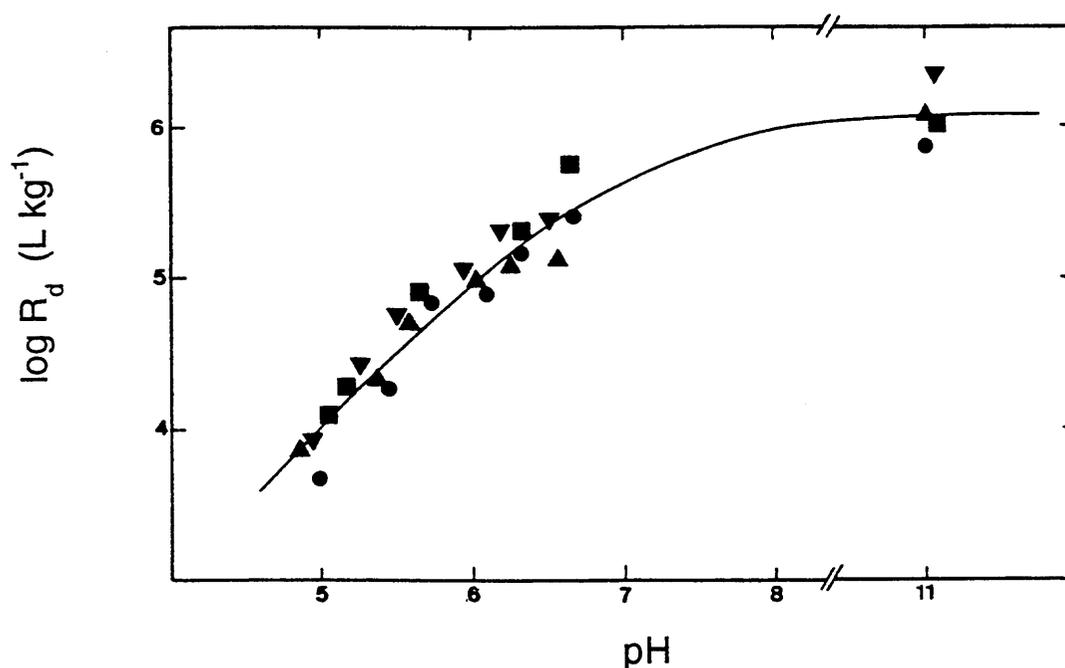


Figure 14: Distribution ratios (L kg^{-1}) versus pH in Boom clay (210 m) at 1% (●), 0.1% (▲), 0.01% (▼) and 0.003% (■) Eu-loadings. (Taken from BAEYENS 1982, Figure 6.17.)

6.3.2 Tetravalent actinides and zirconium

Th, U, Pu

The only directly relevant sets of data for the sorption of tetravalent actinides at high pH which could be found in the open literature were those from BERRY et al. (1991) and BASTON et al. (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) at pH values between ~8 and ~11. The tabulated data in their original work have been plotted here in Figures 15 to 17. These data show that within the scatter of the measurements the sorption for all three actinides is very high on the different sedimentary rocks with very little dependency on pH in the range 8 to 12.

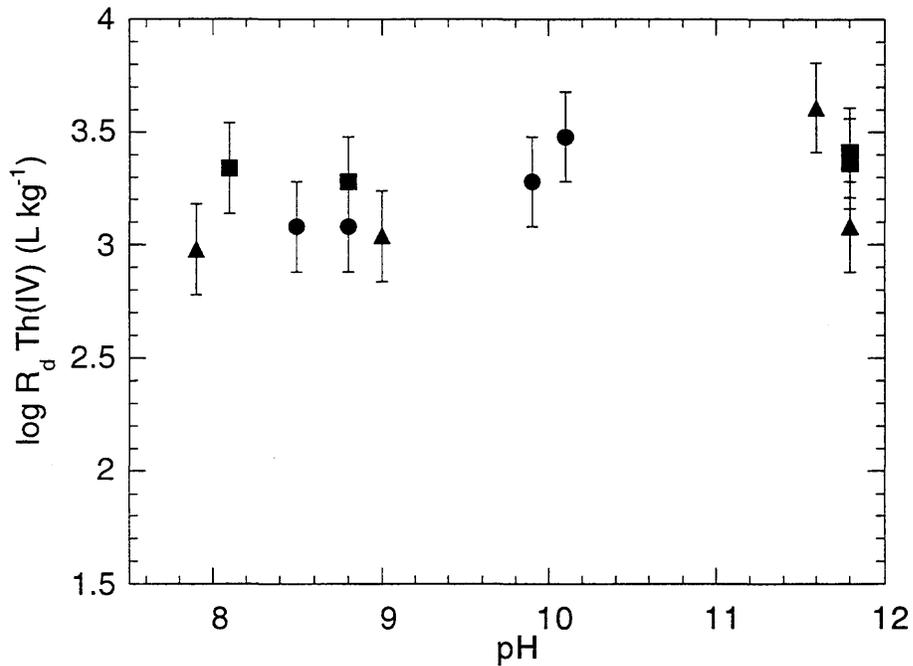


Figure 15: Sorption of Th(IV) on London clay (●), Caithness flagstone (▲) and St. Bees sandstone (■) as function of pH. (Taken from BASTON et al. 1992.)

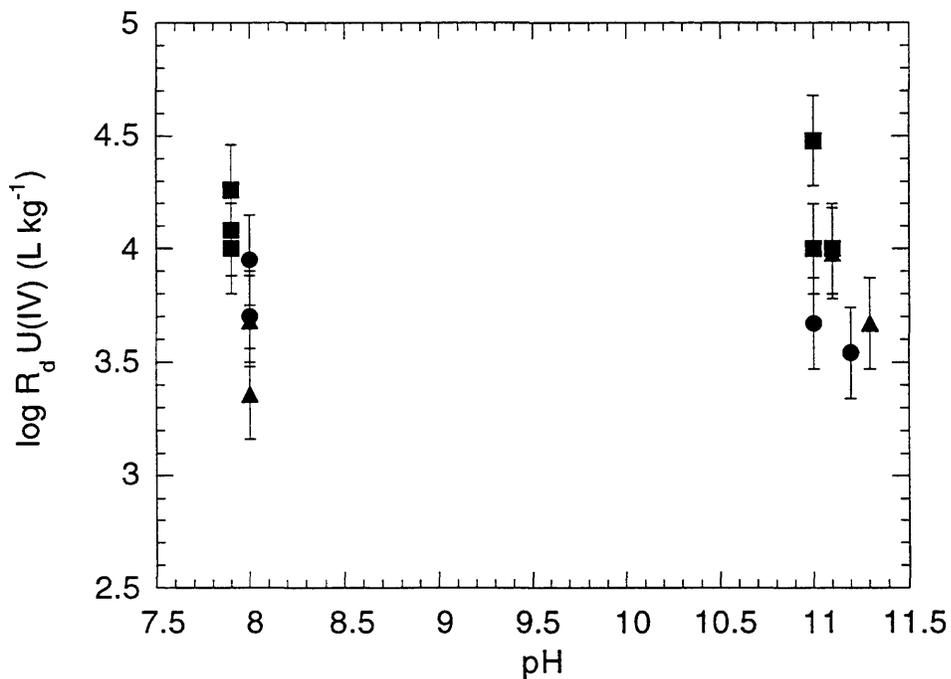


Figure 16: Sorption of U(IV) on London clay (●), Caithness flagstone (▲) and St. Bees sandstone (■) as function of pH. (Taken from BASTON et al. 1992.)

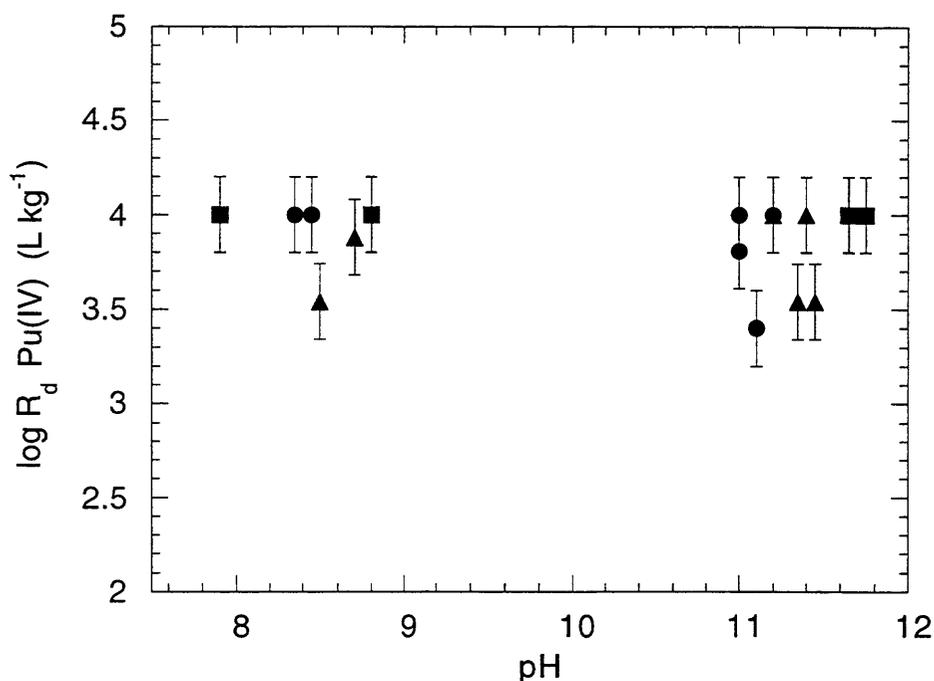


Figure 17: Sorption of Pu(IV) on London clay (●), Caithness flagstone (▲) and St. Bees sandstone (■) as function of pH. (Taken from BERRY et al. 1991 and BASTON et al. 1992)

Np, Zr

Little or no relevant sorption data could be found for Np and Zr and Th has been taken as their chemical analogue.

Recommendation

The arguments presented in BRADBURY & BAEYENS (1997) for the selection of sorption values for Th, U, Pu Np and Zr on marl are essentially valid at higher pH values and can be used for disturbed marl without modification.

