



TECHNICAL REPORT 02-20

Cementitious Near-Field Sorption Data Base for Performance Assessment of an ILW Repository in Opalinus Clay

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

PREFACE

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

The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

NOTE: The Nagra Technical Report contains in addition two appendices.

- In the main part, which is simultaneously issued as a PSI report (Chapters 1 to 8), the sorption values for safety-relevant radionuclides of both their reduced and oxidised forms have been deduced according to the chemical conditions anticipated for a cementitious near field without specifying reference redox potentials.
- Appendix I is a compilation from the main part of this report and includes sorption data for the reference redox conditions assumed for the two waste groups ILW-1 and ILW-2.
- Appendix II is a summary of the data used for safety assessment calculations within the Project Opalinus Clay (Entsorgungsnachweis) and includes comments to allow tracing the data in the compilation back to Appendix I and the main part (Chapters 1 to 8) of this report.

ISSN 1015-2636

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ABSTRACT

The present report describes a cement sorption data base (SDB) for the safety-relevant radionuclides to be disposed of in the planned Swiss repository for long-lived intermediate-level radioactive wastes (ILW). This report is an update on earlier SDBs, which were compiled for the cementitious near field of a repository for low- and intermediate-level radioactive wastes (L/ILW) by BRADBURY & SAROTT (1995) and BRADBURY & VAN LOON (1998).

The radionuclide inventories are determined by the waste streams to be disposed of in the ILW repository. A list of the safety-relevant radionuclides was provided based on the currently available information on ILW inventories. The compositions of the cement porewaters in the near fields of the L/ILW and ILW repositories, which had been calculated using well-established codes for modelling cement degradation, were compared to identify any differences in the near-field conditions and to assess their influence on radionuclide sorption.

Sorption values were selected based on the previously reported SDBs for the near field of the L/ILW repository. Sorption values were revised if new information and/or data were available which allowed changes to or re-appraisals of the data to be made. The sorption values recommended in this report were either selected on the basis of data from in-house experimental studies or from literature data.

For some key radioelements, i.e., Cs(I), Sr(II), Ni(II), Eu(III), Th(IV) and Sn(IV), new data were available from in-house measurements. These elements had been selected for experimental studies due to their relevance to safety assessment and/or their importance as appropriate chemical analogues.

Degradation products of bitumen and cellulose, concrete admixtures and cement-derived near-field colloids were taken into account as the main potential perturbations, which could reduce radionuclide sorption in the near field. Possible impacts of the perturbing factors on radionuclide mobility were considered and quantified in terms of sorption reduction factors.

ZUSAMMENFASSUNG

Der vorliegende Bericht umfasst eine Zementsorptionsdatenbasis (SDB) für sicherheitsrelevante Radionuklide, die in der Schweiz im geplanten geologischen Tiefenlager für langlebige mittelaktive radioaktive Abfälle (ILW) gelagert werden sollen. Mit diesem Bericht werden frühere SDBs, die von BRADBURY & SAROTT (1995) und BRADBURY & VAN LOON (1998) für ein geologisches Tiefenlager für schwach- und mittelaktive radioaktive Abfälle (L/ILW) erstellt wurden, dem neusten Wissensstands angepasst.

Die sicherheitsrelevanten Radionuklide sind durch die in einem Tiefenlager ILW zu entsorgenden Abfallströme gegeben. Die Zusammensetzungen der Zementporenwässer in den Nahfeldern der L/ILW und ILW Tiefenlager wurden mit Hilfe von Rechencodes, die zur Modellierung der Zementdegradation verwendet werden, berechnet. Die so gefunden chemischen Zusammensetzungen der Zementporenwässer in den beiden Nahfeldern wurden verglichen, um Unterschiede in den Nahfeldbedingungen zu identifizieren und deren Bedeutung auf die Radionuklidsorption abschätzen zu können.

Die Sorptionswerte für die Radionuklide wurden aus den bereits früher erstellten SDBs für das geplante Tiefenlager L/ILW ausgewählt. Diese Werte wurden jedoch geändert falls neue Informationen oder Daten zum Sorptionsverhalten der Radionuklide vorhanden waren, die entsprechende Änderungen oder Neubeurteilungen ermöglichten. Die in diesem Bericht vorgeschlagenen Sorptionswerte stammen entweder aus eigenen experimentellen Studien oder wurden aus Literaturdaten ausgewählt.

Für einige Elemente, wie Cs(I), Sr(II), Ni(II), Eu(III), Th(IV) und Sn(IV), waren neue Sorptionsdaten aus eigenen experimentellen Untersuchungen vorhanden. Diese Elemente waren wegen ihrer Bedeutung für den Entsorgungsnachweis und als chemische Homologe ausgewählt worden.

Produkte aus dem Abbau von Zellulose und Bitumen, sowie Betonzusatzmittel und zementartige Nahfeldkolloide wurden als mögliche Störfaktoren berücksichtigt. Diese können die Radionuklidsorption in einem Nahfeld reduzieren. Mögliche Einflüsse der Störfaktoren auf die Radionuklidmobilität wurden auf der Basis von Sorptionsreduktionsfaktoren berücksichtigt und quantifiziert.

RÉSUMÉ

Ce rapport décrit une base de données de sorption (sorption data base ou SDB) pour le ciment, prenant en compte les radionucléides importants pour la sûreté d'un dépôt géologique en profondeur destiné aux déchets de moyenne activité à vie longue (DMAL), tel qu'il est prévu en Suisse. Ce rapport met à jour les bases de données compilées précédemment par BRADBURY & SAROTT (1995) et BRADBURY & VAN LOON (1998) dans la perspective d'un dépôt géologique en profondeur pour déchets de faible et de moyenne activité (DFMA).

La liste des radionucléides a été dressée sur la base des inventaires des déchets qu'il est prévu de stocker dans le dépôt. Les compositions chimiques respectives des eaux interstitielles dans le champ proche des dépôts pour DFMA et DMAL ont été calculées à partir de codes couramment utilisés pour la modélisation de la dégradation du ciment, puis comparées entre elles pour mettre en lumière d'éventuelles différences au niveau des conditions régnant dans le champ proche, et pour estimer l'impact de ces différences sur la sorption des radionucléides. Les coefficients de sorption pour les radionucléides sont issus des SDB compilées pour le champ proche d'un dépôt de DFMA. Ces chiffres ont été modifiés lorsque de nouvelles informations autorisaient un changement ou une réévaluation des données. Les coefficients de sorption recommandés dans ce rapport ont été sélectionnés soit parmi les données obtenues lors d'expériences dans notre laboratoire, soit dans les publications.

Pour certains radioéléments, notamment Cs(I), Sr(II), Ni(II), Eu(III), Th(IV) et Sn(IV), des expériences réalisées dans notre laboratoire ont fourni de nouvelles mesures. Ces éléments ont été sélectionnés en raison de leur importance pour les analyses de la sûreté et en tant qu'homologues chimiques.

Les substances résultant de la dégradation du bitume et de la cellulose, les adjuvants pour le béton, de même que les colloïdes du champ proche provenant du ciment, ont été identifiés comme les principaux éléments susceptibles de réduire la sorption des radionucléides dans le champ proche. Les facteurs de réduction de la sorption correspondant à l'impact potentiel de ces substances sur la mobilité des radionucléides ont été estimés.

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1 INTRODUCTION

The use of cementitious materials is foreseen in the planned Swiss repository for long-lived intermediate-level radioactive wastes (ILW) in the Opalinus clay (OPA) host rock of Northern Switzerland. Cement is used to condition the waste materials and to construct the engineered barrier systems (container, backfill and liner materials). In safety assessment (PA) studies, sorption values for the safety-relevant radionuclides are key input data. Sorption has a strong influence on the retardation of radionuclides in the waste matrix and, consequently, determines the mobile portion in the near field. This report documents the procedures whereby sorption values for the cementitious ILW near field have been chosen, taking into account the present design of the ILW repository.

The current report should be read in conjunction with earlier cement sorption databases (SDBs) compiled for the cementitious near field of the planned repository for low- and intermediate-level radioactive wastes (L/ILW). These reports will be referred to as CEM-94 (BRADBURY & SAROTT 1995) and CEM-97 (BRADBURY & VAN LOON 1998). Thus, the current ILW SDB is viewed as being an update on the previous ones with emphasis on application to the ILW repository. In the compilation of the ILW SDB, we followed the procedures outlined and recommended in CEM-94 and CEM-97 to ensure continuity in the methodology and transparency concerning the selection of sorption values. Additional aspects have only been addressed if they were new or were required for clarity. Thus, in line with the previous cement SDBs, the selection procedure was based on the following considerations:

- 1) A list of the safety-relevant radionuclides was drawn up using the present information on ILW inventories (NAGRA 2002b).
- 2) The composition of the cement porewaters for the L/ILW and ILW near fields predicted on the basis of well-established models (BERNER 1990; NEALL 1994) were compared to identify similarities and differences of the chemical conditions of the cementitious ILW and L/ILW near fields.
- 3) Sorption data for the safety-relevant radionuclides in the planned ILW repository were compiled in conjunction with the L/ILW SDB for the first two stages of the cement degradation. The sorption values of the radioelements previously compiled in the L/ILW SDB were revised if new information and/or data were available that allowed well-justified changes to or re-appraisals of the data to be made. Otherwise, the sorption values were taken as given in the L/ILW SDB.

- 4) New data were available from in-house studies on Cs(I), Sr(II), Ni(II), Eu(III), Th(IV) and Sn(IV) uptake by cement. Sorption values were recommended based on chemical analogy, where experimental data were lacking.
- 5) The selection process was carried out in a manner to assign realistic sorption values to the safety-relevant radionuclides using the pool of experimental information available from in-house measurements and the open literature. Thus, the development of this SDB aimed at selecting realistic and defensible sorption values rather than choosing the lowest published value. Uncertainty ranges were assigned to the selected sorption values taking into account uncertainties on the experimental data.
- 6) Degradation products of bitumen and cellulose, concrete admixtures and cement-derived near-field colloids were considered to be the main sources affecting radionuclide sorption. Their effect was quantified in terms of sorption reduction factors. Radionuclide uptake onto aggregate materials or corrosion products has not been taken into account for this report. A first appraisal of their potential contribution is given in CEM-97.

In CEM-94 it was outlined that the usefulness of sorption data in view of developing a SDB critically depends on the availability of complete sets of experimental data, including measurements of isotherms, studies on the dependence of sorption values on the solid to liquid ratio, and on how well the experimental conditions are defined. Single-point measurements in which sorption has been determined for one set of conditions and at one concentration are viewed as being considerably less useful than sorption data deduced from measurements carried out under different experimental conditions (CEM-94). Note that, at the present time, the vast majority of sorption values still results from single point measurements. Information on uptake mechanisms in cement systems, however, is lacking to a large extent. As previously noted in CEM-94, the only chance of being able to justify fully the selection of a sorption value for a SDB is when the underlying uptake mechanism and the uptake-controlling phase are known, and the process can be expressed in terms of a thermodynamically-based model. For this purpose, macroscopic studies on cement systems have to be complemented by advanced spectroscopic and microscopic techniques to discern uptake processes on a molecular level. With this information at hand, one may be able to deduce a fully justified SDB in the future. For the time being, however, we had to rely on expert judgement with a view to selecting realistic and defensible sorption values for the SDB.

2 ILW REPOSITORY

2.1 Cementitious materials

The present design of the ILW repository in Opalinus Clay (OPA) foresees tunnels with a total length of about 200 m for waste emplacement (NAGRA 2002a). The waste types to be disposed of in this repository consist of intermediate-level waste streams originating from reprocessing, which are incorporated mostly in a cementitious matrix with smaller amounts incorporated in bitumen. Waste packages will be placed in containers made of a concrete cage structure, and voids between packages, containers and within the cavern are to be backfilled with mortar. Thus, waste packages, backfill and construction materials constitute the main components of the near field of an ILW repository.

Cement will be used to condition the waste materials and to construct the engineered barrier system. The retardation of safety-relevant radionuclides by cement is taken into account in PA studies because the source term for radionuclide migration into the host rock is determined by a combination of solubility and sorption constraints in the cementitious near field. Thus, the uptake of radionuclides by hardened cement paste (HCP) plays a decisive role in limiting and retarding the release from the near field. Uptake is expressed in terms of a sorption value or distribution ratio, respectively, and the values compiled in this report are given in units of m^3 per kg HCP^1 . It is to be noted that the cements used for conditioning and construction may have different chemical compositions. Nevertheless, due to the very limited information published on uptake mechanisms in cement systems for the safety-relevant radionuclides, namely the nature of the uptake-controlling processes and the cement phases involved, no connection can presently be made between differences in cement compositions and their effects on the sorption behaviour of radionuclides. Therefore, differences in sorption between various types of cements and concrete have to be ignored in this study in line with the previous SDBs.

Estimates of the total mass of HCP in the near field and the porosity of the near field are required to assess the effect of the cellulose degradation products on radionuclide sorption. The porosity of the near field is estimated to be 30 %. The overall density is assumed to be 2 kg dm^{-3} . BERNER (1999) estimates the total amount of hydrated cement for the basic concept of the ILW design to be 30 weight (wt) %. This value is adopted for the present design of the ILW repository.

¹ Note that information on the mass of HCP per m^3 repository volume is required to calculate the retention factor of radionuclides under near-field conditions.