6.3.3 Protactinium (V)

BERRY et al. (1988) report Pa(V) sorption values of 1 to 1000 m³ kg⁻¹ on London clay at a pH ~9. These were the only sorption data on a relevant sedimentary rock which were found in the open literature.

General comment

For the reasons given in (BRADBURY & BAEYENS, 1997), and for consistency with the sorption data selections made there for marl, it was preferred to take Np(V) as a chemical analogue for Pa(V) and the results of MEYER et al. (1985) on illite to deduce trends in sorption values with increasing pH. Their data clearly demonstrate a strong increase in sorption with increasing pH up to ~10.5, Figure 18.

Recommendation

On the basis of the above discussion, the sorption values deduced for Pa(V) for marl represent conservative values for disturbed marl.

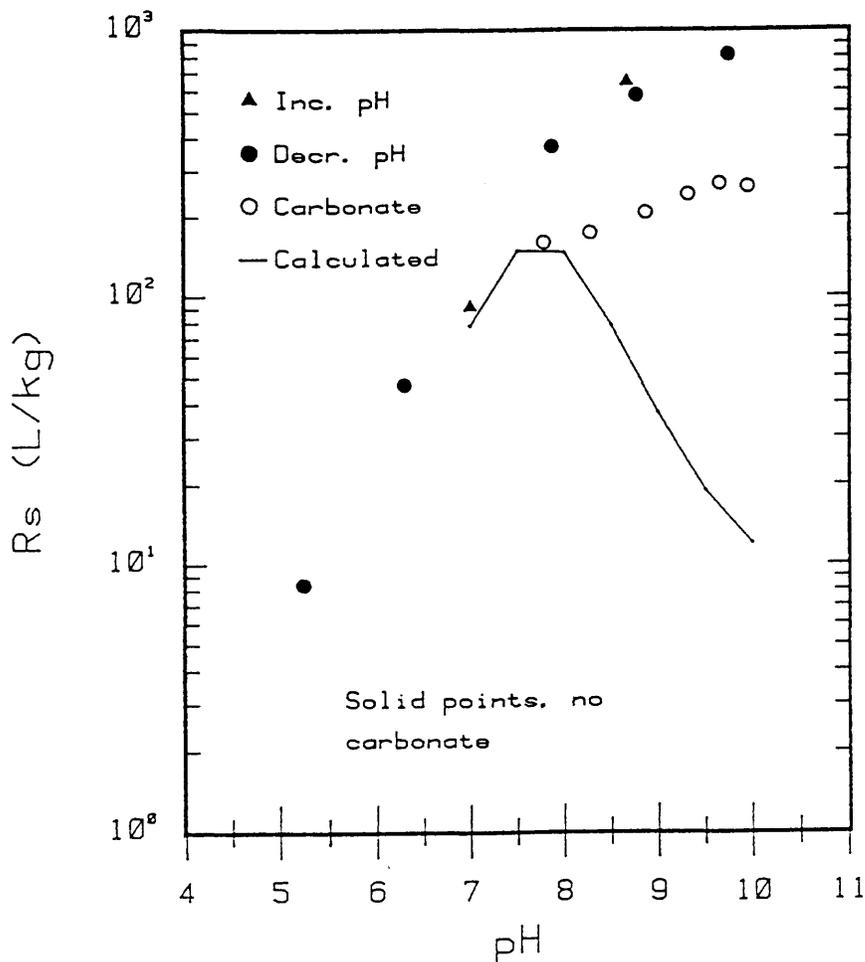


Figure 18: Sorption of Np(V) on illite at 0.1 M NaCl as function of pH in the presence and absence of carbonate. (Taken from MEYER et al. 1985, Figure 1)

6.4 Anionic species

Cl, I, Se, Mo, Nb

All measurements reported in the open literature on the sorption of anionic species indicate that the uptake tends to decrease with increasing pH irrespective of the sorbent, see for example DAVIS & KENT (1990). Although examples of anion sorption edges measured on clay minerals are sparse they do show the expected behaviour. (See for example THENG 1971, NEAL et al. 1987a and 1987b). As an illustrative example, sorption edges for MoO_4^{2-} on soil clays (THENG 1971) are given in Figure 19.

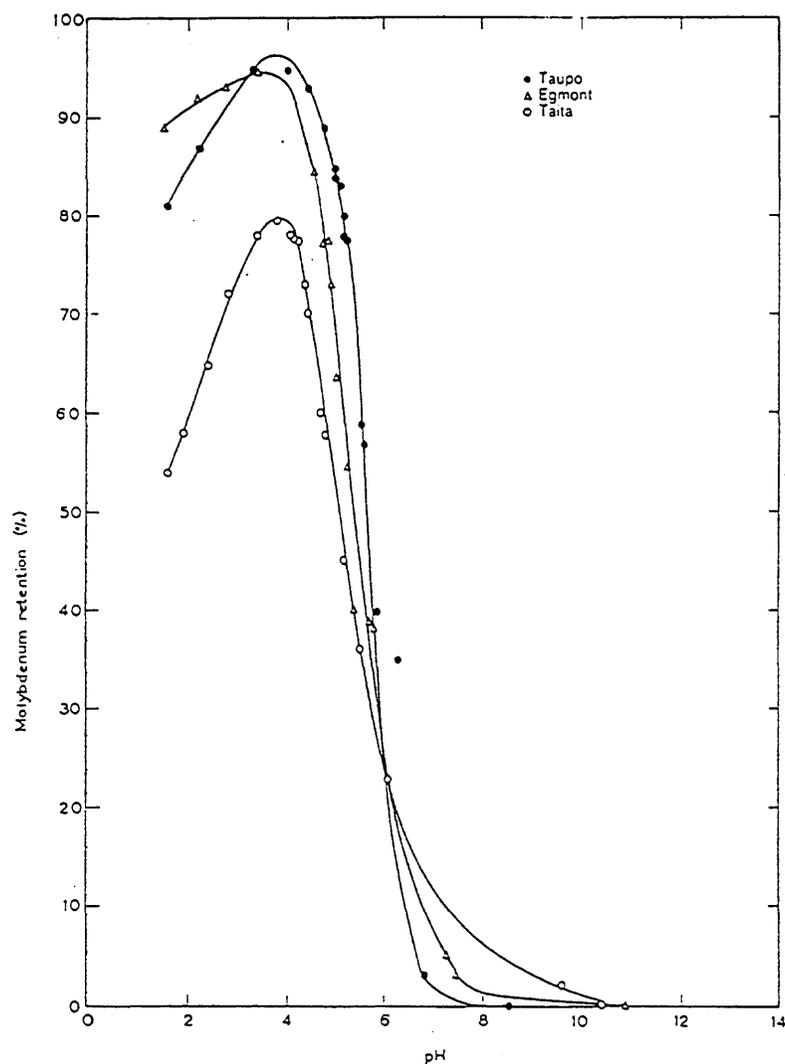


Figure 19: Molybdenate sorption on soil clays. (Taken from THENG 1971, Figure 2)

General comment

For anions sorbing via a ligand exchange mechanism, the universal experience is that the uptake onto mineral surface decreases with increasing pH. The pH at which the sorption becomes effectively zero may vary with radionuclide and solid phase but generally for clay minerals the boundary lies around 8 to 9.

Recommendation

At elevated pH values the sorption values for the radionuclides I, Cl, Se, Mo and Nb should be set to zero.

Sn

According to the Eh-pH equilibrium diagram for the Sn-water system (POURBAIX 1974), the dominant aqueous species is the stannate anion. (At pH=11, SnO_3^{2-} is the stable species down to an Eh of -600 mv.) Based on these considerations, molybdenate (MoO_4^{2-}) was taken as the chemical analogue for the oxyanionic stannate species.

General comment

It should however be noted that the above may be exceedingly conservative. BASTON et al. (1990) report Sn distribution ratios of 10 to 100 $\text{m}^3 \text{kg}^{-1}$ for London clay in the pH range 9 to 11. Such a result is incompatible with SnO_3^{2-} as the sorbing species but might be conceivable if tetravalent Sn were to be reduced to the strongly hydrolysable 2+ state. Alternatively, precipitation effects could be playing a role. In view of the generally poor level of understanding of Sn chemistry and sorption mechanisms, the above conservative approach was chosen.

Recommendation

Using Mo as a chemical analogue for Sn implies that the sorption value of the latter is zero.

^{14}C as $^{14}\text{CO}_3/\text{H}^{14}\text{CO}_3$

Following the approach given in BRADBURY & BAEYENS (1997), the sorption of ^{14}C existing in solution as $^{14}\text{CO}_3/\text{H}^{14}\text{CO}_3$ is considered to take place via an isotope exchange mechanism at the surface of calcite. The extent

to which this occurs depends on the inactive concentrations of CO_3/HCO_3 evolving in the groundwater. As the pH increases the tendency will be for the CO_3/HCO_3 concentrations to decrease. First, because the solubility of calcite decreases with rising pH, and secondly, because there may be significant Ca levels in solution arising from the portlandite in the cement which will tend to reduce the CO_3/HCO_3 concentrations via the common ion effect. Any decreases in carbonate concentrations would tend to result in increased sorption of ^{14}C existing in solution as $^{14}\text{CO}_3/\text{H}^{14}\text{CO}_3$.

Recommendation

At pH <11 the sorption data given for ^{14}C as $^{14}\text{CO}_3/\text{H}^{14}\text{CO}_3$ in the marl data bases are taken as conservative values for disturbed marl systems.

6.5 Sorption data base for disturbed marl, pH<11

Sorption data bases for mineralogies MIN-A, MIN-B and MIN-C in NaCl and NaHCO_3 groundwaters at pH<11 are given in Tables 2 and 3 respectively. Sorption values for fault gouge in both groundwater types are presented in Table 4.

Table 2: CONSERVATIVE sorption values selected for disturbed marl (pH <11) in the NaCl-type groundwater. All data in $\text{m}^3 \text{kg}^{-1}$.

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

Table 3: CONSERVATIVE sorption values selected for disturbed marl (pH<11) in the NaHCO₃-type groundwater. All data in m³ kg⁻¹.

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

Table 4: CONSERVATIVE sorption values selected for disturbed fault gouge (pH<11) in the NaCl- and NaHCO₃-type groundwaters. All data in m³ kg⁻¹.

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

7 SORPTION DATA FOR ALTERED MARL (pH>11)

7.1 Introduction

In this pH region we have assumed that clay minerals have dissolved and the main sorbing phases are calcite and secondary minerals. From the information contained in section 2.4 the most abundant newly formed minerals are likely to be of the CSH-gel type.

As will be described in section 7.3, the approach adopted for the altered marl is different from that used for disturbed marl and calcite, Chapters 6 and 8 respectively. The reasons for this lie mainly with the uncertainties associated with the altered marl system and the general lack of relevant measured data. The aim was to construct a robust SDB for altered marl.

7.2 Sources of sorption data relevant for an altered marl system

In order to provide information on the sorption properties of the likely alteration products, literature studies addressing the retention characteristics of CSH and CASH phases (TITS 1994) and another corresponding one on zeolites (VALKE & CREMERS 1994), were carried out. Although these surveys provided valuable background information (briefly summarised below), one of the main results was to highlight the almost total lack of relevant sorption data in the pH region of interest.

7.2.1 Calcium silicate hydrate phases

Cation exchange seems to be an important nuclide uptake mechanism for CSH/CASH phases and their exchange capacities are generally greater than those of illites and marls. Where comparative sorption values are available, they are generally larger for CSH/CASH phases. However, these data only relate to pH values less than 9.

GULIS & TIMULAK (1986) measured the sorption of Cs and Co on unsubstituted and Al substituted tobermorites at pH values between 12.5 and 13.4 in high ionic strength solutions, 1–2.6 M. The sorption values for Cs

ranged from $\sim 2 \times 10^{-3}$ to $\sim 2 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$. No trends with pH were observed, which would be expected for a cation exchange mechanism. R_d values for Co of $\sim 3.5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ were given at pH ~ 12.7 , falling to zero at pH ~ 13.4 .

EWART et al. (1990) measured the sorption of Pu and Am on synthetic CSH gels and a tobermorite. The Ca:Si ratio for the CSH phases varied between 1.25:1 to 1.7:1. The initial aqueous concentrations of Pu and Am in the sorption experiments were $5 \times 10^{-12} \text{ M}$ and 10^{-11} M , respectively. The results of the sorption measurements are shown in Table 5. (Although the authors mention that they measured the pH, no values were given in the paper.)

Table 5: Sorption of Am and Pu on crystalline (tobermorite) and amorphous CSH phases. (Taken from EWART et al. 1990)

Sorbent	R_d (Am) ($\text{m}^3 \text{ kg}^{-1}$)	R_d (Pu) ($\text{m}^3 \text{ kg}^{-1}$)
Tobermorite	20 (± 10)	400 (± 50)
CSH gels	60 (± 20)	20 (± 10)

One final important point to emerge from the literature study was that the incorporation of cations and anions into CSH/CASH phases during their formation may be a potentially significant retention mechanism. (This is discussed in Appendix B.)

Because so little relevant sorption data was available in the open literature, an experimental programme was started at PSI with the aim of producing a first broad overview of the sort of sorption values which might be expected. Since the results from this programme are important components in the development of the sorption data bases, it is worthwhile to briefly outline the concept and some of the main experimental points.

The groundwater chemistry was assumed to correspond to that emerging from the near field during the initial 10^4 to 5×10^4 years of the repository lifetime i.e. a (Na,K)OH solution saturated with calcite and portlandite at pH ~ 13.3 (BERNER 1992). At such an extreme pH, it was further assumed that all clay minerals within and immediately adjacent to water bearing fractures would

dissolve and be replaced by calcium silicate hydrates (CSH) and calcium aluminium silicate hydrates (CASH). (See, for example, BATEMAN et al. 1995.) Calcite was considered to be stable.

The experimental programme centred around sorption measurements of Cs, Sr, Ni, Eu/Am and Th, on calcite, CSH and CASH minerals, in the gel and crystalline (tobermorite) form. The sorption data quoted later in this chapter for CSH phases and calcite (Chapter 8) were taken mainly from the above work (TITS et al. 1997, 1998b).

7.2.2 Zeolites

Zeolites are known to be very powerful cation exchange media and there is a vast amount of data on their sorption characteristics. However, their exchange (sorption) properties can vary widely depending on composition and structure. Hardly any data are available on the pH dependency of sorption and no data at all could be found corresponding to hyperalkaline conditions. The exception to this was some Cs sorption data on clinoptillolite and mordenite tuffs, $12.5 < \text{pH} < 13.4$, where distribution ratios between $3.5 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ and $1.2 \times 10^{-1} \text{ m}^3 \text{ kg}^{-1}$ were given.

As the hyperalkaline plume is increasingly buffered to lower pH values by interaction with the marl minerals during its migration, the likelihood for the formation of zeolites becomes greater. There are some indications from natural analogue studies at Maqarin, Jordan (see for example ALEXANDER & MAZUREK 1996) and some laboratory studies (CRAWFORD & SAVAGE 1994) that zeolites (mordenite for example) do indeed form. However, there may be water chemistry ranges where both CSH and zeolite phases can co-exist. Exactly which zeolites form where and when and to what extent and under what water chemistry conditions is unclear at the moment.

Because of the generally high degree of uncertainty surrounding zeolites, we were not in a position to assess their relevance. Hence, this class of minerals, which can potentially precipitate out as secondary phases, is not treated further.

7.2.3 Hardened cement paste (HCP)

Extensive use was made of the SDB for cementitious materials (BRADBURY & VAN LOON 1998, Table 7) to deduce the likely impact of the formation of CSH and CASH type phases on the sorption behaviour in altered marl.

7.3 Sorption data selection procedure

By comparing the sorption data for marl given in BRADBURY & BAEYENS (1997) with corresponding values for HCP (BRADBURY & VAN LOON 1998) and measured data on CSH phases (e.g. TITS et al. 1998a) a minimum aim was to present arguments indicating whether the sorption values in altered marl at $\text{pH} > 11$ are likely to be higher or lower than in the unaltered system. Following this, a further aim was to construct a conservative SDB, and to suggest a realistic SDB, taking into account the various mineralogies and water chemistries for the different flow paths in marl.

The assessments are based on data summaries such as those given in Tables 6 to 9. For example, in Table 6 the second column contains the ranges of sorption values selected for the three main mineral combinations present in flow features in undisturbed marl for the NaCl-type reference water chemistry, MIN A, B and C (BRADBURY & BAEYENS 1997, Table 9). In the third column corresponding sorption values selected for HCP are listed, (BRADBURY & VAN LOON 1998, Table 7) and scaled according to the proposal given in section 5.2.2. In the fourth column measured sorption data on CSH phases for alkaline (Cs) and alkaline earth (Sr) metals, a divalent transition metal (Ni) and a tetravalent actinide (Th), taken from the work of TITS et al. (1998a) are given together with data for Am and Pu (EWART et al. 1990).

Using such data summary tables the assessment/selection procedure was briefly as follows.

1. If the marl and scaled cement sorption values were similar, and the tendency was for the CSH values to be higher, then the marl values were chosen as conservative values for the altered marl.
2. If the scaled cement sorption values were greater or very much greater than the marl values and the CSH values even higher, then

the marl sorption values would represent a very conservative choice for the altered marl.

3. Where marl values were greater than the corresponding scaled cement values, the latter were preferred as best estimates for altered marl, even in cases where the scaled CSH values tended to be greater than or equal to the marl values.
4. The considerations listed in points 1 to 3 above led to the proposals for conservative sorption values for altered marl presented in column 5 of the tables.
5. As the alteration of the marl progresses, the scaled cement sorption values would tend to become more representative for the real system, i.e. the scaled cement sorption values given in the third column in Tables 6 to 9 may be considered to a first approximation as realistic for an extensively altered marl system.
6. For the sorption of ^{14}C as $^{14}\text{CO}_3/\text{H}^{14}\text{CO}_3$ in NaCl/NaHCO₃-type groundwaters the discussion given in section 6.4 is also considered to be valid here. Hence the recommendation for altered marl/fault gouge is the same i.e. the sorption data for ^{14}C as $^{14}\text{CO}_3/\text{H}^{14}\text{CO}_3$ in the marl data bases may be taken as representing conservative values.

7.4 Sorption data bases for altered marl

The selected sorption values for the four altered marl systems, MIN-A,-B,-C and NaCl; MIN-A,-B,-C and NaHCO₃; fault gouge and NaCl; fault gouge and NaHCO₃, are presented in column 5 in Tables 6 to 9 respectively.

Table 6: The selected sorption values for altered marl in an NaCl-type groundwater at pH>11 are given in bold type in column 5.

Sorption values for the marl/NaCl groundwater system (BRADBURY & BAEYENS 1997), scaled cement sorption values (BRADBURY & VAN LOON 1998) and sorption values for CSH phases (TITS et al. 1998a; EWART et al. 1990) are also given for comparison. All data in $\text{m}^3 \text{kg}^{-1}$.