2.2 Nuclide inventories

The safety-relevant radionuclides present in the various types of ILW wastes include actinides and their daughters with half-lives that are significant in view of the safety case as well as fission products. The latter have been selected according to their quantities in the waste types and their biotoxicity (NAGRA 2002b).

The radioelements considered in PA studies for the ILW repository are listed in Table 1 according to their chemical properties. This list has been established based on an analysis of the waste streams, which is given elsewhere (NAGRA 2002b). Most of the radionuclides were previously classified as being safety-relevant for a L/ILW repository in CEM-94 and CEM-97. Some radionuclides specifically appear in the ILW inventory, such as Eu and Sm, due to differences in the compositions of the L/ILW and ILW streams.

TABLE 1: Safety-relevant radioelements in an ILW repository^{1,2} (NAGRA 2002b).

Group I and II elements	H(HTO), Cs, Sr, Ra
Transition elements (first and second series)	Co, Ni, Zr, Nb, Mo, Tc
Group IV, V, VI and VII elements	C, Sn, Pb, Se, Po, Cl, I
Lanthanides and actinides	Sm, Eu, Ac, Th, Pa, U, Np, Pu, Am, Cm

¹ Some radioelements, i.e., Na, K, Mn, Ho, included in CEM-94 and CEM-97 are not discussed in this study due to minor relevance to the ILW streams.

² The list of radioelements discussed in this report is larger than the list of safety-relevant radioelements considered in the safety assessment calculations for the following reason: The simple screening analysis for the derivation of the list of safety-relevant nuclides described in Appendix 5 of Nagra (2002b) was modified at a later stage in Project Opalinus Clay (Entsorgungsnachweis); i.e. after the bulk of the work described in this report had been undertaken. Therefore, in addition to the elements given in this table, the sorption behaviour of Be, Ca, Fe, Ru, Sb, Pd, Ag and Pm has been assessed in the context of this study.

The sorption behaviour of a radioelement is influenced by the oxidation state of the dominant aqueous species. In this study, sorption values are given for reduced and oxidised species of a radioelement to account for possible variations of the redox potential in the cementitious near field. Note that, after repository closure, reducing conditions are expected to predominate due to the presence of large quantities of steel in the near field (CEM-94).

The expected valence states of the ILW-specific radioelements are listed in Table 2. Note that the oxidation states of all other redox-sensitive radioelements, above all the actinides, are given in CEM-94.

TABLE 2: Oxidation states of the redox-sensitive ILW-specific radioelements under alkaline conditions.

Element	Oxidising conditions	Reducing conditions
Fe	+III	+II
Ru	+VI	+III
Sb	+V	+III

2.3 Model prediction of the composition of the porewater in the ILW repository

Cement undergoes chemical degradation in contact with infiltrating groundwater. In general, three stages of the cement degradation are distinguished (e.g., ATKINSON et al. 1988; BERNER 1992): The cement porewater (CPW)² composition is dominated by the release of alkali hydroxides (NaOH and KOH) in the first stage of cement degradation (stage I), which results in a pH of about 13.3. In stage II, the chemical composition of the alkali-depleted CPW is controlled by the solubility of portlandite, which fixes $[\text{Ca}]_{\text{tot}}$ at $\sim 2 \cdot 10^{-2}$ M and the pH at ~ 12.5 . In stage III, the buffer capacity of portlandite is exhausted, and pH drops continuously to lower pH values. In this stage the incongruent dissolution of calcium silicate hydrates (CSH) and other cement phases determines the pH buffering capacity.

Models of cement degradation have been developed and used to predict the evolution of the cement material and CPW compositions in the near field of the planned Swiss L/ILW repository (BERNER 1990; BERNER 1992; NEALL 1994; PFINGSTEN & SHIOTSUKI 1998). NEALL (1994) used a mixing tank model to estimate the CPW composition of the L/ILW near field in contact with infiltrating groundwater of different compositions, i.e., a NaHCO_3 -type and a NaCl -type groundwater. The model developed by this author uses the cement degradation model as proposed by BERNER (1990). The study of NEALL (1994) shows that the cementitious near field of the L/ILW repository will be in the stage I of cement degradation typically for a few thousand years and in the stage II typically for more than one hundred thousand years, based on the boundary conditions (e.g., hydraulic conductivity, pressure gradients) and features (e.g., cement composition, porosity) expected for the L/ILW near field (NAGRA 1994). It is anticipated that the timescales are even longer in OPA as diffusion is the dominant transport process in this host rock (NAGRA 2002b).

² Cement porewater (CPW) is taken as a general expression for porewater in contact with the cement matrix, whereas artificial cement porewater (ACW) denotes a cement porewater synthesized from chemicals and used for laboratory experiments.

PFINGSTEN (2001) published a study of the 2-D modelling of a porous cement block in contact with a NaHCO_3 -type groundwater. The results indicate that cement dissolution causes calcite precipitation at the rock-cement interface. Depending on the assumed boundary conditions and the background flow field, changes in the overall porosity and the hydraulic conductivity in the cement block, caused by a reduction of the local porosity, are expected. Self-sealing of the near field is expected to be effective over very long time periods due to the large capacity of the high-pH buffer, i.e., portlandite in the cement matrix. Since a reduction in radionuclide migration from the near field into the far field is induced, this self-sealing effect is beneficial for the safety of a repository.

The modelling approach given in NEALL (1994) was adopted for the prediction of the CPW composition of the ILW near field by SCHWYN et al. (2003). These authors based their calculations of the ILW near-field chemistry on the following assumptions:

Solid phase: Average Swiss Portland cement composition including Na/K hydroxides, calcium silicate hydrates (CSH), portlandite, hydrogarnet, ettringite and brucite.

Initial water composition: The input water for stage I is “distilled” water in equilibrium with calcite and fluorite to fix the equilibrium concentrations of carbonate and fluoride. Modelling of the composition of CPW in stage II is based on sequential replacements of the pore volume of HCP with the OPA groundwater. The composition of the OPA input water is given in WABER et al. (1998).

SCHWYN et al. (2003) calculated the chemical equilibria using MINEQL/DISSOLVE with the Nagra/PSI chemical thermodynamic data base (HUMMEL et al. 2002). The CPW compositions of the ILW near field given in Table 3 are results from these calculations. The CPW compositions of the L/ILW near field previously published in NEALL (1994) are listed in Table 4 to allow comparisons with the predicted ILW porewaters to be made.

2.4 Comparison of the composition of the porewaters in the L/ILW and ILW repositories

In stage I of cement degradation, the pH is determined by the Na/K hydroxides, which are contributed from the cement matrix. Tables 3 and 4 show that L/ILW and ILW CPWs have similar alkali concentrations and, consequently, pH values (pH = 13.44 and 13.51 for the L/ILW CPW and pH = 13.44 for the ILW CPW). Alkali hydroxides are assumed to have been washed out of the matrix in the stage II of the degradation

process. In this stage, Na^+ and K^+ concentrations correspond to the alkali inputs from the groundwaters. The model predicts similar pH values for stage II, i.e., pH ranging between 12.50 and 12.56 for the L/ILW CPW and 12.55 for the ILW CPW, due to a control by portlandite solubility. Thus, the model calculations lead to consistent pH values for both stages of the cement degradation. The small differences in pH are disregarded for radionuclide speciation and, consequently, for sorption.

Differences in the concentrations of CO_3^{2-} (CO_3 in Tables 3 and 4) for the corresponding L/ILW and ILW CPWs are within a factor of about two. Differences are caused by small changes in calcite solubility with pH and Ca concentration. The concentration of F^- (F in Tables 3 and 4) is controlled by fluorite solubility (CaF_2) in the model. CaF_2 was not included in the previous calculations of the L/ILW CPW (NEALL 1994). However, because CaF_2 solubility is expected to be the controlling process in both near fields, and moreover, Ca concentrations are similar for the L/ILW and ILW CPWs, no significant differences in F^- concentrations are anticipated. For the stage II of cement degradation, SCHWYN et al. (2003) report about an order of magnitude higher SO_4^{2-} concentrations in the ILW CPW compared to the L/ILW CPW (SO_4 in Tables 3 and 4). According to these authors, the higher value accounts for differences between model calculations and experimental data. However, the stability of SO_4^{2-} complexes was found to be too weak to exert any significant effect on radionuclide speciation at the given concentration levels of SO_4^{2-} . On the basis of the above we can ignore possible effects on uptake processes caused by differences in the CO_3^{2-} , SO_4^{2-} and F^- concentrations of the L/ILW and ILW CPWs in this study.

NEALL (1994) does not report Cl^- concentrations (Cl in Tables 3 and 4) for the L/ILW CPWs. Nevertheless, the Cl^- concentrations can be estimated from the input groundwaters, i.e., $[\text{Cl}^-] \sim 3 \cdot 10^{-4}$ M for the NaHCO_3 -type groundwater and $[\text{Cl}^-] \sim 0.47$ M for the NaCl -type groundwater (Table 3). Note, however, that Cl^- concentrations deduced in this manner are maximum values. The interaction of infiltrating Cl^- with the cement matrix and the formation of Cl-bearing cement phases (GUNKEL 1992), e.g., Friedel's salt ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$), may further reduce the Cl^- concentration. Thus, the high Cl^- concentrations are only justified on the assumption that the capacity of HCP to bind Cl^- in the form of Friedel's salt is limited. Despite the high Cl^- concentrations reported by SCHWYN et al. (2003), the stability of Cl^- complexes of the relevant radioelements were found to be too weak to exert any significant effect on radionuclide speciation at $\text{pH} > 12.5$ except for Ag and Pd (BERNER 2002).

The model calculations reported by NEALL (1994) and SCHWYN et al. (2003) reveal differences in the Al and Si concentrations (Al and H_2SiO_4 in Tables 3 and 4) for the stage I CPWs as well as differences in the Na, K, and Al concentrations for the stage II CPWs. Differences in alkali concentrations can be attributed to differences of the respective input groundwaters. In the case of Al and Si, however, SCHWYN et al. (2003) selected the lower concentration for the ILW CPWs based on experimental evidence. Irrespective of this choice, the effect of Al and $\text{H}_2\text{SiO}_4^{2-}$ on the radionuclide uptake by HCP can be ignored.

On the basis of the above it is concluded that the chemical conditions prevailing in the L/ILW and ILW near fields may be similar for the same type of groundwater. Nevertheless, the development a SDB using the available data pool is based on few assumptions: The effect of CO_3^{2-} , SO_4^{2-} , F⁻, Cl⁻ and $\text{H}_2\text{SiO}_4^{2-}$ on the speciation of metal cations is considered to be negligible as OH⁻ is the dominant complexant. Differences in ionic strength caused by differences in the Na and K concentrations and possible consequences for uptake process are ignored. Note, however, that the lower K concentration and, by contrast, higher Ca concentration in the stage II compared to the stage I of cement degradation will be taken into account when assigning sorption values to Cs⁺ and Sr²⁺. These considerations are important due to the well-established competitions between K⁺ - Cs⁺ and Ca²⁺ - Sr²⁺, respectively, in cement systems. Finally, differences in the chemical compositions of cements are ignored because they are expected to exert no significant effect on the CPW compositions (BERNER 1990).

Since variations in two of the main parameters, that is pH and the concentrations of inorganic ligands, are small for the L/ILW and ILW CPWs, no significant effect on radionuclide speciation and uptake processes is anticipated. The sorption values selected in CEM-94 and CEM-97 for a L/ILW repository are considered to be applicable to an ILW repository, and thus, were taken unless new information and/or experimental data for a specific radioelement were available.

In the next section, in-house uptake studies for selected radionuclides will be reported. These experiments were conducted under conditions corresponding to the stage I of cement degradation. Thus, the artificial cement porewater (ACW) employed in the studies had the following chemical composition: pH = 13.3, $[\text{Na}]_{\text{tot}} = 0.114 \text{ M}$, $[\text{K}]_{\text{tot}} = 0.182 \text{ M}$, $[\text{Ca}]_{\text{tot}} = 1.6 \cdot 10^{-3} \text{ M}$, $[\text{Si}]_{\text{tot}} = 4 \cdot 10^{-5} \text{ M}$, $[\text{Al}]_{\text{tot}} = 5 \cdot 10^{-5} \text{ M}$, $[\text{S}]_{\text{tot}} = 3 \cdot 10^{-3} \text{ M}$, $[\text{CO}_3]_{\text{tot}} = 1.2 \cdot 10^{-4} \text{ M}$. This composition has been chosen based on the calculations reported by BERNER (1990). Note that the composition of ACW is similar to the CPW composition predicted for the initial phase of the ILW repository.

TABLE 3: Predicted composition of CPW in the stage I and II of cement degradation for different input groundwaters (SCHWYN et al. 2003). Repository in the OPA host rock.

Component	Stage I	Stage II
	Early porewater [mmol L ⁻¹]	OPA [mmol L ⁻¹]
Na	101	169
K	303	5.7
Ca	0.84	20.1
Mg	<10 ⁻⁴	10 ⁻⁴
Al	0.01	0.005
CO ₃	0.20	0.01
SO ₄	0.75	0.10
Cl	-	160
F	0.76	0.10
H ₂ SiO ₄	0.05	0.016
pH	13.44	12.55

TABLE 4: Predicted composition of CPW in the stage I and II (after about 70 exchange cycles) of cement degradation for a repository in marl (NEALL 1994).