Radionuclide	MIN A, B & C	CEMENT SDB* (scaled values)	Measured data on CSH	SELECTED VALUES
Cinorg.	$9-15 \times 10^{-4}$	10^{-3}		10^{-3}
Corg.	0	0		0
Cl	0	10^{-3}		0
K	$1.5-4 \times 10^{-4}$	0		0
Co	$6-20 \times 10^{-3}$	2×10^{-2}		6×10^{-3}
Ni	$1-3 \times 10^{-2}$	2×10^{-2}	1×10^{-1}	10^{-2}
Se	$2-4 \times 10^{-4}$	0		0
Sr	$8-25 \times 10^{-5}$	2×10^{-4}	6×10^{-1}	8×10^{-5}
Zr	$5-15 \times 10^{-2}$	1		5×10^{-2}
Nb	$4-10 \times 10^{-2}$	0.2		4×10^{-2}
Mo	$2-5 \times 10^{-3}$	0		0
Tc	$7-20 \times 10^{-4}$	0.2		7×10^{-4}
Pd	$1-3 \times 10^{-2}$	2×10^{-2}		10^{-2}
Ag	0	0		0
Sn	$2-5 \times 10^{-3}$	0.2		2×10^{-3}
I	0	2×10^{-3}		0
Cs	$3-8 \times 10^{-2}$	4×10^{-4}	2×10^{-3}	4×10^{-4}
Pb	$1.5-5 \times 10^{-1}$	10^{-1}		10^{-1}
Po	0	0		0
Ra	$8-25 \times 10^{-5}$	10^{-2}		8×10^{-5}
Ac	$8-20 \times 10^{-1}$	0.2		2×10^{-1}
Th	$5-15 \times 10^{-2}$	1	>50	5×10^{-2}
Pa	$4-10 \times 10^{-3}$	1		4×10^{-3}
U	$3-7 \times 10^{-1}$	1		3×10^{-1}
Np	$5-15 \times 10^{-2}$	1		5×10^{-2}
Pu	$3-7 \times 10^{-1}$	1	~20	3×10^{-1}
Am**	$8-20 \times 10^{-1}$	0.2	>50	2×10^{-1}
Cm	$8-20 \times 10^{-1}$	0.2		2×10^{-1}

* Region 1, reducing; Table F-1 (BRADBURY & SAROTT 1994)

** Measured distribution ratios for Eu on CSH-gels were $>100 \text{ m}^3 \text{kg}^{-1}$. Eu is considered to be a chemical analogue for Ac, Am and Cm.

Table 7: The selected sorption values for altered marl in a NaHCO₃-type groundwater at pH>11 are given in bold type in column 5.

Sorption values for the marl/NaHCO₃ groundwater system (BRADBURY & BAEYENS 1997), scaled cement sorption values (BRADBURY & VAN LOON 1998) and sorption values for CSH phases (TITS et al. 1998a; EWART et al. 1990) are also given for comparison. All data in m³ kg⁻¹.

Radionuclide	MIN A, B & C	CEMENT SDB* (scaled values)	Measured data on CSH	SELECTED VALUES
C _{inorg.}	7-10 x 10 ⁻⁴	6 x 10 ⁻³		10⁻³
C _{org.}	0	0		0
Cl	0	10 ⁻³		0
K	1.5-4 x 10 ⁻³	0		0
Co	3-7 x 10 ⁻¹	2 x 10 ⁻²		2 x 10⁻²
Ni	5-15 x 10 ⁻¹	2 x 10 ⁻²	1 x 10 ⁻¹	2 x 10⁻²
Se	1.5-3 x 10 ⁻⁵	0		0
Sr	1-3 x 10 ⁻²	2 x 10 ⁻⁴	6 x 10 ⁻¹	2 x 10⁻⁴
Zr	5-15 x 10 ⁻²	1		5 x 10⁻²
Nb	4-10 x 10 ⁻²	0.2		4 x 10⁻²
Mo	6-15 x 10 ⁻⁴	0		0
Tc	7-20 x 10 ⁻⁴	0.2		7 x 10⁻⁴
Pd	5-15 x 10 ⁻¹	2 x 10 ⁻²		2 x 10⁻²
Ag	1-3 x 10 ⁻³	2 x 10 ⁻⁴		2 x 10⁻⁴
Sn	6-15 x 10 ⁻⁴	0.2		6 x 10⁻⁴
I	0	2 x 10 ⁻³		0
Cs	5-15 x 10 ⁻²	4 x 10 ⁻⁴	2 x 10 ⁻³	4 x 10⁻⁴
Pb	4-10 x 10 ⁻²	10 ⁻¹		4 x 10⁻²
Po	0	0		0
Ra	1-3 x 10 ⁻²	10 ⁻²		10⁻²
Ac	4-10	0.2		2 x 10⁻¹
Th	5-15 x 10 ⁻²	1	>50	5 x 10⁻²
Pa	7-20 x 10 ⁻³	1		7 x 10⁻³
U	3-7 x 10 ⁻¹	1		3 x 10⁻¹
Np	5-15 x 10 ⁻²	1		5 x 10⁻²
Pu	3-7 x 10 ⁻¹	1	~20	3 x 10⁻¹
Am ^{**}	4-10	0.2	>50	2 x 10⁻¹
Cm	4-10	0.2		2 x 10⁻¹

* Region 1, reducing; Table F-2 (BRADBURY & SAROTT 1994)

** Measured distribution ratios for Eu on CSH-gels were >100 m³ kg⁻¹. Eu is considered to be a chemical analogue for Ac, Am and Cm.

Table 8: The selected sorption values for altered fault gouge in an NaCl-type groundwater at pH>11 are given in bold type in column 5.

Sorption values for the fault gouge/NaCl groundwater system (BRADBURY & BAEYENS 1997), scaled cement sorption values (BRADBURY & VAN LOON 1998) and sorption values for CSH phases (TITS et al. 1998a; EWART et al. 1990) are also given for comparison. All data in $\text{m}^3 \text{kg}^{-1}$.

Radionuclide	FAULT GOUGE NaCl	CEMENT SDB* (scaled values)	Measured data on CSH	SELECTED VALUES
Cinorg.	9×10^{-4}	10^{-3}		0
Corg.	0	0		0
Cl	0	10^{-3}		0
K	10^{-3}	0		0
Co	4×10^{-2}	2×10^{-2}		2×10^{-2}
Ni	8×10^{-2}	2×10^{-2}	1×10^{-1}	2×10^{-2}
Se	2×10^{-4}	0		0
Sr	6×10^{-4}	2×10^{-4}	6×10^{-1}	2×10^{-4}
Zr	4×10^{-1}	1		4×10^{-1}
Nb	3×10^{-1}	0.2		2×10^{-1}
Mo	10^{-2}	0		0
Tc	5×10^{-3}	0.2		5×10^{-3}
Pd	8×10^{-2}	2×10^{-2}		2×10^{-2}
Ag	0	0		0
Sn	10^{-2}	0.2		10^{-2}
I	0	2×10^{-3}		0
Cs	2×10^{-1}	4×10^{-4}	2×10^{-3}	4×10^{-4}
Pb	1	10^{-1}		10^{-1}
Po	0	0	0	0
Ra	6×10^{-4}	10^{-2}		6×10^{-4}
Ac	5	0.2		2×10^{-1}
Th	4×10^{-1}	1	>50	4×10^{-1}
Pa	3×10^{-2}	1		3×10^{-2}
U	2	1		1
Np	4×10^{-1}	1		4×10^{-1}
Pu	2	1	~20	1
Am**	5	0.2	>50	2×10^{-1}
Cm	5	0.2		2×10^{-1}

* Region 1, reducing; Table F-1 (BRADBURY & SAROTT 1994)

** Measured distribution ratios for Eu on CSH-gels were $>100 \text{ m}^3 \text{kg}^{-1}$. Eu is considered to be a chemical analogue for Ac, Am and Cm.

Table 9: The selected sorption values for altered fault gouge in an NaHCO₃-type groundwater at pH>11 are given in bold type in column 5.

Sorption values for the fault gouge/NaHCO₃ groundwater system (BRADBURY & BAEYENS 1997), scaled cement sorption values (BRADBURY & VAN LOON 1998) and sorption values for CSH phases (TITS et al. 1998a; EWART et al. 1990) are also given for comparison. All data in m³ kg⁻¹.

Radionuclide	FAULT GOUGE NaHCO ₃	CEMENT SDB* (scaled values)	Measured data on CSH	SELECTED VALUES
Cinorg.	7 x 10 ⁻⁴	6 x 10 ⁻³		10⁻³
Corg.	0	0		0
Cl	0	10 ⁻³		0
K	10 ⁻²	0		0
Co	2	2 x 10 ⁻²		2 x 10⁻²
Ni	3	2 x 10 ⁻²	1 x 10 ⁻¹	2 x 10⁻²
Se	2 x 10 ⁻⁵	0		0
Sr	8 x 10 ⁻²	2 x 10 ⁻⁴	6 x 10 ⁻¹	2 x 10⁻⁴
Zr	4 x 10 ⁻¹	1		4 x 10⁻¹
Nb	3 x 10 ⁻¹	0.2		2 x 10⁻¹
Mo	4 x 10 ⁻³	0		0
Tc	5 x 10 ⁻³	0.2		5 x 10⁻³
Pd	3	2 x 10 ⁻²		2 x 10⁻²
Ag	8 x 10 ⁻³	2 x 10 ⁻⁴		2 x 10⁻⁴
Sn	4 x 10 ⁻³	0.2		4 x 10⁻³
I	0	2 x 10 ⁻³		0
Cs	4 x 10 ⁻¹	4 x 10 ⁻⁴	2 x 10 ⁻³	4 x 10⁻⁴
Pb	3 x 10 ⁻¹	10 ⁻¹		10⁻¹
Po	0	0		0
Ra	8 x 10 ⁻²	10 ⁻²		10⁻²
Ac	25	0.2		2 x 10⁻¹
Th	4 x 10 ⁻¹	1	>50	4 x 10⁻¹
Pa	5 x 10 ⁻²	1		5 x 10⁻²
U	2	1		1
Np	4 x 10 ⁻¹	1		4 x 10⁻¹
Pu	2	1	~20	1
Am**	25	0.2	>50	2 x 10⁻¹
Cm	25	0.2		2 x 10⁻¹

* Region 1, reducing; Table F-2 (BRADBURY & SAROTT 1994)

** Measured distribution ratios for Eu on CSH-gels were >100 m³ kg⁻¹. Eu is considered to be a chemical analogue for Ac, Am and Cm.

8 SORPTION ON CALCITE AT ELEVATED pH

8.1 Introduction

The sorption of cations and anions on calcite is a well reported subject in the open literature e.g. McBRIDE 1979, 1980, GAMSJAGER et al. 1984, COMANS & MIDDELBURG 1987, DAVIS et al. 1987, COWAN et al. 1990, ZACHARA et al. 1991, STIPP 1992. Unfortunately the majority of the measurements have been carried out at pH values less than 9. No sorption data at all could be found for actinides and no relevant data at elevated pH (~12 to 13) for any safety relevant radionuclide seems to be available. Although "low pH" sorption data may be used as indicators of behaviour, it should be realised that sorption mechanisms might be different at extreme pH values and the low pH (<10) behaviour may not be directly transferable to higher values. Also, in nature calcite is unlikely to be present as pure CaCO₃ and seldom if ever occurs alone. It may well be the case that the other minerals associated with calcite, especially at high pH where reactions are likely, will determine the sorption properties so that laboratory sorption data measured on pure calcite may not always be relevant to the real situation.