Component	Stage I		Stage II	
	NaHCO ₃ water [mmol L ⁻¹]	NaCl water [mmol L ⁻¹]	NaHCO ₃ water [mmol L ⁻¹]	NaCl water [mmol L ⁻¹]
Na	143	587	17.5	461
K	370	375	0.05	0.71
Ca	0.82	1.01	16.3	35.1
Mg	< 10 ⁻⁴	< 10 ⁻⁴	< 10 ⁻⁴	10 ⁻⁴
Al	1.34	1.14	0.13	0.13
CO ₃	0.33	0.50	0.007	0.012
SO ₄	1.27	1.16	0.008	0.013
Cl	-	-	-	-
F	-	-	-	-
H ₂ SiO ₄	0.77	0.39	0.017	0.014
pH	13.51	13.44	12.56	12.50

3 SELECTED SORPTION DATA FOR UNPERTURBED CEMENT

3.1 Uptake processes on cement

The immobilization potential of cement originates from its selective binding properties for radioelements. Cation and anion binding by cementitious materials can be classified into particular uptake mechanisms (e.g., COCKE & MOLLAH 1993; GOUGAR et al. 1996): 1) precipitation or surface precipitation, i.e., the formation of a solid phase of pure or mixed composition without forming a solid solution, 2) solid-solution formation and co-precipitation, i.e., incorporation of foreign ions in the structure of a solid phase by precipitation with or diffusion into an existing solid phase, and 3) specific and non-adsorption, i.e., the formation of covalent bonds between the sorbing species and the solid surface (inner-sphere surface complexation) or replacement of one adsorbed, readily exchangeable ion by another (ion exchange, outer-sphere complexation). According to the same authors, calcium aluminates (AFm- and AFt-type phases) and calcium silicate hydrates (CSH phases) are prime candidates for cation and anion binding in the cement matrix because of their abundance and appropriate structures. Note that often the mechanisms cannot be absolutely delimited from each other, and the categories represent limiting cases of sorption. The state of knowledge of the different type of uptake processes on a microscopic level and the thermodynamic description of the processes is not well advanced to date. In addition, little is known about the kinetics and reversibility of these processes.

In general, radionuclide uptake by HCP is described in terms of a distribution ratio, R_d :

$$R_d = \frac{\text{Quantity of a radionuclide sorbed per unit mass cement}}{\text{Equilibrium concentration of the radionuclide in CPW}} \quad [\text{m}^3 \text{kg}^{-1}] \quad (1)$$

In a broader sense, the distribution ratio (in this study also denoted as “sorption value”) accounts for the partitioning of a radionuclide between the mobile and immobile phase. Note that a sorption value does not include mechanistic information, e.g., speciation of the sorbing and dissolved cations and anions or the binding mechanism involved.

The pool of sorption data reported in this study was obtained primarily from batch-type sorption experiments. It is to be noted that sorption values can also be deduced from dynamic tests, e.g., column and through-diffusion experiments. In general, it is assumed that the R_d value is constant irrespective of the solid content of the experimental system, i.e., the solid to liquid (S/L) ratio. That kind of characteristic behaviour is consistent

with a sorption-type uptake mechanism at low surface coverage, such as linear sorption or the formation of solid solutions. Nevertheless, systematic investigations of the dependence of sorption values on the S/L ratio of cement systems are largely lacking to date. In those studies where solid concentration effects have been addressed (e.g., PILKINGTON & STONE 1990), solid contents vary over one order of magnitude at maximum, which provides no conclusive information on the S/L dependence and, therefore, the mode of ion uptake by HCP. For this reason, the potential effect of the S/L ratio on R_d values has specifically been addressed in this study (see discussion in the following section).

An important feature of cementitious systems is the presence of trace element impurities, which are inherently associated with the cement matrix. Cement is manufactured by blending a calcareous material, typically limestone, with an argillaceous one, typically clay or shale. Both constituents contain impurity elements at trace levels. In the large body of existing sorption studies conducted on cementitious systems, the solution compositions are given, if at all, only in terms of the main parameters and components, e.g., pH and the concentrations of cement-derived elements such as Na, K, Ca, Al, Mg, Si and S. Information on the inventory of trace elements in solution is almost always lacking. It is worth noticing that the concentrations of stable isotopes may be significant in CPW and exceed the concentrations of radioisotopes added to CPW for uptake studies by orders of magnitudes. Thus, lack of information on trace element inventories gives rise to uncertainties concerning the nature of the uptake processes at trace levels. For example, the partitioning of a radioisotope occurs via isotopic exchange, irrespective of the chemical process involved, if the stable isotope concentration of a radioelement (e.g., Ni) is higher than the inventory of the radioisotope used to determine the sorption value (e.g., ^{63}Ni). Moreover, stable isotope concentrations are relevant in connection with solubility limits, which may be fixed according to the total concentration of an element (stable and unstable isotopes) rather than the concentration of the radioisotope alone.

In the following, sorption values will be deduced for the two main stages of an evolving cementitious near field, i.e., the stage I and II of cement degradation. The study by NEALL (1994) indicates that the cementitious near field of the L/ILW repository will be in the stage I of cement degradation for a few thousand years and, for very much longer time, in the stage II. The time spans may be even longer for an ILW repository as a consequence of the favourable boundary conditions in the OPA (NAGRA 2002b).

Owing to the long lifetime of the high pH conditions ($\text{pH} > 11$), the third stage of the cement degradation is considered to be of minor relevance to an ILW repository in OPA.

3.2 In-house sorption measurements

Over the past years, in-house investigations on the uptake of Cs(I), Sr(II), Ni(II), Eu(III), Sn(IV) and Th(IV) by a sulfate-resisting Portland cement (Haute Teneur en Silice (HTS) cement) have been carried out under conditions relevant to the near field of a repository for nuclear waste (e.g., SAROTT 1996; WIELAND et al. 1997; 1998; 2000; 2002). HTS cement has been used now for many years to solidify and stabilise low- and intermediate-level waste in Switzerland. Cs(I), Sr(II), Ni(II), Eu(III), Sn(IV) and Th(IV) were selected as representatives for important groups of elements, i.e., Cs(I) and Sr(II) for the alkali and earth-alkali metals including Ra, respectively, Ni(II) for the bivalent transition metals, Eu(III) for the trivalent lanthanides and actinides, and Th(IV) for the tetravalent actinides. Sn(IV) is a representative for the strongly hydrolysing tetravalent metal cations. In addition to uptake studies on HTS cement, studies on the interaction of some of the above-mentioned elements with CSH phases have been conducted over the past years (TITS et al. 1998; 2000). Moreover, complementary information on the uptake of Cs(I), Ni(II), Cl(-I) and I(-I) by HTS cement is available from through-diffusion experiments (SAROTT et al. 1992; JAKOB et al. 1999; JAKOB 2002; TITS et al. 2003a). Due to the large body of in-house data available and the well-defined conditions under which the experiments have been conducted, it was decided to use the sorption values of the afore-mentioned radioelements as guideline data for the present study. Thus, uptake of these radioelements by HTS cement will be discussed in more detail prior to selecting sorption values for other safety-relevant radionuclides.

3.2.1 Materials and methods

Uptake studies on HTS cement were conducted as previously described in WIELAND et al. (1998; 2000; 2002). For this, a HCP material was manufactured from HTS cement as described by SAROTT et al. (1992). It is to be noted that this material was prepared using a high water to cement ratio (w/c) of 1.3. Uptake studies were carried out on crushed material, which was prepared from bulk samples by grinding in a mortar under CO_2 free conditions and subsequently sieving the material to collect the size fraction $\leq 70 \mu\text{m}$. The N_2 -BET surface area of the powder material was determined to be $46 \pm 4 \text{ m}^2 \text{ g}^{-1}$. Appropriate amounts of crushed HCP material were added to ACW in 40 mL polyallomere centrifuge tubes according to the S/L ratio of the samples. ACW has the chemical composition of a porewater in equilibrium with HCP in the stage I of

cement degradation (see Section 2.4). Prior to the uptake studies, stability tests for HCP immersed in ACW were conducted to assess equilibrium conditions with respect to the main cement-derived elements, i.e., Na, K, Ca, Al, Si and S³. The partitioning of a radioelement between HCP and ACW was then determined by adding small aliquots of standard tracer solution to the suspensions to give a total volume of 40 mL. Standard solutions of the following radioisotopes were used for studies of tracer partitioning: ¹³⁴Cs, ⁸⁵Sr, ⁶³Ni, ¹⁵²Eu, ^{228/234}Th and ¹¹³Sn. The standard solutions were commercially available except carrier-free ²³⁴Th, which was prepared using the ion exchange method described in DYRSSEN (1950). Radiotracers were added at concentrations well below the solubility with respect to potentially solubility-limiting phases under the given conditions. Initial concentrations ranged from about 10⁻¹⁰ M, e.g., for the Eu and Th experiments, to about 10⁻⁸ M, e.g., for the Sn experiments. The suspensions were equilibrated end-over-end for appropriate time periods. For each radioelement, the time period was selected based on the results from kinetic measurements. The time required to reach equilibrium typically ranged from 7 to 30 days. After equilibration, the solid and liquid phases were separated by centrifugation (95000 g for 60 min). Aliquots were withdrawn from the supernatant solution for activity measurements. In the case of Eu, Th and Sn, the total activities of the suspensions were determined prior to centrifugation to account for wall sorption on the centrifuge tubes. Note that all preparation and equilibration steps were carried out in a glove box under a N₂ atmosphere (O₂ and CO₂ < 5 ppm). Radionuclide assays were performed using a Packard Cobra 5003 auto gamma counter for ⁸⁵Sr, ¹⁵²Eu, ²²⁸Th and ¹¹³Sn, and a Canberra Packard Tri-carb 2250 CA liquid scintillation analyser for ¹³⁴Cs, ⁶³Ni and ²³⁴Th.

³ For this, powdered HCP material was mixed with ACW, which had the composition of a porewater in equilibrium with HCP with respect to the main cement-derived cations at pH 13.3, i.e., Na, K, Ca. Such a system, however, involves an initial disequilibrium between HCP and ACW with respect to the minor elements, e.g., Al, S and Si. It was observed that, after contacting HCP with ACW, these elements were immediately released into the porewater to establish equilibrium porewater conditions. For all elements except Ni it was found that the distribution ratios agree within the uncertainties of the data irrespective of the initial porewater conditions, that is, whether or not equilibrium conditions were established when starting the uptake experiments. For this reason, we report R_d values for both initial set-ups in the case of Ni, e.g. in Fig. 1 c. For the other elements, however, only R_d values obtained under equilibrium conditions are shown.

3.2.2 Results

3.2.2.1 Cesium

Cs sorption on HCP is expected to be weak for both stages of the cement degradation (CEM-94 and references therein). The high concentrations of (Na,K)OH appear to exhibit a strong competitive effect on Cs uptake by HCP in the stage I of cement degradation. Note that sorption values were found to be significantly higher on concretes, which contained large amounts of sandy aggregate material (HIETANEN et al. 1984). Fig. 1a shows that, under the conditions of a stage I CPW, batch R_d values range in value between $2 \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $4 \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ on HCP (TITS 2002). The values are slightly lower than those previously reported by ALLARD et al. (1984) ($R_d \sim 10^{-3} \text{ m}^3 \text{ kg}^{-1}$). Note, however, that TITS et al. (1998) report higher sorption values for Cs uptake by CSH phases in ACW at pH = 13.3 ($2 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ and $4 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$). Finally, through-diffusion studies indicate R_d values ranging between $\sim 8 \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $\sim 3 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ (SAROTT et al. 1992; JAKOB et al. 1999) (Fig. 1a).

No in-house measurements currently exist for conditions of a stage II CPW. However, it is expected that the competitive effect of Na and K is diminished in stage II due to the lower concentrations of (Na/K)OH. This explains the higher R_d values reported for Cs under these conditions (CEM-94). Sorption values ranging between $\sim 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ and $\sim 0.2 \text{ m}^3 \text{ kg}^{-1}$ have been reported for concrete and HCP samples depending on the type of ballast material used and the K and Na concentrations of the solutions in contact with the cement materials (e.g., CEM-94 and references therein; IDEMITSU et al. 1991; JOHNSTON & WILMOT 1992; SHIMOOKA et al. 1989). Low sorption values result at high Na and K concentrations (mmolar range) as shown by Johnston and co-worker. Finally, HOLLAND & LEE (1992) determined the R_d value for Cs uptake by a sulfate-resistant Portland cement to be $0.017 \text{ m}^3 \text{ kg}^{-1}$ under the conditions relevant to the stage II of cement degradation.

The sorption values obtained from in-house studies are lower than those recommended in CEM-97 for the stage I of cement degradation. Note that the values given in CEM-94 and CEM-97 were selected based on a literature survey. In view of the new information available, R_d values are reduced to $5 \cdot 10^{-4} \text{ m}^3 \text{ kg}^{-1}$ for the stage I and $5 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ for the stage II, respectively, of cement degradation. These sorption values are selected based on the results from experimental in-house batch and diffusion studies on HCP. Note that a difference in the distribution ratio by one order of magnitude between the stage I and II is justified taking into account the reduced competitive effect of K in the stage II.