8.2 Sources of sorption for calcite

The general trend in the sorption of cationic species on calcite is to increase with increasing pH. This is illustrated in Figure 19 by the data of ZACHARA et al. (1991) who measured the sorption of 7 bivalent metals on calcite. Only one element (Co) showed a decrease in sorption at higher pH.

In common with other sorbates, the uptake of anionic species by calcite decreases with increasing pH (see for example Figure 20).

Because of this exceedingly meagre pool of relevant sorption data for calcite at elevated pH an experimental programme centred around sorption measurements of Cs, Sr, Ni, Eu/Am and Th on commercially available calcite and calcite from Wellenberg was initiated (TITS et al. 1997, 1998b). The water chemistry in these tests was an artificial cement porewater, see section 7.2.1. Many of the sorption values in the calcite SDB were deduced from data generated in these studies.

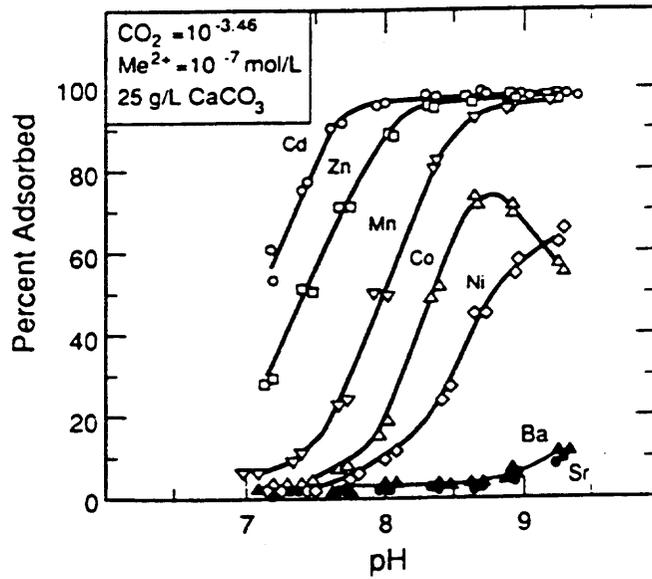


Figure 19: Sorption of 7 bivalent metals on calcite as function of pH. (Taken from ZACHARA et al. 1991, Figure 2a.)

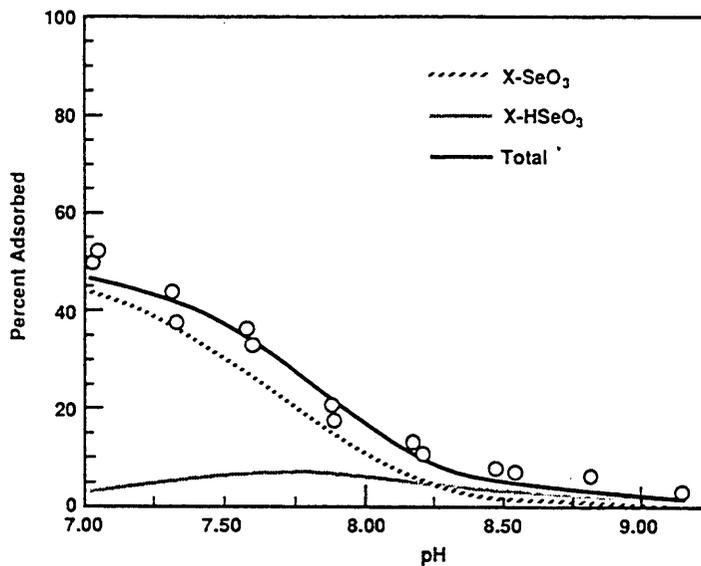


Figure 20: Sorption of Se on calcite. (Taken from COWAN et al. 1990, Figure 2)

8.3 Selection of sorption data for calcite at elevated pH

8.3.1 Procedure

The methodology adopted for estimating sorption values will be based again upon the identification of sorption trends with increasing pH within groups of chemically similar radionuclides and comparison with the data in the marl MIN-D SDB (BRADBURY & BAEYENS 1997). It is important to realise here that the data in the marl SDB apply to in situ conditions i.e. the laboratory measurements have been multiplied by a factor of 0.05 (the Lab->Field transfer factor⁺ for calcite) to produce the in situ sorption values. This is important when comparing SDB data and the laboratory measurements on calcite at high pH. Also, the variation in particular radionuclide sorption values in the marl SDBs for the calcite/NaCl and calcite/NaHCO₃ systems essentially arise from the pH difference in these two groundwater types. As far as the uptake of radionuclides by calcite is concerned, water composition is mainly (but not always) a second order effect. In view of this, sorption on calcite at elevated pH values will depend primarily on pH and consequently only two SDBs (pH<11 and pH>11) are given. Where undisturbed marl values are selected as being conservative, the sorption values for the higher pH NaHCO₃ system are chosen.

8.3.2 Alkaline and alkaline earth metals

Cs

No sorption of Cs on CaCO₃ was measurable at pH~13.3 in the concentration range 10⁻⁶ to 10⁻¹⁰ M (TITS et al. 1998b).

Recommendation

Cs is treated as being non-sorbing in the MIN-D marl SDB and the evidence is that it is also non-sorbing at high pH.

⁺ A factor for scaling crushed rock sorption values to values appropriate to bulk rock. It is defined as the ratio of the N₂-BET determined surface area of intact rock to the surface area of crushed rock. (BRADBURY & BAEYENS 1998b)

Sr and Ra

In the work of ZACHARA et al. (1991) there are clear indications that Sr (and Ba) sorb on calcite and that the sorption appears to be increasing at pH values above ~9, Figure 19.

On the other hand, TITS et al. (1998b) were not able to detect any uptake of Sr on CaCO₃ at pH~13.3.

Recommendation

For disturbed marl (pH <11) the Sr and Ra sorption values for MIN-D marl are recommended as being conservative, whereas at pH values above ~13 these radionuclides do not appear to sorb at all on CaCO₃.

8.3.3 Transition and heavy metals

Ni, Co, Pd, Pb

The data of ZACHARA et al. (1991) indicate that the sorption of transition metals increases with pH up to values of ~9.5, Figure 19. The exception to this is Co which shows a downturn in sorption above a pH of ~9 possibly due to the formation of negatively charged carbanato complexes.

Relatively low sorption values of ~10⁻³ m³ kg⁻¹ have been measured by TITS et al. (1998b) for Ni on CaCO₃ at pH~13.3 at high solid to liquid ratios (S:L = 50 g L⁻¹). This result may be compatible with the data of ZACHARA et al. (1991) if the other transition metals behave similarly to Co, but at a higher pH. Hyperalkaline conditions could then be sufficient to reduce sorption significantly through the formation of inorganic complexes.

Recommendation

For pH values less than 11, the MIN-D marl sorption values for transition/heavy metals represent conservative values for disturbed marl.

For altered marl a value of 10⁻³ m³ kg⁻¹ is selected as the best available laboratory value. The selected value in the SDB is 5 x 10⁻⁵ m³ kg⁻¹ taking into account the Lab->Field transfer factor.

Tc, Ag

No sorption data could be found for Tc and Ag on calcite. We assume zero sorption across the whole pH range.

8.3.4 Actinides

Trivalent Actinides

Ac, Am, Cm

Although the uptake mechanism of Am on CaCO_3 is uncertain, CaCO_3 appears to be extremely efficient at removing this trivalent actinide from solution.

BEALL & ALLARD (1981) measured the sorption of Am on calcite and dolomite in the pH range 7 to 9. The R_d values ranged between 10 to 50 $\text{m}^3 \text{kg}^{-1}$ and the trend in the data was of increasing sorption with increasing pH. TITS et al. (1997) measured the sorption of Am on synthetic CaCO_3 (Merck) in the pH range 11 to 13.3 and no pH dependency in the sorption data was observed. The distribution ratios were in all cases higher than 100 $\text{m}^3 \text{kg}^{-1}$. These data are supported by the results from similar measurements carried out using Eu which exhibited equally high sorption values and a linear sorption behaviour at equilibrium concentrations $< 10^{-9} \text{ M}$, TITS et al. (1998b).

Tetravalent actinides and Zr

Th, U, Np, Pu, Zr

The only data available for the sorption of tetravalent actinides on calcite at elevated pHs are those for Th on CaCO_3 (TITS et al 1998b). Again the sorption values at trace Th concentrations ($\sim 10^{-11} \text{ M}$) at $\text{pH} \sim 13.3$ are high, $R_d \gg 10 \text{ m}^3 \text{kg}^{-1}$.

Recommendation

The trend in the uptake of tri- and tetravalent radionuclides onto CaCO_3 is of increasing sorption values with increasing pH. The same sorption values for actinides as given for calcite in the undisturbed case can be used as conservative values in both pH regions i.e. $\text{pH} < 11$ and $\text{pH} > 11$.

8.3.5 Protactinium (V)

No data for the sorption of Pa on calcite were found.

In accord with previous practice, Np(V) was taken as a chemical analogue. The data of ALLARD (1982) indicated only a weak tendency for the sorption of Np(V) on calcite to rise with increasing pH.

Recommendation

The same sorption value for Pa as given for the calcite/ NaHCO_3 system in the undisturbed case can be used in both pH regions.

8.3.6 Anionic species

Cl, I, Se, Mo, Nb, Sn

As in other systems, the tendency is for anions to sorb less on CaCO_3 as the pH increases. This is illustrated for example in Figure 20 for Se.

Sn and Nb have been included with the anionic species since under the most probable Eh/pH conditions they are present in solution as negatively charged species; SnO_3^{2-} and $\text{Nb}(\text{OH})_6^-$ respectively.

Recommendation

At elevated pH values (> 9) the sorption values for the radionuclides I, Cl, Se, Mo, Nb and Sn should be set to zero.

8.3.7 Wellenberg calcite

A final point worth mentioning here is that "Wellenberg calcite" contains quartz, and there will be a strong tendency for CSH phases to form at high pH. Such phases may well dominate the sorption behaviour in calcareous marl/limestone layers.

In parallel to the sorption measurements of Cs, Sr, Ni, Eu, Am and Th at pH=13.3 on CSH phases and a synthetic CaCO_3 (Merck), a natural calcite sample from Wellenberg was also investigated. A comparison of the sorption

values obtained for the above radionuclides for the synthetic CaCO_3 and the natural Wellenberg calcite is given in Table 10.

Table 10: Distribution coefficients ($\text{m}^3 \text{kg}^{-1}$) for Cs, Sr, Ni, Eu, Am and Th on a synthetic CaCO_3 (Merck) and on Wellenberg calcite at $\text{pH}=13.3$ (TITS et al. 1997, 1998b).

	Cs	Sr	Ni	Eu	Am	Th
CaCO_3 (Merck)	0	0	10^{-3}	>100	>100	>10
Calcite (Wellenberg)	0	3	0.5	>100	>100	>10

From the results presented in this table it is clear that for Sr and Ni sorption on the natural calcite is considerably higher than on the Merck calcite. For the trivalent and tetravalent cations sorption is high on both solid phases.

Table 11: CONSERVATIVE sorption values selected for disturbed marl MIN-D (pH<11) and for altered marl MIN-D (pH>11) in the NaCl/NaHCO₃-type groundwaters. All data in m³ kg⁻¹.

Radionuclide	MIN-D pH < 11	MIN-D pH > 11
C(inorg.)	1.5 x 10 ⁻³	1.5 x 10 ⁻³
C(org.)	0	0
Cl	0	0
K	0	0
Co	2 x 10 ⁻³	5 x 10 ⁻⁵
Ni	5 x 10 ⁻⁴	5 x 10 ⁻⁵
Se	0	0
Sr	5 x 10 ⁻⁵	0
Zr	7 x 10 ⁻¹	7 x 10 ⁻¹
Nb	0	0
Mo	0	0
Tc	0	0
Pd	5 x 10 ⁻⁴	5 x 10 ⁻⁵
Ag	0	0
Sn	0	0
I	0	0
Cs	0	0
Pb	5 x 10 ⁻⁴	5 x 10 ⁻⁵
Po	0	0
Ra	5 x 10 ⁻⁵	0
Ac	1	1
Th	7 x 10 ⁻¹	7 x 10 ⁻¹
Pa	10 ⁻¹	10 ⁻¹
U	7 x 10 ⁻¹	7 x 10 ⁻¹
Np	7 x 10 ⁻¹	7 x 10 ⁻¹
Pu	7 x 10 ⁻¹	7 x 10 ⁻¹
Am	1	1
Cm	1	1

9 ORGANICS IN A DISTURBED/ALTERED MARL FAR-FIELD

9.1 Background

The principal organic ligands which could influence the uptake of radionuclides onto the disturbed/alterd marl minerals are cement additives and cellulose degradation products from the cementitious near-field. It was argued in BRADBURY & VAN LOON (1998), Chapter 14, that of all the organic ligands present, those from these two sources will have potentially the greatest effect.

The experimental measurements and discussions presented here will centre on ISA, which has been shown to be the major strongly complexing cellulose degradation product (VAN LOON et al. 1996), and GLU, which is taken to be a conservative representative for the behaviour of the organic cement additives. Currently available experimental evidence indicates that GLU forms the strongest organic ligand-radionuclide complexes of all the organic additives likely to be present in cement, see EWART et al. (1991) and GLAUS et al. (1995). However, this has not yet been unambiguously proven.

Having identified the two most potentially influential organic ligands, it must be said that the experimental data available quantifying their effects on sorption processes are relatively sparse. Before summarising the main results below, the sorption characteristics of ISA and GLU themselves will be briefly described since these are key factors in understanding their effects on sorption and being able to assess their influence.

9.2 The sorption of iso-saccharinic acid and gluconate in cementitious systems

The sorption characteristics of ISA and GLU have been described and discussed in detail elsewhere (VAN LOON et al. 1997; BRADBURY & VAN LOON 1998) and only the main relevant points will be listed here.

ISA and GLU sorb rapidly and to a significant extent on cementitious materials at pH values around 13. Their sorption in the concentration range from 10^{-6} to 10^{-2} M can, to a first approximation, be described by a Langmuir type

isotherm. The measurements indicate that the sorption capacity of hardened HTS ** cement paste for ISA is $\sim 0.2 \text{ mol kg}^{-1}$, whereas a value of $\sim 0.6 \text{ mol kg}^{-1}$ was deduced from the GLU data. (The above value for ISA should be compared with the global estimate for cement of 0.3 mol kg^{-1} given in BRADBURY & SAROTT (1994), section 6.2.2.) Preliminary measurements have also indicated that these two organic ligands sorb strongly on CSH-type phases, as would be expected (TITS et al. 1998a).

One of the main consequences of this is that the concentrations of ISA and GLU in the repository may be orders of magnitude lower than would be calculated on the basis of inventories and cellulose degradation rates alone. This is important because both of these organic ligands can form very strong complexes with safety relevant radionuclide and lower concentrations in cement porewaters automatically mean that they can have less of an influence on sorption (see section 9.5).

9.3 The influence of iso-saccharinic acid and gluconate on sorption at pH<11

BASTON et al. (1992) investigated the sorption of the actinides Th(IV), U(IV), and Pu(IV) on London clays as a function of pH in the presence and absence of ISA and GLU. (The mineralogical composition of London clay is comparable to that of Palfris marl.) Their main results are summarised in Figure 21.

In Figure 21 the shaded areas represent the range of sorption values measured in the absence of organic ligands and the data points correspond to measurements made in the presence of $2 \times 10^{-3} \text{ M}$ gluconate or "authentic degradation products", ADP. The ADP was prepared by mixing 1 kg paper tissues with 10 kg cement (1:9 OPC:BFS*) and 1 kg water and reacting in an autoclave at $105 \text{ }^\circ\text{C}$ for 30 days. On the basis of the available information, and taking into account ISA sorption on the OPC and the solubility of $\text{Ca}(\text{ISA})_2$, we estimate that the concentration of ISA was in the range 10^{-3} to 10^{-2} M in these tests.

** HTS = Haut Teneur en Silice, a French sulphate resisting cement.

* OPC/BFS= Ordinary Portland Cement/Blast Furnace Slag

The results indicate that the levels of cellulose degradation products in the ADP have little or no influence on the sorption of Th(IV), U(IV), and Pu(IV) on London clays at pH values up to ~11. In this context it should be noted that the complexation behaviour of cellulose degradation products (ISA) with actinides, especially Pu, tends to be significantly stronger than with any other safety relevant radionuclides (PILKINGTON & STONE 1990; GREENFIELD et al. 1992). Or, in other words, the influence of equivalent ISA concentrations on the uptake of other radionuclides will be effectively zero.

GLU, on the other hand, does appear to have an adverse effect, but only at the highest pHs in the case of Th(IV) and Pu(IV). For U(IV) an effect is apparent over the whole pH range investigated. (Sorption reduction factors are of the order of 10.) However, as will be shown later, the GLU concentrations used here were at least an order of magnitude greater than those expected in practice.

Similar trends in sorption behaviour were also determined in complementary experiments performed with two other sedimentary rocks, Caithness flagstones and St. Bees sandstone.

In a more recent study, BASTON et al. (1994), the effects of organic ligand concentrations on the sorption of Th(IV) and Pu(IV) on tuffs were investigated at pHs of ~8 and ~12. (The data for pH ~12 are reproduced in Figures 22 and 23.) These authors concluded that the presence of GLU and ISA at concentrations $<2 \times 10^{-4}$ M reduces the sorption of Th(IV) and Pu(IV) by factors of the order unity. Only at concentrations of $\sim 2 \times 10^{-3}$ M and above were significant decreases in sorption measured. (For GLU over the whole pH range and for ISA only at the highest pH.)