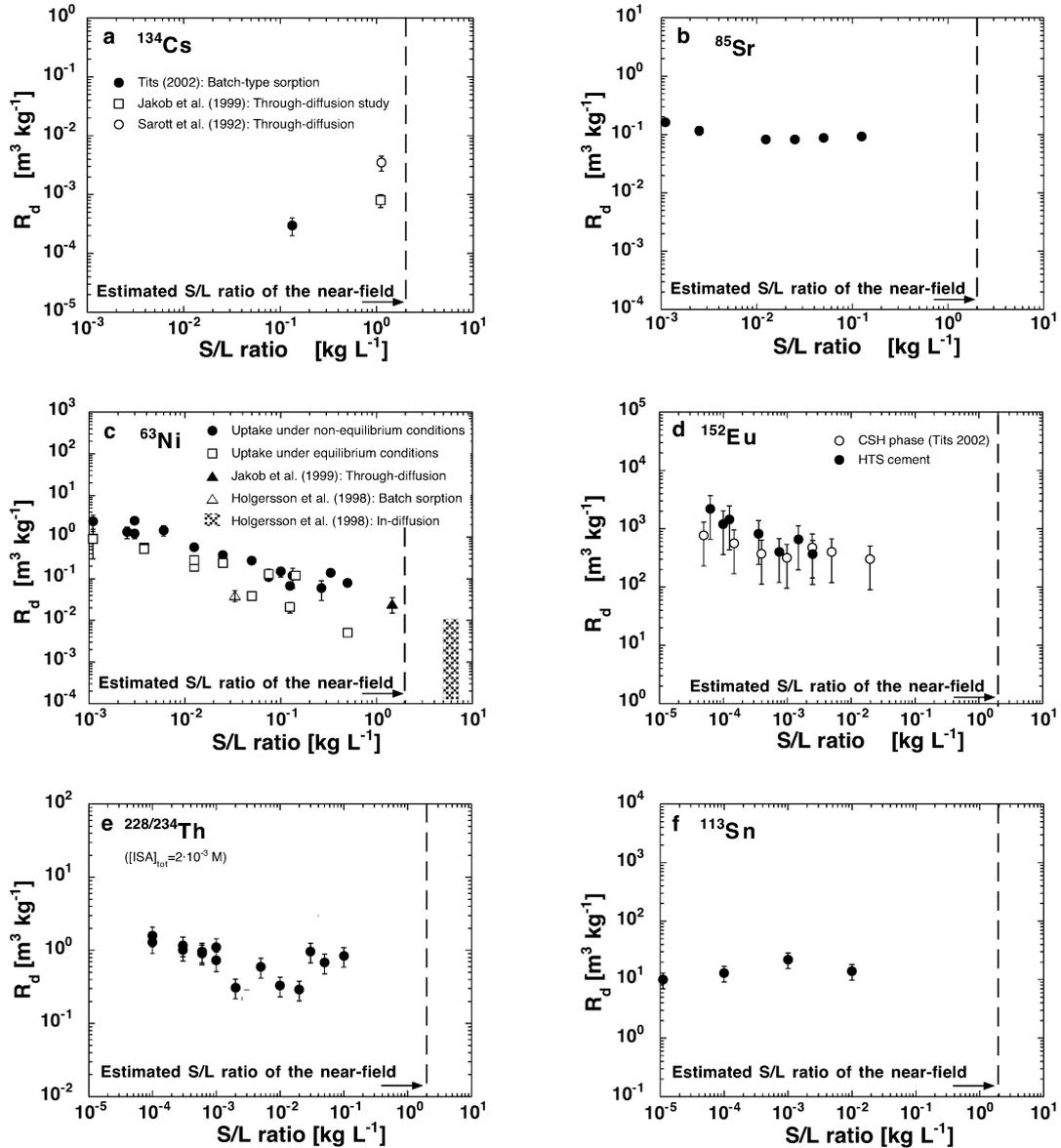


FIGURE 1: Dependence of the R_d values determined for a) ^{134}Cs , b) ^{85}Sr , c) ^{63}Ni , d) ^{152}Eu , e) $^{228/234}\text{Th}$ and f) ^{113}Sn on the S/L ratio. All experiments were carried out using HCP in contact with ACW at pH = 13.3 (stage I of cement degradation). In the case of Eu, sorption data on CSH phases are shown by way of comparison. The initial concentrations range from about 10^{-10} M to about 10^{-8} M depending on the radionuclide used. Equilibration times are as follows: 15 days for Cs, 30 days for Sr and Ni, 7 days for Eu, Th and Sn. The S/L ratio of the ILW near field is estimated to be $\sim 2 \text{ kg L}^{-1}$ (see section 2.1).

3.2.2.2 Strontium

In CEM-94 and CEM-97 an R_d value of $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was assigned to Sr in the stage I of cement degradation. Note that this value was selected based on experimental studies carried out under conditions corresponding to the stage II of cement degradation, i.e., pH ~12.5 instead of pH = 13.3 $[\text{Ca}]_{\text{tot}} \sim 20 \text{ mM}$ instead of $\sim 2 \text{ mM}$. Thus, taking into account an adverse effect of Ca on Sr uptake as indicated from studies on CSH phases (TITS et al. 1998), the realistic sorption value is expected to be greater than the conservative value given in the previous SDBs. Indeed, an R_d value of $0.1 \text{ m}^3 \text{ kg}^{-1}$ was obtained from in-house measurements under conditions corresponding to the stage I of cement degradation (pH = 13.3, $[\text{Ca}]_{\text{tot}} \sim 2 \text{ mM}$) (WIELAND et al. 2000). Moreover, the R_d value was found to be constant for S/L ratios ranging between $10^{-3} \text{ kg L}^{-1}$ and 0.1 kg L^{-1} (Fig. 1b).

EWART et al. (1985), HIETANEN et al. (1984) and SHIMOOKA et al. (1989) investigated Sr sorption under conditions relevant to the stage II of cement degradation. R_d values were found to range in value between $1 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ and $4 \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$. Similar sorption values stem from diffusion studies on concrete materials (IDEMITSU et al. 1991). A study recently published by SUGIYAMA & FUJITA (1999) indicates sorption values ranging between $\sim 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ and $\sim 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ under conditions corresponding to a stage III CPW (pH < 12).

The difference in sorption values reported for the two stages of cement degradation are attributed to the competitive effect of Ca on Sr uptake (CEM-94; TITS et al. 1998). Note that Sr is expected to be associated predominantly with CSH phases in the cement matrix⁴. Based on the available information, R_d values of $0.1 \text{ m}^3 \text{ kg}^{-1}$ and $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ are assigned to Sr uptake in the stages I and II of cement degradation.

3.2.2.3 Nickel

A sorption value of $0.1 \text{ m}^3 \text{ kg}^{-1}$ was assigned to Ni for both stages of cement degradation in CEM-94 and CEM-97. The value also agrees with in-house measurements on HCP ($R_d \sim 0.1 \text{ m}^3 \text{ kg}^{-1}$ to $\sim 0.3 \text{ m}^3 \text{ kg}^{-1}$ determined at a S/L ratio of $2.5 \cdot 10^{-2} \text{ kg L}^{-1}$) (WIELAND et al. 2000). Nevertheless, sorption measurements carried out in suspensions with varying S/L ratios reveal a strong decrease of the R_d value with increasing S/L ratio (Fig. 1c). This finding contradicts the notion of an adsorption-type

⁴ Hydrated cement consists of about 40 - 60 wt % CSH phases (TAYLOR 1997).

uptake process. It is to be noted that evidence for a solubility-controlled uptake process was previously provided by HIETANEN et al. (1984), PILKINGTON & STONE (1990), ATKINS et al. (1993) and OCHS et al. (1998). To further prove the possibility of Ni uptake by a solubility-limiting process, investigations of the behaviour of stable Ni in cement systems were conducted. In these studies, equilibrium concentrations of stable Ni were determined in ACW, which was in contact with HCP at different S/L ratios of the suspensions. The results show that the Ni concentration in ACW is almost constant (range $\sim 5 \cdot 10^{-8}$ M to $\sim 2 \cdot 10^{-7}$ M) regardless of the S/L ratio (Fig. 2). This finding supports the idea that the partitioning of stable Ni is controlled by a solubility-limiting process rather than a sorption-type process. Recent results obtained from X-ray absorption spectroscopy (XAS) studies on Ni precipitates in cement systems further substantiate this finding (SCHEIDEGGER et al. 2000). The authors show that mixed Ni-Al layered double hydroxides (LDH) may form in cement systems, and thus, Ni-Al LDHs are regarded as solid phases being potentially present in the waste matrix and governing Ni uptake. The work of JOHNSON & GLASSER (2003), however, indicates that $\text{Ni}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 2\text{H}_2\text{O}$, which has a LDH-type structure, is unlikely to account for the limited solubility of Ni in cement systems. Nevertheless, it is still unknown as to the relevance of CO_3^{2-} -containing LDHs in the complex cement matrix due to the limited inventory available during hydration. Thus, at the present time, the composition of the Ni-containing solid phase, which is responsible for the low Ni concentrations determined in cement systems at pH = 13.3, is still unknown.

The possibility of Ni uptake due to solubility limitation could further be substantiated when the Ni data shown in Fig. 2 were tentatively modelled in terms of an adsorption-type process assuming an R_d value of $0.1 \text{ m}^3 \text{ kg}^{-1}$. This sorption value was taken from CEM-97 and, moreover, corroborated by in-house measurements. Model predictions of the partitioning of stable Ni between HCP and CPW can be based on mass balance considerations for Ni given by:

$$I_t = I_s^0 + I_l^0 = I_{s,\text{eq}} + I_{l,\text{eq}} = m_c c_s^0 + V_l c_l^0 = m_c c_{s,\text{eq}} + V_l c_{l,\text{eq}} \quad [\text{mol}] \quad (2)$$

- I_t : total inventory of the HCP suspension [mol]
- I_s^0 : initial inventory of the HCP matrix [mol]
- I_l^0 : initial inventory of CPW [mol]
- $I_{s,\text{eq}}$: inventory of the HCP matrix at equilibrium [mol]
- $I_{l,\text{eq}}$: inventory of CPW at equilibrium [mol]
- m_c, V_l : mass of HCP [kg] and volume of porewater [L]
- c_s^0, c_l^0 : initial concentrations of HCP [mol kg^{-1}] and CPW [M]
- $c_{s,\text{eq}}, c_{l,\text{eq}}$: equilibrium concentrations of HCP [mol kg^{-1}] and CPW [M]

Re-arranging Eq. 2 and replacing $c_{s,eq}$ by $R_d \times c_{1,eq}$ (R_d in $L \text{ kg}^{-1}$) according to Eq. 1 yields the following expression for the equilibrium Ni concentration, $c_{1,eq}$:

$$c_{1,eq} = \frac{m_c c_s^0 + V_1 c_1^0}{m_c R_d + V_1} \quad [\text{mol L}^{-1}] \quad (3)$$

The Ni concentration in HCP was determined to be 19.9 ppm ($c_s^0 = 3.39 \cdot 10^{-4} \text{ mol kg}^{-1}$). The initial concentration in ACW (c_1^0) was set to $4 \cdot 10^{-8} \text{ M}$. Fig. 2 shows that the expected concentrations of stable Ni (solid line) are significantly above the experimental data at S/L ratios $>10^{-4} \text{ kg L}^{-1}$. This indicates that the partitioning of stable Ni in the cement system cannot be interpreted in terms of a reversible adsorption-type process ($R_d = 0.1 \text{ m}^3 \text{ kg}^{-1}$), further supporting solubility limitation of Ni in these systems.

More detailed information on the processes taking place at the atomic/molecular level is required to substantiate the experimental findings presented in Fig. 1c and to develop a mechanistic model of the Ni uptake by HCP. Based on our present understanding of Ni immobilization in cement systems, however, we infer that:

- 1) The R_d value of $0.1 \text{ m}^3 \text{ kg}^{-1}$, which was previously reported in CEM-97 and supported from in-house batch-type sorption studies, is not considered to be representative for Ni uptake by HCP. As a consequence, we refrain from assigning an R_d value to Ni and recommend the use of solubility limits for PA calculations instead.
- 2) The Ni concentration in CPW appears to be controlled by a solubility-limiting process. The maximum concentration of Ni in CPW (pH = 13.3) is estimated to be $\sim 2 \cdot 10^{-7} \text{ M}$, which is lower than the Ni concentration predicted based on $\text{Ni}(\text{OH})_2$ solubility at pH = 13.3, i.e., $[\text{Ni}]_{\text{tot}} = 3 \cdot 10^{-6} \text{ M}$ (BERNER 1999). At the present time, however, the nature of the Ni-containing solid phase is still unclear. Evidence has been provided for the formation of a solid solution with Ni-Al LDH-type compounds.
- 3) The question arises whether or not the concept presented for Ni also holds for other transition metals. In Section 3.4 it will be shown that the behaviour of Co, for which Ni is considered to be an appropriate chemical analogue, can be interpreted in a similar manner. Detailed uptake studies with other bivalent metal cations may help to clarify this open question.

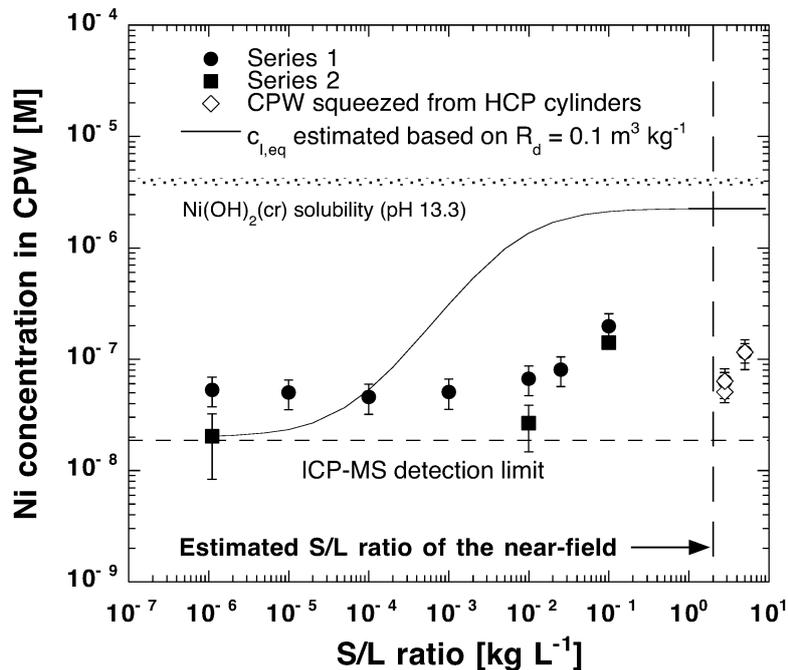


FIGURE 2: Ni concentration measured in solution shown as a function of the S/L ratio of the suspensions. The samples with S/L ratios $< 0.1 \text{ kg L}^{-1}$ were prepared by varying the HCP content in contact with ACW (pH = 13.3). After 30 days equilibration, HCP and ACW were separated by centrifugation, and the Ni concentration was measured in the supernatant by ICP-MS. The Ni concentrations at S/L ratios $> 2 \text{ kg L}^{-1}$ were determined for CPW which was squeezed from HCP. The solid line indicates Ni concentrations predicted from mass balance calculations.

3.2.2.4 Europium

Eu(III) is the only stable redox state of Eu under alkaline conditions. WIELAND et al. (1998) and OCHS et al. (1998) published investigations of Eu uptake by HCP as well as measurements of the solubility of Eu in ACW. Ochs and co-workers determined the solubility of Eu in both fresh and degraded cementitious systems. Eu shows a higher solubility in a stage I CPW (pH = 13.2) than in a porewater of pH = 12.5. The Eu concentrations in ACW were determined to be $\sim 2 \cdot 10^{-9} \text{ M}$ at pH 13.2 and to $< 6.6 \cdot 10^{-10} \text{ M}$ (detection limit of ICP-MS) at pH = 12.5. Thermodynamic calculations indicate that $\text{Eu}(\text{OH})_3$ is the solubility-limiting phase in both cases. However, it should be noted that thermodynamic calculations of Eu speciation were based on thermodynamic data for Am. Moreover, OCHS et al. (1998) provide no supporting evidence for the presence of a solubility-limiting phase.

WIELAND et al. (1998) report uptake studies with Eu on HTS cement at pH = 13.3. The total Eu concentration added in these experiments was well below the critical concentration with regard to the formation of radiocolloids or $\text{Eu}(\text{OH})_3$, i.e., $[\text{Eu}]_{\text{tot}} \leq 10^{-9}$ M. Moreover, the concentration of stable Eu in cement systems was found to be below the detection limit of ICP-MS, i.e., $[\text{Eu}]_{\text{tot}} \leq 3 \cdot 10^{-11}$ M. WIELAND et al. (1998) observed a strong uptake of Eu by HCP resulting in R_d values $\geq 1000 \text{ m}^3 \text{ kg}^{-1}$ at a S/L ratio of $10^{-5} \text{ kg L}^{-1}$. The very low S/L ratios were chosen to allow accurate measurements of the Eu activities in ACW. Lower R_d values were determined at a S/L ratio of $10^{-4} \text{ kg L}^{-1}$ ($R_d > 100 \text{ m}^3 \text{ kg}^{-1}$). Sorption studies on CSH phases at pH = 13.3 yield consistent R_d values, i.e., $R_d > 100 \text{ m}^3 \text{ kg}^{-1}$ at a S/L ratio of $10^{-4} \text{ kg L}^{-1}$ (TITS et al. 1998; 2000) (Fig. 1d). Note that CSH phases are expected to be important sorbing phases for Eu in the cement matrix primarily due to their abundance, and consequently, their sorption capacity. Thus, the sorption values of Eu are expected to be similar in value on HCP and CSH phases.

A study recently published by POINTEAU et al. (2001) indicates Eu incorporation into the structure of CSH phases. Using time-resolved laser fluorescence spectroscopy (TRLFS), the authors were able to characterise two main sorption sites for Eu on CSH phases representing different coordination environments. The sites were distinguished according to the time dependence of the emission decay for Eu surface species. The authors ascribe the site with a long lifetime to Eu being incorporated in the structure, whereas the site with a shorter lifetime is considered to reveal the characteristics of a chemical environment like that in $\text{Eu}(\text{OH})_3$. Note that the wet chemistry data published by POINTEAU et al. (2001) further support a strong uptake of Eu ($R_d \geq 90 \text{ m}^3 \text{ kg}^{-1}$).

The results of TITS et al. (2003b) corroborate the findings of POINTEAU et al. (2001). TITS and co-workers were able to identify three different types of sorbed Cm species on CSH phases. Note that Cm is considered to be an appropriate chemical analogue for Eu. TITS et al. (2003b) propose a structural model for Cm and Eu incorporation in CSH phases based on the substitution of these elements for Ca at two different types of sites in the CSH structure. Recent TRLFS measurements finally show that, in the case of Cm and Eu, CSH phases are the uptake-controlling phase in the cement matrix (STUMPF 2002).

Due to consistency of the data obtained for the different solid phases, we feel justified in assigning a high sorption value to Eu in cement systems ($R_d = 100 \text{ m}^3 \text{ kg}^{-1}$). It is to be noted that studies on Eu uptake by calcite under hyperalkaline conditions (TITS et al.

2002) and by feldspar at pH = 13.3 (VAN LOON & GLAUS 1998) corroborate the strong interaction of Eu with solid phases (R_d values $\geq 100 \text{ m}^3 \text{ kg}^{-1}$). Investigations of the dependence of the R_d value on the HCP content of cement systems indicate a weak trend to lower R_d values with increasing S/L ratio of the suspensions (Fig. 1d). Note, however, that uncertainties on R_d values are large due to the low quantities of HCP used in these experiments. Thus, the trend to lower sorption values, which appears in Fig. 1d, is not considered to be significant. Studies on CSH phases further support the finding of constant R_d values with varying solid concentrations of the suspensions (open symbols in Fig. 1d; TITS 2002). Thus, we ignore the solid concentration effect and assign an R_d value of $100 \text{ m}^3 \text{ kg}^{-1}$.

3.2.2.5 Thorium

Th sorption on HTS cement at pH = 13.3 was reported by WIELAND et al. (1998; 2002). Similar to Eu, strong uptake by HCP was observed, i.e., $R_d \geq 1000 \text{ m}^3 \text{ kg}^{-1}$ at a S/L ratio of $10^{-5} \text{ kg L}^{-1}$. The Th concentration added in the experiments was below the critical concentration with regard to the formation of radiocolloids ($[\text{Th}]_{\text{tot}} \sim 10^{-9} \text{ M}$). Moreover, the experiments were carried out at very low S/L ratios due to the high affinity of Th for HCP. At a S/L ratio = $10^{-4} \text{ kg L}^{-1}$, the R_d value was found to be about one order of a magnitude lower ($R_d \sim 100 \text{ m}^3 \text{ kg}^{-1}$ to $500 \text{ m}^3 \text{ kg}^{-1}$). Note that sorption studies on CSH phases at pH = 13.3 yielded similar R_d values (TITS et al. 1998; 2000). In addition, no significant dependence of the R_d value on the solid concentration was observed for cement systems in the S/L range between $10^{-4} \text{ kg L}^{-1}$ and $10^{-2} \text{ kg L}^{-1}$ (Fig. 1e). Note that these experiments were carried out in ACW at a total isosaccharinic acid (ISA) concentration of $2 \cdot 10^{-3} \text{ M}$. In this case, Th uptake by HCP is reduced (WIELAND et al. 1998; 2002). R_d values range in value between $\sim 0.2 \text{ m}^3 \text{ kg}^{-1}$ and $\sim 3 \text{ m}^3 \text{ kg}^{-1}$ at $[\text{ISA}]_{\text{tot}} = 2 \cdot 10^{-3} \text{ M}$ instead of $R_d > 100 \text{ m}^3 \text{ kg}^{-1}$ as observed in the absence of ISA. Nevertheless, with adsorption as the uptake-controlling process, the sorption value is expected to be constant at varying S/L ratios regardless of the presence or absence of ISA.

The in-house determined R_d values for Th are found to be one to two orders of magnitude larger than the values previously reported by ALLARD (1985) and HÖGLUND et al. (1985). Note, however, that a higher S/L ratio ($S/L = 2 \cdot 10^{-2} \text{ kg L}^{-1}$) was employed by these authors, which could explain the lower R_d value determined in these systems. Note further that R_d values $\geq 100 \text{ m}^3 \text{ kg}^{-1}$ have been reported for Th uptake by calcite under hyperalkaline conditions (TITS et al. 2002) and by feldspar at

pH = 13.3 (VAN LOON & GLAUS 1998). Thus, based on the above information, we feel justified in assigning a high sorption value to Th ($R_d = 100 \text{ m}^3 \text{ kg}^{-1}$).

3.2.2.6 Tin

Sn is expected to exist in the tetravalent state, i.e. Sn(IV), under the conditions prevailing in a repository environment (SÉBY et al. 2001). Sn readily hydrolyses in the pH range > 8 (AMAYA et al. 1997). In-house studies show a strong uptake of Sn by HCP at pH = 13.3 (Fig. 1f). The experiments were carried out at Sn concentrations well below the solubility limit with regard to sparingly soluble Ca-stannate ($\text{CaSn}(\text{OH})_6(\text{s})$) (OCHS et al. 1998). R_d values ranging between $10 \text{ m}^3 \text{ kg}^{-1}$ and $20 \text{ m}^3 \text{ kg}^{-1}$ were determined irrespective of the concentration of HCP in the system (Fig. 1f). Note that BAKER et al. (1994) observed higher sorption values for Sn on HCP ($R_d \geq 30 \text{ m}^3 \text{ kg}^{-1}$) under conditions of a stage II CPW.

The experimental data for Sn and Th show that both tetravalent metal cations sorb strongly onto HCP in spite of differences in speciation at pH = 13.3. In the case of Sn, $\text{Sn}(\text{OH})_5^-$ and $\text{Sn}(\text{OH})_6^{2-}$ are the dominant hydrolytic species at pH > 8 , whereas Th predominately exists in the form of $\text{Th}(\text{OH})_4$ in alkaline media. In the case of Sn, finally, XAS measurements indicate that CSH phases may not be the uptake-controlling phase in the cement matrix. An alternative structure model for Sn binding in HCP was proposed based on XAS results and on the assumption that ettringite is the uptake-controlling phase (BONHOURE et al. 2003).

Based on the in-house data, we assign an R_d value of $10 \text{ m}^3 \text{ kg}^{-1}$ for both stages of cement degradation.

3.2.2.7 General considerations

In CEM-94 it was argued that the magnitude of sorption of a radionuclide qualitatively correlates with its tendency to hydrolyse. Indeed, there are examples given in the literature, which demonstrate the significant influence of the chemical characteristics of metal cations on the adsorption behaviour. For example, SCHINDLER et al. (1976) and SCHINDLER (1984) show that the stability constants of surface complexes ($K_{\text{int}}^{\text{s}}$) on silica correlate excellently with the stability constants of the aqueous mono-hydroxo complexes (i.e., the first hydrolysis constant) of metal cations. Linear free-energy relationships (LFER) have been reported for other oxides such as $\alpha\text{-FeOOH}$, amorphous $\text{Fe}(\text{OH})_3$ and $\gamma\text{-Al}_2\text{O}_3$. Thus, in all these cases, the tendency of a metal cation to adsorb

on the surface of metal(hydr)oxides can be related to the stability of the first hydrolysis product in line with LFER.

At the present time, however, the LFER approach cannot be applied to cement systems in the narrower sense. The thermodynamic description and mechanistic understanding of uptake processes are still insufficient. Nevertheless, we expect a qualitative understanding of the metal-cement interaction when comparing the sorption values with the chemical characteristics of the metal centres. In this study, a charge-to-size relationship given by the ratio of the cation charge, z , to the M-O inter-atomic distance, d , which is the sum of ionic radii, $d = r_{M^{z+}} + r_{OH^-}$ (SHANNON & PREWITT 1969), is used as characteristic parameter. The parameter is a measure of the polarising effect of cations on anionic counter-ions comparable to the ionic potential (HUHEEY 1975). For example, BAES & MESMER (1986) used this parameter to group the hydrolysis constants of metal cations.

The sorption values reported for Cs, Sr, Eu, Sn and Th on HCP at pH = 13.3 are tentatively grouped according to the above approach in Fig. 3. Note that Ni is not included in Fig. 3 since Ni immobilization is expected to be controlled via solubility limitation. For the few data of this study, Fig. 3 reveals a general trend to stronger uptake by HCP with increasing charge-to-size relationships (z/d) of the metal centre. Note, however, that grouping R_d values in terms of the polarising effect of a metal centre implicitly emphasises the ionic character of the bonding irrespective of the underlying uptake mechanism. The trend displayed in Fig. 3 implies that the magnitude of sorption of a metal cation on HCP is influenced by the chemical nature of the metal centre, e.g., the oxidation state. Again, it should be noted that the correlation is qualitative in the sense that no account is taken of the specific binding mechanisms involved (i.e., ion exchange and surface complexation), the mineral phases involved and speciation at high pH. Although the correlation is of limited use, it reveals a general trend in the immobilization of metal cations by HCP.