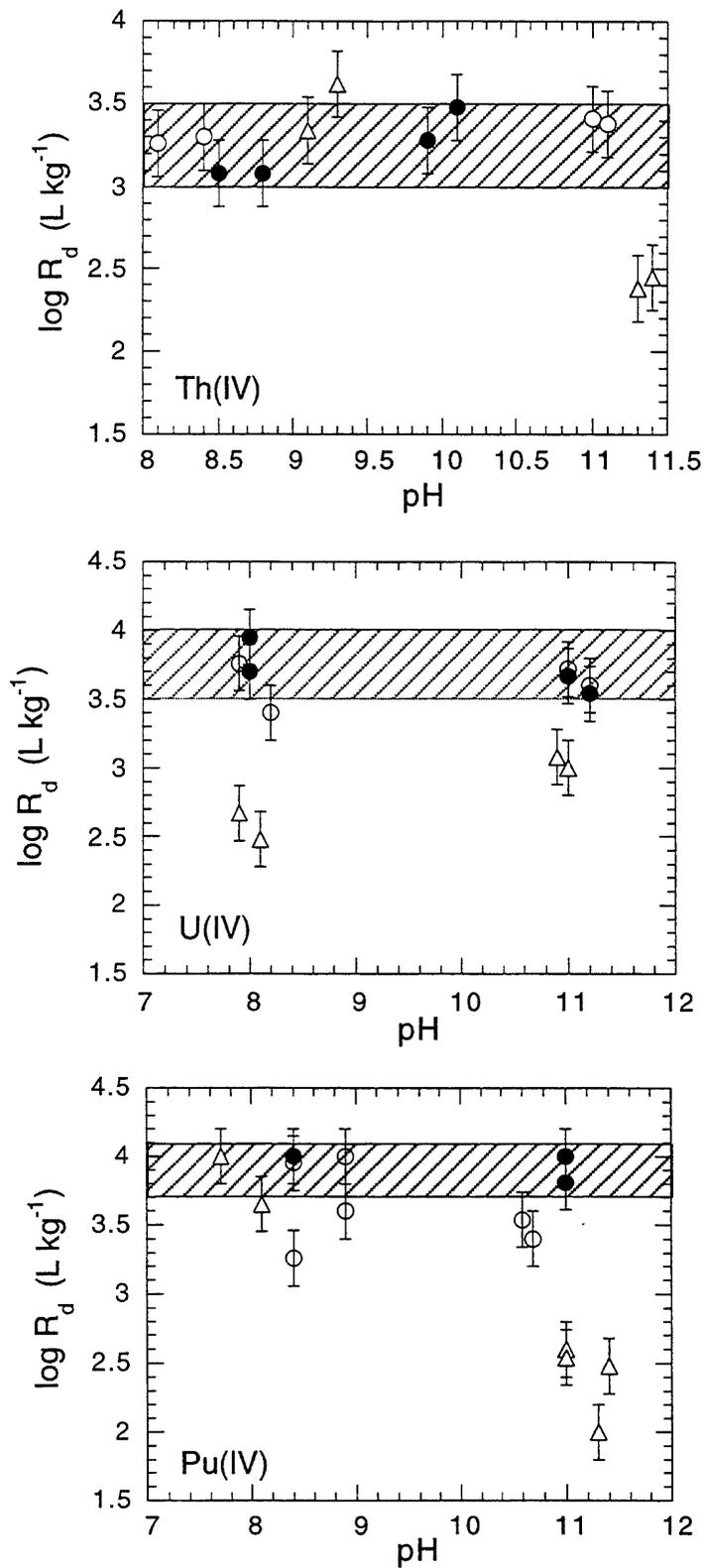


Figure 21: Effect of authentic degradation products and gluconate on Th, U and Pu sorption on London clay. No organics (●), ADP (○) GLU (Δ). (Taken from BASTON et al. 1992)

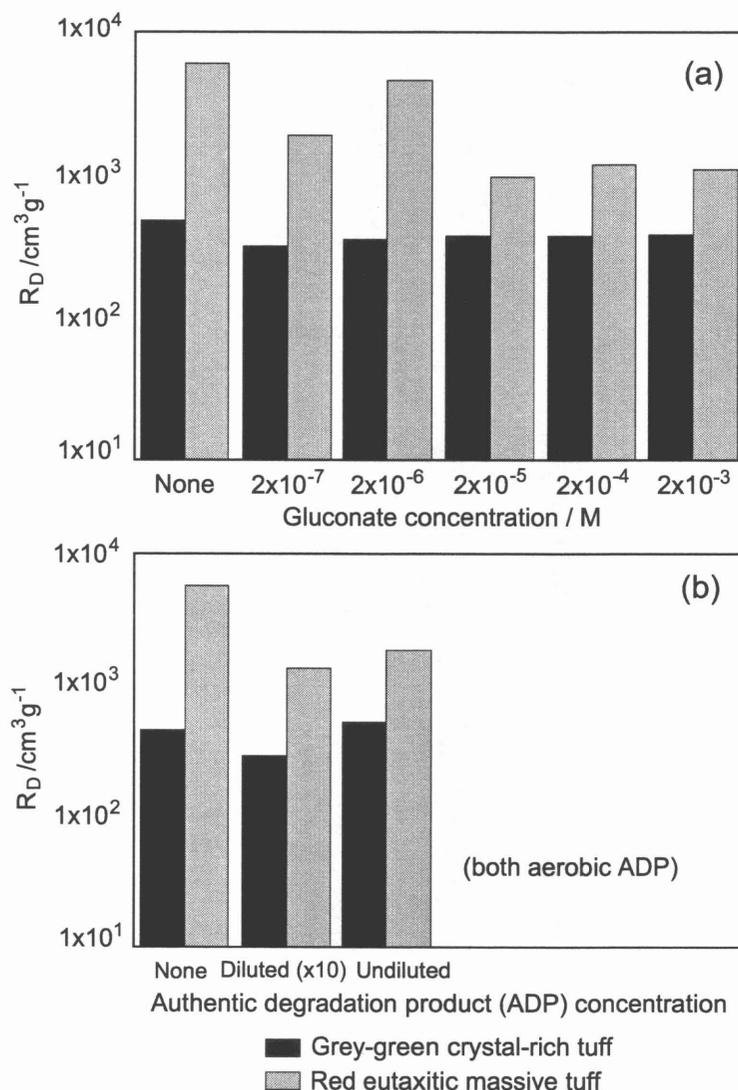


Figure 22: Effect of organics, (a) GLU; (b) ADP on the sorption of Th(IV) on tuffs at pH ~12. (Taken from BASTON et al. 1994, Figure 5.)

9.4 The influence of iso-saccharinic acid and gluconate at pH > 11

CSH-PHASES

TITS et al. (1998a) investigated the effects of initial GLU concentrations of $\sim 10^{-4}$ M on the sorption of Ni, Eu and Th on amorphous CSH phases at pH ~13.3. The main result from this work was that no adverse influence on the sorption of these bi-, tri- and tetravalent radionuclides could be detected. In the case of Ni the short term sorption values in the presence of GLU were higher than the values measured in its absence. Tests were also carried out with Cs and Sr and, as expected, GLU had no influence.

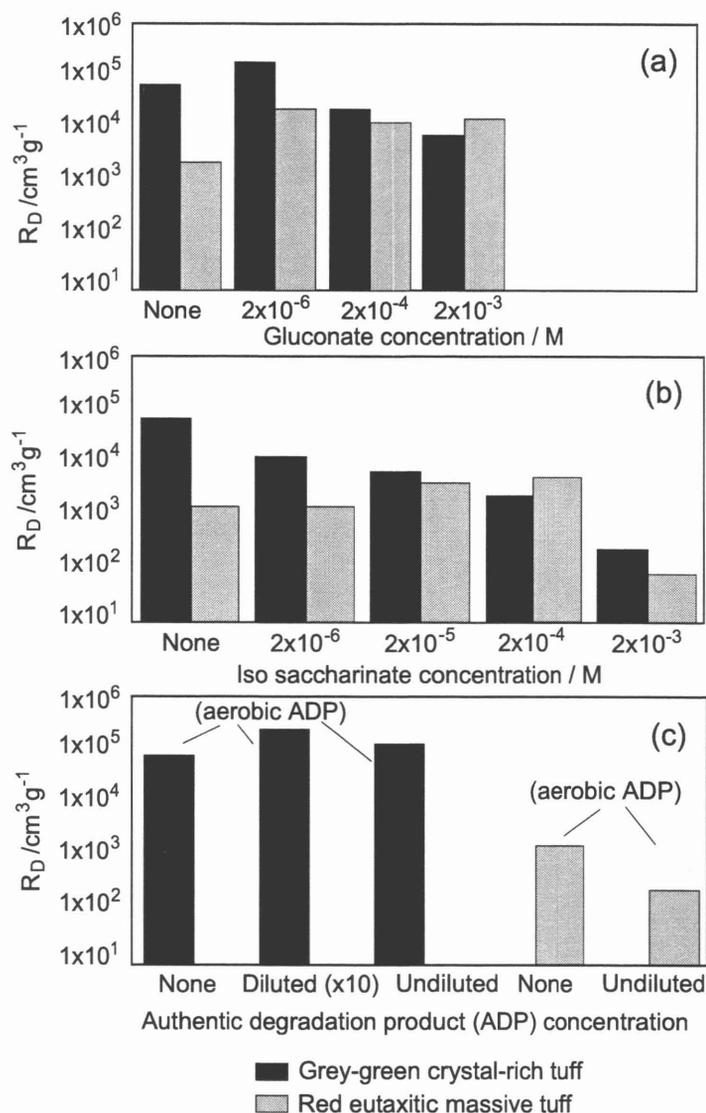


Figure 23: Effect of organics, (a) GLU; (b) ISA; (c) ADP on the sorption of Pu(IV) on tuffs at pH ~12. (Taken from BASTON et al. 1994, Figure 3.)

Synthetic CaCO_3

Similar experiments to those above were performed using CaCO_3 as the sorbent. In contrast to CSH phases, significant reductions in the uptake of Eu and Th by CaCO_3 were recorded. The sorption of Eu and Th was reduced by a factor of ~1000.

In the case where CaCO_3 was the solid phase, the complexation of GLU with Eu and Th appears to be strong, with the consequence that significant reductions in sorption are observed. However, for the CSH experiments, where the water chemistry was essentially the same and therefore the complexation with GLU should have been equally strong, there was practically no influence at all on sorption. The question posed by these two sets of data is: "Why are the results so different?"

The explanation of this apparent anomaly proposed by TITS et al. (1998a) lies in the sorption behaviour of GLU and also (possibly) the complexes it forms with radionuclides. These authors showed that GLU does not sorb at all on CaCO_3 but sorbs strongly on CSH phases. This has the effect of severely reducing the GLU concentrations in sorption experiments conducted with the latter solid phase and thereby also the influence of any adverse effects due to complexation. (Whether the radionuclide-organic complexes also sorb remains an open question at the moment.) In the sorption tests with CaCO_3 the full effects of complexation are observed.

Hardened cement paste

WIELAND et al. (1998) investigated the influence of ISA concentration on the sorption of mono-, bi-, tri- and tetravalent radionuclides on a hardened HTS cement paste. For ISA concentrations up to $\sim 6 \times 10^{-3}$ M, and over equilibration times as long as 56 days, no effects on the sorption of Cs, Sr and Ni were detected.

Eu exhibited a very high affinity for HCP surfaces with distribution ratios of $\sim 3 \pm 2 \times 10^3 \text{ m}^3 \text{ kg}^{-1}$. Equilibrium concentrations of ISA up to 10^{-4} M produced only slight reductions in these sorption values and even raising the levels to 10^{-3} M only caused a reduction by a factor of ~ 6 .

The uptake of Th onto HCP was not quite as strong as Eu but nevertheless the measured sorption values were $> 10^3 \text{ m}^3 \text{ kg}^{-1}$. A reduction in sorption by a factor of ~ 2 resulted from ISA concentrations at the 10^{-4} M level. However, increasing the equilibrium ISA concentration by a factor of ten to 10^{-3} M reduced the sorption to less than $5 \text{ m}^3 \text{ kg}^{-1}$ i.e. a reduction of ~ 40 fold. The reason for this disproportionate effect on sorption is not clear at the moment.