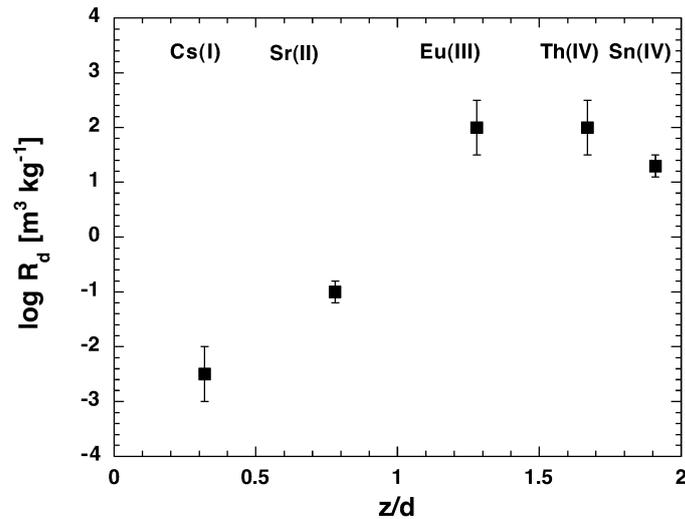


FIGURE 3: Sorption values for selected elements on HCP displayed as a function of the charge-to-size ratio (z/d). z denotes the cation charge of the metal centre, and d is the inter-atomic distance M-O, which is the sum of ionic radii, $d = r_{M^{z+}} + r_{O^{2-}}$, in [Å].

3.3 Chemical analogues

Internal consistency of the sorption values is an important aspect of the SDB. To check consistency in the sorption behaviour of radioelements, we rely on the aspect of chemical analogy. In CEM-94 radioelements were grouped according to their position in the periodic table and their major chemical characteristics, i.e., redox sensitivity, hydrolysis and ion-pair formation. We retain the proposed groups of chemical analogues in this study. To check internal consistency of the proposed sorption values for metal cations, we use the trend displayed in Fig. 3 as an additional criterion. In the following, sorption values are assigned to elements where no experimental data are available based on the principle of chemical analogy.

3.4 Selection of sorption values for safety-relevant radioelements

In CEM-94 and CEM-97 sorption data were deduced for the safety-relevant radionuclides of a L/ILW repository. In the following, discussions will be confined to those elements that specifically appear in the ILW waste (Section 3.4.1). Also, discussions will be confined to those areas where advances in knowledge and understanding have occurred which enables us to modify the sorption values recommended in CEM-94 and CEM-97 (Section 3.4.2). No new information or

understanding is available for some elements, which would justify modifications of the previously recommended sorption values to be made. In these cases, sorption values are the same as given in CEM-94 and CEM-97 (Section 3.4.3).

3.4.1 New elements

Be, Ca, Fe, Ru, Sb, Pm, Sm and Eu (discussed in Section 3.2.2.4) are ILW-specific elements (see Table 1), which were not considered in CEM-94 and CEM-97.

3.4.1.1 Beryllium

Be shows a unique chemical behaviour within the group II elements (earth-alkali group). Its chemistry is characterised by the covalent rather than ionic nature of its compounds. Hydroxide and fluoride are the only ligands that may form strong complexes with Be^{2+} in aqueous solution. Thus, under conditions relevant to a repository, i.e., at very low fluoride concentrations, speciation of Be at high pH is dominated by $\text{Be}(\text{OH})_3^-$ and $\text{Be}(\text{OH})_4^{2-}$ (BAES & MESMER 1986). To the best of our knowledge, no sorption data have been reported for this element under conditions relevant to cement systems.

Using the trend displayed in Fig. 3, significant uptake by HCP is expected based on the ionic potential of Be^{2+} ($z/d = 1.21$), which is high due to the small size of the cation ($r = 0.27 \text{ \AA}$). The formation of $\text{Be}(\text{OH})_3^-$ and $\text{Be}(\text{OH})_4^{2-}$ species at high pH is expected to exhibit a competitive effect on uptake, thus reducing the overall sorption value. Although uptake of Be by HCP is very likely, we take a conservative view and set the sorption value to zero.

3.4.1.2 Calcium

Ca is a major constituent of the cement matrix⁵. The total Ca concentration is fixed by portlandite solubility at $\sim 2 \text{ mM}$ in the stage I and $\sim 20 \text{ mM}$ in the stage II of cement degradation. We anticipate that the uptake of ^{41}Ca present in the waste matrix occurs via isotopic exchange with stable Ca rather than adsorption. Thus, the concentration of the ^{41}Ca in CPW is expected to be controlled by isotopic dilution with stable Ca in cement systems. We refrain from assigning an R_d value to Ca and recommend the use of concentration limits and taking into account isotopic exchange for PA calculations instead.

⁵ CaO contributes to about 55 wt % to the HTS cement (WIELAND, unpublished data).

3.4.1.3 Iron

The aqueous chemistry of iron is dominated by the Fe(II)/Fe(III) redox couple. For example, redox conditions in the bentonite buffer are assumed to be controlled by the magnetite/Fe(II) equilibrium where the dissolved Fe(II) concentration corresponds to that in the groundwater of the surrounding host rock, e.g., $[\text{Fe(II)}] = 5 \cdot 10^{-6}$ M (WABER et al. 1998; WERSIN et al. 2003). Iron is an important component both of the cementitious and metallic waste materials in the near field of a repository. NEALL (1994) estimates the contribution of steel, which is present in the form of waste canisters, decommissioning waste and concrete reinforcing, to be about 4 wt % of the total mass of the L/ILW near field. Moreover, cement contains several percent of iron oxides (typically ~3 wt %) mostly as ferrite phases (TAYLOR 1997). Ferrites can be prepared with any composition as solid solution of the type $\text{Ca}_2(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_5$. They are converted into monosulfate-type or ettringite-type products during hydration of the clinker material. Both product phases tend to undergo further alteration to form hydrogarnet-type phases. Fe^{3+} may partially replace Al^{3+} in the structure of these products. Note further that several investigations indicate the presence of iron(III) hydroxides in the cement matrix (TAYLOR 1997). The above considerations show that Fe is an intrinsic constituent of the cement matrix, and thus, Fe uptake by HCP may occur via solid solution formation with Fe-containing phases rather than adsorption onto the surface of cement minerals. We infer from this that:

- 1) The Fe concentration in CPW is presumably controlled by a solubility-limiting process, e.g., due to the presence of iron(III) oxides and hydroxides, or a solid solution with Fe-containing cement phases rather than adsorption.
- 2) Large Fe inventories are available in the cementitious near field, which allows saturation with respect to a solubility-limiting Fe phase to be achieved in CPW.

Since no sorption data for Fe in cement systems are available, and moreover, evidence for a solubility-limiting process can be given, we recommend the use of concentration limits for PA calculations instead. Analyses of CPW squeezed from HCP samples show that the concentration of total Fe ranges in value between $5 \cdot 10^{-7}$ M and $5 \cdot 10^{-6}$ M, which is in good agreement with the data obtained from leaching studies (BERNER 2002).

3.4.1.4 Ruthenium

Standard potential-pH equilibrium diagrams for the system ruthenium-water at 25° C reveal that Ru(O), Ru(IV) and Ru(VI) are the dominant oxidation states under alkaline conditions (BAES & MESMER 1986). Note that existence of Ru(IV) was also reported by POURBAIX (1974). Information on the hydrolysis products is either conflicting or lacking at all (BAES & MESMER 1986). To date, no sorption values for Ru are available to the best of our knowledge. In this study, the distribution ratios of the Ru species are set to zero due to the vague information available on the speciation in aqueous solution under alkaline conditions.

3.4.1.5 Antimony

Sb(III) is stable under reducing conditions and at ambient pH values, whereas Sb(V) predominates under oxidising conditions. Sb is expected to exist primarily in the oxidation state V in a repository (pH range 12 to 14). To the best of our knowledge, no sorption data have been reported for Sb(III) and Sb(V) in cement systems.

Sb(OH)₅ is represented as antimonic acid, which has a strong tendency to form polymers upon hydrolysis (BAES & MESMER 1986). Sb(OH)₆⁻ was reported to be the dominant species above pH 5 (BAES & MESMER 1986). It was further indicated that Sb(V) may exist in the form of an oxy anion, i.e., SbO₃⁻·3H₂O, by POURBAIX (1974) and LEGOUX et al. (1992). Because no sorption data are available for Sb(V) under conditions relevant to cement systems, selection of the R_d value has to be based on chemical analogy, if at all. Emphasising the anionic character of Sb(V) (SbO₃⁻·3H₂O) and, in addition, considering the hydrolysis behaviour of antimonic acid, we assume a sorption behaviour typically observed for anions, such as Tc(VII) and Se(IV/VI) (R_d range between 10⁻³ m³ kg⁻¹ and 3·10⁻² m³ kg⁻¹) (CEM-94 and references therein). We thus assign a sorption value based on the analogy with Tc(VII) (R_d = 10⁻³ m³ kg⁻¹) for both stages of cement degradation.

Under very reducing conditions, however, Sb(III) may form. Cationic compounds of Sb(III) are mostly of the so-called “antimonyl” ion type, SbO⁺. Sb(III) hydrolyses in a manner typically observed for metal cations (BAES & MESMER 1986). Hydrolysis products of Sb(III) include Sb(OH)₂⁺, Sb(OH)₃ and Sb(OH)₄⁻. Note that Sb(OH)₄⁻ is the dominant species above pH 11. The z/d ratio of Sb(III) is estimated to be 1.38. The ionic potential of SbO⁺ is lower (z/d ~0.9). Based on the trend displayed in Fig. 3 and based on our best estimates for the ionic potentials, the sorption value is expected to range in

value between $0.1 \text{ m}^3 \text{ kg}^{-1}$ and $100 \text{ m}^3 \text{ kg}^{-1}$. We take a conservative view of Sb(III) sorption and assign a nominal sorption value of $0.1 \text{ m}^3 \text{ kg}^{-1}$.

3.4.1.6 Promethium, Samarium

Selection of the sorption value of Eu(III) is discussed earlier (Section 3.2.2.4). Eu(III) is considered to be an appropriate chemical analogue for Pm(III) and Sm(III). For this reason and because of missing experimental data for Pm(III) and Sm(III), we assign the same R_d value to the lanthanides.

3.4.2 Revised sorption values

Because new information is existing, we feel justified in re-assessing the sorption characteristics of tritium (HTO), Se, I, Cs, Sr, Ra, Ni, Co, Sn, Zr, Ac, Th, Pa, Pu, Np, U, Am and Cm on HCP. Selection of the sorption values for Cs, Sr, Ni, Sn and Th is described in Section 3.2.2.

3.4.2.1 Tritium

New experimental information is available for tritium (HTO). In-house studies were carried out to assess the migration and sorption behaviour of non-sorbing and weakly sorbing tracers in the stage I of cement degradation (TITS et al. 2003a). In these studies, the sorption values of HTO on HCP were determined to be $(0.8 \pm 0.2) \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ from batch-type experiments and, in excellent agreement, $(0.8 \pm 0.1) \cdot 10^{-3} \text{ m}^3 \text{ kg}^{-1}$ from through-diffusion experiments (JAKOB 2002). The diffusion experiments consisted of a through-diffusion test followed by an out-diffusion test. Earlier diffusion studies reported by JOHNSTON & WILMOT (1992) and HOLGERSSON et al. (1998) indicate R_d values of about $10^{-4} \text{ m}^3 \text{ kg}^{-1}$ or lower. Discrepancies in the sorption values resulting from the different studies could be due to differences in sample characteristics, e.g., the water/cement (w/c) ratio used to prepare the HCP, or parameter evaluation. The diffusion experiments reported by JAKOB (2002) and TITS et al. (2003a) were conducted on HCP material prepared at w/c ~ 1.3 . It is to be noted that the w/c ratios of HCP were significantly lower in the studies of JOHNSTON & WILMOT (1992) (w/c ~ 0.35) and HOLGERSSON et al. (1998) (w/c ~ 0.5). Moreover, in these studies, parameter evaluation was only based on through-diffusion data rather than a combined set of through- and out-diffusion data. Note that including a set of diffusion data, i.e., from through- and out-diffusion experiments, adds additional constraints on the modelling, which finally results in well-bound sorption values (JAKOB 2002; TITS et al. 2003a).

We feel justified in considering some uptake of HTO by HCP based on the in-house data presently available. Nevertheless, there are discrepancies on the exact value when comparing the results from the different studies. For this reason, we assign a (low) nominal sorption value of $10^{-4} \text{ m}^3 \text{ kg}^{-1}$ to HTO for both stages of cement degradation.

3.4.2.2 Selenium

SeO_3^{2-} is the dominant species in a cementitious near field under moderately reducing conditions (oxidation state IV). A first series of in-house sorption studies indicate a significant uptake of SeO_3^{2-} by HCP at $\text{pH} = 13.3$ (WIELAND, unpublished data). Kinetic studies of Se(IV) uptake by HCP were carried out in cement suspensions at a S/L ratio of $2.5 \cdot 10^{-2} \text{ kg L}^{-1}$. An R_d value of $\sim 0.1 \text{ m}^3 \text{ kg}^{-1}$ was deduced from these experiments. In addition, the R_d value was found to vary by only a factor of about 3 ($0.03 \text{ m}^3 \text{ kg}^{-1}$ to $0.1 \text{ m}^3 \text{ kg}^{-1}$) in the S/L range between $10^{-3} \text{ kg L}^{-1}$ and 0.1 kg L^{-1} . Note that in a recent study published by JOHNSON et al. (2000) even stronger uptake of SeO_3^{2-} by HCP ($R_d \sim 0.3 \text{ m}^3 \text{ kg}^{-1}$ to $\sim 0.9 \text{ m}^3 \text{ kg}^{-1}$) is indicated.