9.5 Summary of the influence of cellulose degradation products and cement additives on sorption in an disturbed/alterd marl far-field

Both ISA and GLU have been shown to exhibit significant sorption on hardened cement paste (see VAN LOON et al. 1997). A conservative calculation given in BRADBURY & VAN LOON (1998) indicated that their

maximum concentrations in the cement pore water in the near-field are $\sim 3 \times 10^{-4}$ M for ISA and $\sim 5 \times 10^{-5}$ M for GLU.

Since additives are present at roughly the same levels everywhere within the cement in the repository, the above value can be taken as an estimate of the maximum concentration which can leave the near field. According to the arguments given in Chapter 4, much of the GLU originally existing in the cement pore water will already have left the repository and moved out into the far-field before any of the sorbing radionuclides see the altered far field. In addition GLU will be sorbing strongly onto the secondary CSH minerals. These two processes are likely to reduce the GLU concentrations in the far field to levels which are significantly below those originally existing in the near field. If the results given previously on the influence of GLU on sorption are considered, then the concentrations of GLU entering the disturbed/altered far field are probably so low that they no longer have any adverse influences on sorption processes.

The ISA on the other hand arises from degradation reactions taking place within the waste drums and must first leave the drum and then migrate through the various cementitious barriers to reach the far field. Because of its relatively high sorption it will be retarded with respect to the leading edge of the pH plume. Also, in a similar way to GLU, ISA will be sorbing strongly onto the secondary CSH minerals, again a process which will lower its aqueous phase concentration. In addition, there are strong indications from the work of WIELAND et al. (1998) that even at the highest estimates for the concentration of ISA in the near field, there is little or no influence on the uptake of radionuclides on hardened cement paste (CSH gel) surfaces.

All of the information currently available indicates the concentrations of cement additives and cellulose degradation products are likely to be too low to adversely influence the sorption properties of radionuclides in an altered marl far field.

The one region in which "organics" might conceivably be important is the jointed calcareous marl/limestone layers where the retardation is principally via sorption on calcite. The results given in Chapter 9 indicated that GLU and iso-saccharinic acid had significant effects on the sorption on CaCO_3 even at

low concentrations. However, even here the effect of organics will not be as great as might be anticipated because "Wellenberg calcite" contains ~10 wt.% quartz and under the hyperalkaline conditions CSH phases will most probably form here as well. These CSH phases provide strong sinks for organic ligands such as ISA and GLU and are likely to significantly reduce their concentrations in solution and hence their influence on sorption.

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APPENDIX A SIMPLIFIED MINERALOGIES FOR THE MAIN FLOW PATHS IN THE PALFRIS MARL FORMATION

MAZUREK et al. (1994) have described the dominant flow paths in the Palfris marl formation and classified them into three broad types viz. cataclastic zones, thin discrete shear zones, and jointed calcareous marl or limestone layers. 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 simplified mineralogies. In order to provide continuity with the work of MAZUREK et al. (1994), 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% Calc./Ank./Dol.
 ~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 gauge (Porosity ~10%, water conducting feature type 1)

Simplified Mineralogy

~42% Calc./Ank./Dol.
 ~40% Clay minerals
 ~16% Quartz

MIN-C

Calc./marl limestone (Porosity ~0.8%, water conducting feature type 1)

Calc./marl limestone (Porosity ~0.8%, water conducting feature type 3)

Simplified Mineralogy

~71% Calc./Ank./Dol

~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.

APPENDIX B INCORPORATION OF RADIONUCLIDES INTO CSH PHASES DURING THEIR FORMATION

The possibility of the incorporation of radionuclides into CSH phases has been discussed in a previous report (BRADBURY & VAN LOON 1998) describing the compilation of a sorption data base for the cementitious near field of a L/ILW repository. The information presented there is equally relevant to the processes occurring during and after the formation of secondary minerals of the CSH-type in the altered marl far-field. It is given here again, in a slightly amended form, for completeness.

The effectiveness of cementitious materials as near field barriers to the migration of radionuclides has mainly been attributed to sorption on hardened cement paste, in particular to sorption on the CSH-type phase components. However, the good retention characteristics may not be just a question of sorption.

There is an increasing body of evidence, arising predominantly from outside the radioactive waste management community, which is suggesting that chemical incorporation reactions, either during the formation of CSH phases or as a subsequent reaction to surface sorption, are important removal mechanisms for many nuclides. Although most of the published results are for transition and heavy metals, with virtually nothing on trivalent metals and actinides, it is reasonable to believe that these too will take part in such reactions.

An overview paper by COCKE & MOLLAH (1993) summarises the uptake processes for Hg, Pb, Cd, Zn, Cr and Ba on hardened cement paste in the form of a diagram which is reproduced below, Figure B1.

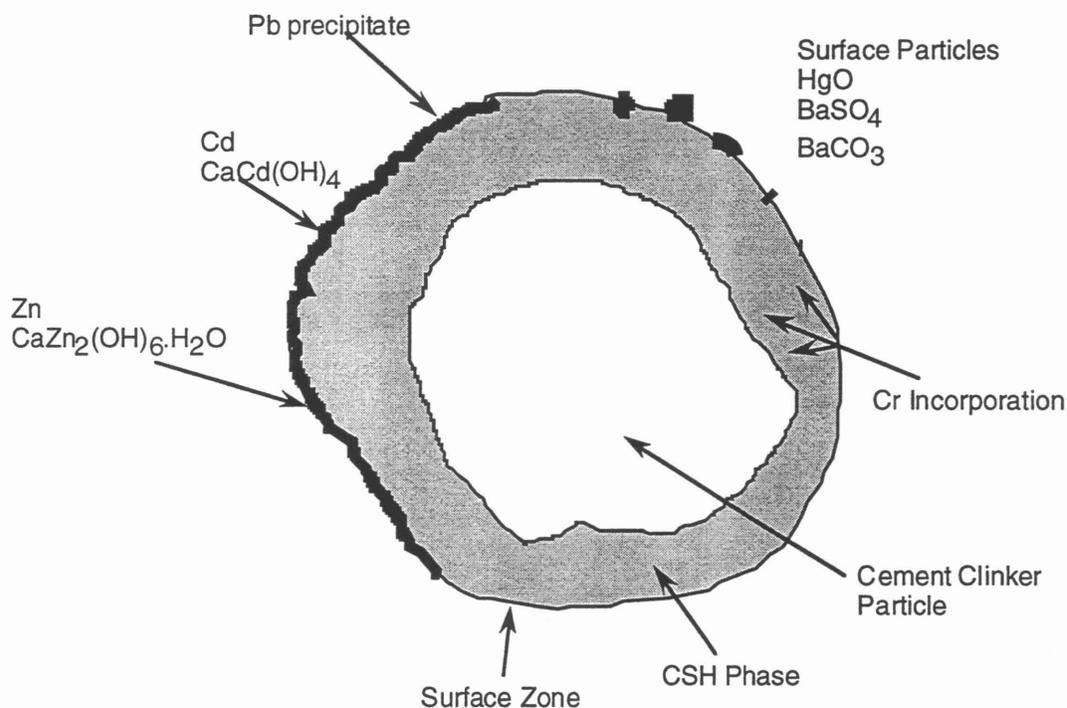


Figure B1: A summary of models for the interaction of metal pollutants with cement. (Figure 8-31 in COCKE & MOLLAH 1993)

BAUMBAUER (1992) in his paper talks of "Speicherminerale" (storage minerals) i.e. minerals which are capable of incorporating heavy metals and certain anions into their structures during their formation. As examples he gives the incorporation of Cl^- and Fe, Cr, Mn, Co, Ni, Zn, Pb, As, Cd in ettringite and/or monosulphate phases.

Other interesting work in this area can be found in COCKE (1990), COCKE et al. (1992), KOMARENI & ROY (1981, 1985), KOMARENI et al. (1982, 1986), KOMARENI et al. (1988), LABHSETWAR & SHRIVASTAVA (1988, 1989), LAMEILLE et al. (1987), TITS (1994).

In a recent report, ALEXANDER & MAZUREK (1996) summarise some preliminary observations from the Maqarin analogue project which tend to indicate that radionuclide/secondary mineral association is taking place in the altered rock. For example, Ra and Sn are definitely associated with CSH and CASH phases (MILODOWSKI et al. 1997); Se appears to form solid solutions with ettringite; Ni has been found in the same mineral, and jennite, tobermorite and ettringite, amongst other secondary minerals, provide sinks for uranium.

Though there is mounting evidence for the "chemical fixation" of radionuclides by CSH phases (and other secondary minerals) forming in the far field providing an important additional retardation mechanism, the extent to which it takes place, and consequently its influence on performance assessment studies, are uncertain at the present time.

APPENDIX C CHEMICAL ANALOGUES, MEASURED VALUES

It should be realised that sorption mechanisms at extreme pH values may not be the same as those occurring at one or two pH units either side of neutral. Also, the aqueous chemistry for many radionuclides becomes very uncertain in hyperalkaline solutions and often there are no directly measured data.

Wherever possible experimentally measured sorption values have been used to compile the SDBs, and only in cases where there was no measured data were sorption values deduced from chemical analogy. Unless there were strong reasons to the contrary, measured data were always preferred over values deduced via a chemical analogue.

This method of proceeding has led to some apparent anomalies and seeming inconsistencies. For example, no reliable sorption data for Sn at $\text{pH} < 11$ could be found and as the current evidence would indicate that Sn is present as the stannate anion, the chemical analogy with Mo, as molybdate, for which there were measurements, was taken. At $\text{pH} > 12.5$ measured data on HCP indicated high Sn sorption values, but no data were available for Mo. However, Mo was taken to have very weak sorption and the analogy with Sn was not invoked. Mo almost certainly still exists as the negatively charged molybdate at high pH (hence low sorption) but the possibility exists for Sn to be reduced to the 2+ state which is strongly hydrolysing and hence also (probably) strongly sorbing. This could explain the high values determined experimentally on HCP.

Finally, it is almost inevitable that such conflicting situations occur where our understanding is weak and where few reliable sorption measurements exist.