BAUR & JOHNSON (2003) found that SeO_3^{2-} sorbs more strongly than SeO_4^{2-} (oxidation state VI) on CSH phases, ettringite and monosulfate⁶, which are the most important constituents of the HCP. The distribution ratios determined for SeO_3^{2-} were similar in value on all cement minerals, ranging between $0.18 \text{ m}^3 \text{ kg}^{-1}$ and $0.38 \text{ m}^3 \text{ kg}^{-1}$. In contrast, SeO_4^{2-} , which is the dominant species under oxidising conditions, was found to sorb specifically on monosulfate whereas sorption on ettringite and CSH phases was weak. Substitution for sulfate was suggested to be the relevant process. Furthermore, the study of BAUR & JOHNSON (2003) indicates that substitution of SeO_4^{2-} for SO_4^{2-} on ettringite is quantitatively unimportant which contradicts results recently published by OCHS et al. (2002).

In view of the new experimental data we feel justified in revising the sorption values of Se(IV) given in CEM-94 and CEM-97 ($R_d = 0$). However, a (conservative) distribution ratio of $0.03 \text{ m}^3 \text{ kg}^{-1}$ is recommended for Se(IV) in line with the in-house measurements. No sorption data are available for Se(VI) on HCP. Nevertheless, uptake of SeO_4^{2-} by HCP is anticipated in view of the results published by BAUR & JOHNSON (2003). Therefore, we further feel justified in revising the distribution ratio for Se(VI) given in CEM-94 and CEM-97 ($R_d = 0$). Because experimental data on HCP are lacking, Se(VI) is tentatively grouped to TcO_4^- (Tc(VII)), for which an R_d value of $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ was

⁶ Hydrated cement consists of about 10 - 20 wt % ettringite and monosulfate (TAYLOR 1997).

selected (CEM-97). The above sorption values for Se(IV) and Se(VI) are assigned to both stages of cement degradation.

3.4.2.3 Iodine

Batch sorption data for iodine were reported by ANDERSSON et al. (1983), ALLARD et al. (1984; 1991), HIETANEN et al. (1984; 1985), HÖGLUND et al. (1985), HOLLAND & LEE (1992) and BAKER et al. (1994). The sorption data given in the early studies were reviewed by LIU & VON GUNTEN (1988). In CEM-97, the sorption value of I was set to $10^{-2} \text{ m}^3 \text{ kg}^{-1}$ on the basis of the results published in the above studies. Note that sorption values obtained from diffusion experiments were found to be about an order of magnitude lower (SAROTT et al. 1992; JAKOB et al. 1999), implying a dependence of the R_d value of I on the S/L ratio as previously indicated in the study of HOLLAND & LEE (1993). At the present time, however, there is no conclusive explanation for the observed discrepancies between batch and diffusion data. The study of BONHOURE et al. (2002) shows that changes in the oxidation state of I can be ruled out as interfering process in uptake studies over time periods relevant to the above experiments. Therefore, redox process may not account for the observed discrepancies. Based on the above considerations we take a conservative view and reduce the distribution ratio of I to $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ for both stages of cement degradation.

3.4.2.4 Radium

Selection of the sorption values for Sr on HTS cement is discussed in Section 3.2.2.2. Sr is considered to be an appropriate chemical analogue for Ra. The sorption values of Ra given in CEM-94 and CEM-97 were selected from the study of BAYLISS et al. (1989), where the experimental conditions correspond to the conditions of a stage II CPW (pH = 12.5). Furthermore, HOLLAND & LEE (1992) determined Ra uptake by a sulfate-resistant Portland cement ($R_d = 0.05 \text{ m}^3 \text{ kg}^{-1}$). The sorption value given in CEM-97 ($R_d = 0.05 \text{ m}^3 \text{ kg}^{-1}$) for a stage II CPW is retained based on the consistent set of data available from the above-mentioned studies and in contrast to the markedly lower R_d value selected for Sr ($R_d = 10^{-3} \text{ m}^3 \text{ kg}^{-1}$). For the stage I of cement degradation, however, we assign similar sorption values to Ra and Sr ($R_d = 0.1 \text{ m}^3 \text{ kg}^{-1}$), assuming chemical similarity of the two radioelements due to lack of back-up from experimental data for Ra.

3.4.2.5 Cobalt

Ni is considered to be an appropriate chemical analogue for Co. The sorption behaviour of Ni in cement systems is discussed in Section 3.2.2.3. Similarities in the behaviour of Ni and Co in cement systems also appear from in-house studies on stable isotope inventories. The behaviour of Co is illustrated in Fig. 4. Changes in the concentration of stable Co as a function of the S/L ratio are given by Eq. 3. Calculations are based on a Co inventory of 3.5 ppm for the HCP matrix and R_d values of $0.1 \text{ m}^3 \text{ kg}^{-1}$ (Ni value given in CEM-97) and $0.01 \text{ m}^3 \text{ kg}^{-1}$ (IDEMITSU et al. 1991). Fig. 4 shows a constant concentration of stable Co in CPW within the uncertainty range of the data irrespective of the S/L ratio of the cement suspensions. Fig. 4 further reveals that the partitioning of stable Co cannot be interpreted in terms of an adsorption-type process using the R_d values given above. This finding suggests that a solubility-limiting process controls Co uptake in cement systems rather than an adsorption-type process.

The maximum Co concentration in the ILW CPW is expected to range in value between $5 \cdot 10^{-8} \text{ M}$ and $2 \cdot 10^{-7} \text{ M}$ at $\text{pH} = 13.3$ (Fig. 4). This value is lower than predicted from solubility calculations assuming $\text{Co}(\text{OH})_2$ as the solubility-limiting phase ($7.6 \cdot 10^{-5} \text{ M}$) (BERNER 1999). Like in the case of Ni, we refrain from assigning an R_d value to Co and recommend the use of concentration limits for PA calculations instead.

3.4.2.6 Zirconium

Sn(IV) is expected to be a possible chemical analogue for tetravalent Zr(IV). The z/d ratio of Zr(IV) is 1.89 which is close to the value estimated for Sn(IV) ($z/d = 1.91$). Note that $\text{Zr}(\text{OH})_5^-$ is the dominant hydrolysis product in alkaline media, whereas $\text{Sn}(\text{OH})_5^-$ and $\text{Sn}(\text{OH})_6^{2-}$ are the main species at $\text{pH} > 8$ for Sn. Thus, based on similar z/d characteristics of the metal centres and similarities in speciation, we assign the same R_d value to Zr and Sn ($R_d = 10 \text{ m}^3 \text{ kg}^{-1}$).

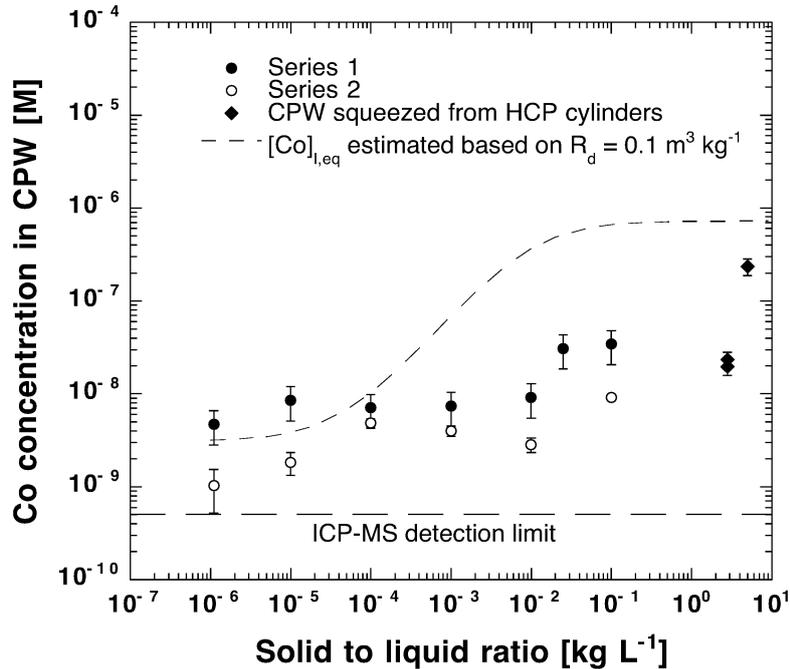


FIGURE 4: Co concentration measured in CPW shown as a function of the S/L ratio of the cement system. Dependence of the stable Co concentration in solution on the S/L ratio is given by Eq. 3 using the following parameters: $c_s^0 = 3.5$ ppm, $R_d = 0.1$ m³ kg⁻¹ (Ni value given in CEM-97) and 0.01 m³ kg⁻¹ (IDEMITSU et al. 1991). For the experimental methods see Fig. 2.

3.4.2.7 Actinium, Protactinium, Plutonium, Neptunium, Uranium

The most stable oxidation states of these actinides are considered to be Ac(III), Pa(IV)/Pa(V), U(IV)/U(VI), Np(IV)/Np(V) and Pu(IV)/Pu(V) (CHOPPIN 1983). The tetravalent states predominate under reducing conditions. Th(IV) is considered to be an appropriate chemical analogue for the tetravalent actinides. Selection of the sorption values for Th(IV) on HTS cement is discussed in Section 3.2.2.5. Ac is stable in the trivalent oxidation state, Ac(III). It is a more nearly analogue of the lanthanides due to similarities in the respective electron configurations. In this study Eu(III) is selected to be a chemical analogue for Ac(III), and therefore, the same sorption value is assigned to the radioelements ($R_d = 100$ m³ kg⁻¹).

We assign the high sorption values selected for Th(IV) to Pa(IV), U(IV) and Np(IV), ($R_d = 100$ m³ kg⁻¹) due to similarities in speciation at high pH. $M(OH)_4$ is the dominant species of the tetravalent metal cations under alkaline conditions. BAES & MESMER (1986) assume the formation of a negatively charged hydroxo complex ($Pu(OH)_5^-$) in the

case of Pu(IV), and therefore, this species was included in the earlier Nagra thermochemical data base (PEARSON et al. 1992). According to the recent NEA review (LEMIRE et al. 2000), however, experimental studies do not support robust thermodynamic data for $\text{Pu}(\text{OH})_5^-$. Thus, $\text{Pu}(\text{OH})_4(\text{aq})$ is considered to be the only and dominant complex under alkaline conditions in the new Nagra/PSI thermochemical data base (HUMMEL et al. 2002). As a consequence of the above, similarities in Th(IV) and Pu(IV) speciations are anticipated, which, for reasons of consistency, requires that the high distribution ratio selected for Th(IV) be assigned to Pu(IV).

As a consequence of the above re-assessment of the sorption behaviour of tetravalent actinides, the sorption values recommended for reducing conditions are significantly higher than in the previous SDBs. Nevertheless, the high sorption values are defensible, taking into account the experimental data and associated uncertainties reported for tetravalent actinides in the open literature, i.e., by ALLARD et al. (1984), ALLARD (1985), HÖGLUND et al. (1985), EWART et al. (1989; 1990) and BAYLISS et al. (1991): $R_d = 3$ to $200 \text{ m}^3 \text{ kg}^{-1}$ for Np(IV), 1 to $70 \text{ m}^3 \text{ kg}^{-1}$ for Pu (redox state not determined), and 5 to $40 \text{ m}^3 \text{ kg}^{-1}$ for U(IV)/U(VI). It is to be noted that some of these data do not unambiguously support the high sorption values determined for Th(IV) on cementitious systems by TITS et al. (1998; 2000) and WIELAND et al. (1998; 2002), and on minerals by TITS et al. (2002) and VAN LOON & GLAUS (1998). In this study, however, we feel justified in selecting a realistic R_d value based on the large pool of new data available from in-house studies and the broadly accepted use of Th(IV) as a chemical analogue for U(IV), Pa(IV), Np(IV) and Pu(IV).

Under oxidising conditions, pentavalent NpO_2^+ , PaO_2^+ and PuO_2^+ as well as hexavalent UO_2^{2+} are considered to be the dominant species. Note that the effective charge of the MO_2^+ and MO_2^{2+} cations is markedly lower than indicated from the oxidation state of the metal centres (CHOPPIN 1983; MORIYAMA et al. 1999). For this reason, the sorption values of MO_2^+ and MO_2^{2+} cations are expected to be similar in value to those of bi- or trivalent metal cations, respectively, rather than the tetravalent metal cations.

The complexation behaviour of NpO_2^+ and bivalent metal cations, especially Ca^{2+} , were found to be similar (GLAUS et al. 1997). The effective charge of the metal cation in NpO_2^+ was reported to be $+2.3 \pm 0.1$ (CHOPPIN 1983). BERRY et al. (1988) studied the partitioning of Pa(V) between a sulfate-resisting Portland cement and ACW (pH ~12.8). The authors determined R_d values ranging between $0.1 \text{ m}^3 \text{ kg}^{-1}$ and $100 \text{ m}^3 \text{ kg}^{-1}$ and suggested that this wide range may be the result of the separation technique used in their study (filtration). No experimental data are available for PuO_2^+ . In view of the limited

information available on the sorption behaviour of pentavalent actinides, we assume that the distribution ratios of NpO_2^+ , PaO_2^+ and PuO_2^+ in cement systems are similar in value to those of bivalent metal cations. The sorption values of bivalent metal cations, e.g., Sr(II) and Pb(II), were reported to range in value between $0.1 \text{ m}^3 \text{ kg}^{-1}$ and $0.5 \text{ m}^3 \text{ kg}^{-1}$. On the basis of the above we assign a nominal sorption value ($R_d = 0.1 \text{ m}^3 \text{ kg}^{-1}$) to Np(V), Pa(V) and Pu(V) for both stages of cement degradation.

Since there is no new information available for a reappraisal of U(VI) sorption on HCP, the value selected in CEM-97 is retained ($R_d = 2 \text{ m}^3 \text{ kg}^{-1}$).

3.4.2.8 Americium, Curium

Am(III) and Cm(III) are expected to sorb strongly on cementitious materials. Measurements of Am sorption were reported by BAYLISS et al. (1991; 1992) for the Nirex reference vault backfill, which is an OPC/lime/limestone aggregate concrete, and individual cement minerals, and by ALLARD et al. (1984) and HÖGLUND et al. (1985) for various concrete materials ($R_d = 1 \text{ m}^3 \text{ kg}^{-1}$ to $100 \text{ m}^3 \text{ kg}^{-1}$ for Am). In these studies the R_d values were found to be generally lower than the value determined for Eu on HTS cement. It is to be noted that, in the above studies, higher S/L ratios and different cement formulations were employed, which could explain the difference between the R_d values of Eu and Am. No data are available for Cm(III).

In this study we rely on the broadly accepted view that Eu(III) is an appropriate chemical analogue for Am(III) and Cm(III) and on the large pool of data from in-house studies using Eu(III). As a consequence of the above, we assign the same sorption value to these radioelements ($R_d = 100 \text{ m}^3 \text{ kg}^{-1}$).

3.4.3 Non-revised sorption values

At the present time, we see no compelling reason to revise the sorption values recommended in CEM-97 for C, Cl, Nb, Mo, Tc, Pb, Po, Ag and Pd.

In the case of C new information on the formation of hydrocarbons in metallic iron/water systems was published by DENG et al. (1997). According to this study, C-14 in the repository is associated primarily with steel, i.e., as an activation product of N-14, which exists in the form of nitrides in steel. It can be assumed that C-14 is associated with carbides. Several volatile hydrocarbons can be formed from carbides (e.g. CH_4 , $\text{CH}_3\text{-CH}_3$, etc.) by a kind of Fischer-Tropsch reaction (JEFFERIES 1990; DENG et al. 1997). Based on this information potential pathways for C-14 release from the

repository can be summarised as follows: If carbides react to form volatile hydrocarbons, C-14 will be released as a gas. The other potential pathway for release is the transformation of carbides into CO₂. In that case, carbonates will be formed in the repository and the fate of C-14 will be controlled by isotopic exchange with stable C of the carbonates, i.e., predominantly calcite (see Section 5.2.7 in CEM-94; BAYLISS et al. 1988; MATSUMOTO et al. 1995).

Nevertheless, there is no information or understanding available, which would justify modifications of the sorption values for the afore-mentioned elements to be made. Consequently, the sorption values are retained as given in CEM-97.

3.5 Differences in R_d values in stage I and II of cement degradation

Changes in the porewater compositions may, in principle, affect the sorption behaviour of radioelements during cement degradation in the near field. Na, K and Ca concentrations as well as pH are the main parameters that change during the evolution of the near field. A lower pH value and lower K concentrations are predicted for a stage II CPW compared to a stage I CPW (Table 3). The Na concentration is fixed by the input groundwater in the stage II of cement degradation. The Ca concentration is fixed by portlandite solubility, which increases with decreasing pH. Thus, the Ca concentration is fixed at ~20 mM in stage II (pH = 12.5) compared to ~2 mM in stage I (pH = 13.3).

A competitive effect of K on uptake was taken into account when assigning sorption values to Cs for the two stages of cement degradation in CEM-94. The K concentration of a stage II CPW is predicted to be markedly lower than in the stage I (Table 3), thus implying higher sorption values for Cs (CEM-94).

A competitive effect of Ca on uptake has been taken into account for Sr and Ra. For other radioelements, however, we anticipate that the higher Ca concentration of a stage II CPW exerts only a minor effect on the uptake by HCP.

Adsorption onto a solid phase and hydrolysis of a metal cation are considered to be counter-acting processes on the basis of mass balance considerations within the framework of the surface complexation model. Speciation of metal cations in alkaline media, i.e., the formation of hydrolysis products, depends on pH whereby the ligand number of the hydrolytic species increases with increasing pH. Note that the ligand number indicates the average number of OH⁻ ions bound to the metal centre. Hydrolysis

products with higher ligand numbers are formed in a stage I CPW (pH = 13.3) compared to a stage II CPW (pH = 12.5), indicating stabilisation of the metal centre in solution (hydrolysis products) rather than on the solid surface (surface complex) with increasing pH. To date, however, no systematic studies are available, which report pH effects on radionuclide uptake in cementitious systems. In this study we ignore pH effects and take a conservative view of sorption when assigning the same sorption values to both stages of cement degradation.

3.6 Uncertainties in sorption values

3.6.1 Experimental uncertainties

Batch-type sorption studies are usually carried out on powdered cement materials. Experimental uncertainties in the sorption values arise from sample manipulations, e.g., the preparation of the solid material and the suspensions, as well as from radiochemical analysis.

Crushing and grinding results in a potential enhancement of the available sorption sites that would normally not be accessible. ROWAN et al. (1988) determined water vapour adsorption on crushed materials with different average particle size ranges (50 - 125 μm , 125 - 250 μm , 0.5 - 1.0 mm) using the BET method. The specific surface areas are reported to fall within the range between 73 $\text{m}^2 \text{g}^{-1}$ and 91 $\text{m}^2 \text{g}^{-1}$ in spite of the markedly different size ranges of the fragmented samples. Moreover, the surface area seems to be dominated by the contribution from the gel pore structure of HCP, which, apparently, is not affected by the crushing and grinding procedure. Based on the study of ROWAN et al. (1988), we anticipate that preparation of the cement materials is a minor source for experimental uncertainties.

A major uncertainty arises from the preparation of cement suspensions. They are usually prepared by mixing crushed HCP materials with ACW. It was observed that the solid content of the suspensions had to be reduced to 10^{-3}kg L^{-1} or lower to allow accurate measurements of the radionuclide activities in solution for the strongly sorbing radionuclides (e.g., VAN LOON & GLAUS 1998; WIELAND et al. 1998; TITS et al. 2002). However, it appears that the preparation of suspensions with S/L ratios of 10^{-4}kg L^{-1} or lower involves large uncertainties in the effective cement content and the homogeneity of the cement material. Variations in the solid contents by up to a factor of 4 were observed at low S/L ratios (TITS 2002), which explains the large uncertainty in R_d values observed for the strongly sorbing radionuclides. In view of the large

uncertainties associated with sample preparation, the subsequent uncertainties associated with activity measurements (radio assay) are negligible.

In this study an uncertainty factor, f_E , is used to estimate upper and lower limits for the sorption values according to:

$$R_{d,\max} = R_d \cdot f_E \quad (4a)$$

$$R_{d,\min} = R_d/f_E \quad (4b)$$

The experimental uncertainties associated with the R_d values listed in Table 5 are estimated as follows: The uncertainty range of the sorption values is assumed to be about one order of magnitude for the strongly sorbing radionuclides, e.g., namely M(III) and M(IV) metal cations with $R_d \geq 10 \text{ m}^3 \text{ kg}^{-1}$. The uncertainty accounts for variations in the solid contents and the homogeneity of the material at very low S/L ratios. Thus, an uncertainty factor, f_E , of about 3.3 is assigned to R_d values $\geq 10 \text{ m}^3 \text{ kg}^{-1}$. R_d values below $10 \text{ m}^3 \text{ kg}^{-1}$ are usually determined at higher S/L ratios, which reduces uncertainties associated with sample preparation. In this case, R_d values are assumed to vary within a factor of 2, which corresponds to an uncertainty factor, f_E , of about 1.4.

3.6.2 Uncertainties associated with the use of batch data for compacted systems

Greater uncertainties arise in connection with the question whether or not sorption values determined on crushed solid materials are applicable as such for describing sorption on the in situ bulk material. In principle, differences in the water chemistry and in the accessibility of the solid surfaces involve uncertainties when assigning batch sorption values to compacted systems. The interaction of HCP with infiltrating groundwater fixes the CPW composition in cementitious systems. Thus, uncertainties associated with changes in the porewater composition can be excluded. Nevertheless, differences in the surface areas between crushed HCP materials used for batch-type sorption studies and intact HCP may impose additional uncertainties on the sorption values. Crushing rock material results in making available sorption sites that would normally only be accessible via diffusion processes. BRADBURY & BAEYENS (1998) found that rocks containing large proportions of hard, brittle minerals and a low porosity show large differences in the specific surface areas of crushed and intact rock materials. Note, however, that HCP prepared at w/c ratio = 0.3, which is typical for cement materials, has a relatively high total porosity (~25 %) and contains no such hard, brittle minerals. Thus, effects related to the porosity and the mineral composition of a material are expected to be of minor importance in the case of HCP. Indeed, ROWAN et al. (1988) determined the surface area of intact cement specimens to be $55 \pm 5 \text{ m}^2 \text{ g}^{-1}$, which

is less than a factor of 2 lower than the surface areas of crushed materials ($73 \text{ m}^2 \text{ g}^{-1}$ to $91 \text{ m}^2 \text{ g}^{-1}$) as reported by the same authors. Note that the surface area of crushed HCP (size range $\leq 70 \text{ }\mu\text{m}$) prepared from HTS cement was determined to be $46 \pm 4 \text{ m}^2 \text{ g}^{-1}$ (WIELAND et al. 1998). Based on the above consideration we infer that differences in the specific surface areas of intact and crushed HCP materials are negligible. Therefore, for HCP, no additional uncertainty is considered to be associated with the use of batch sorption values in compacted systems.

4 IMPACT OF ORGANICS AND COLLOIDS

The presence of organic ligands and colloids in CPW can have an adverse effect on the immobilization of radionuclides in the near field. The formation of water-soluble complexes in the case of organics and the association of radionuclides with colloidal material can, in principle, reduce the uptake of radionuclides by HCP. According to VAN LOON & GLAUS (1998), the effect of organics can be expressed in terms of a sorption reduction factor, F_{red} :

$$F_{\text{red}} = 1 + \frac{\sum_n \beta_n \cdot [L]^n}{A} \quad (5)$$

where β_n is the stability constant of the metal-ligand complex ML_n , $[L]$ is the concentration of the free, i.e. uncomplexed organic ligand L , and A denotes the side reaction coefficient given by:

$$A = 1 + \sum_k \sum_m \beta_m^k \cdot [I^k]^m \quad (6)$$

with β_m^k as the overall stability constant of the $[MI_m^k]$ species and $[I^k]$ as the concentrations of the free, uncomplexed inorganic ligands, e.g., OH^- , CO_3^{2-} , etc. Eq. 5 shows that the sorption reduction caused by a given complexing ligand L depends on the stability constants of the ML_n complexes and the concentration of the free ligand L . If the ML_n complexes dominate the speciation in solution, i.e. if:

$$\sum_n \beta_n \cdot [L]^n \gg A \quad (7)$$

ligand L has a significant effect on the sorption of the radionuclide, M . The type of solid phase does not play a role as long as sorption is reversible and linear, and the ligand L and the ML_n complexes do not sorb.

The reduction of sorption on HCP caused by the presence of colloids can be treated in a similar manner as sorption reduction caused by complexing ligands. The distribution ratio ($R_{\text{d,eff}}$) in the presence of colloids can then be written as (WIELAND 2001):

$$R_{\text{d,eff}} = \frac{R_d}{(1 + R_c m_c)} = \frac{R_d}{F_{\text{red}}} \quad [\text{m}^3 \text{kg}^{-1}] \quad (8)$$

R_d denotes the distribution ratio of the radionuclide onto HCP (immobile material) in the absence of colloids [$\text{m}^3 \text{kg}^{-1}$]. R_c is the distribution ratio of the metal between the colloidal phase and solution [$\text{m}^3 \text{kg}^{-1}$], and m_c is the concentration of colloids in the fluid [kg m^{-3}]. By analogy with the organics, the effect of colloids on radionuclide sorption is expressed in terms of a sorption reduction factor, F_{red} ($F_{\text{red}} = R_d/R_{d,\text{eff}}$). Eq. 8 reveals that the effect of colloids on radionuclide mobilisation in the backfill depends on the stability of the metal-colloid surface complex (expressed by R_c) and the colloid mass concentration (m_c).

4.1 Cellulose and bitumen degradation products

Examination of the material inventory of the ILW repository reveals that bitumen and cellulose are the only important organics to be considered (McGINNES 2002). The degradation of bitumen has been studied intensively in the past and it has been shown that only radiolytic degradation is of importance (VAN LOON & KOPAJTIC 1991). The main degradation product is oxalate. The effect of oxalate on the sorption of radionuclides is negligible for mainly two reasons: 1) complexes between radionuclides and oxalate are relatively weak, and 2) the concentration of oxalate is small owing to the formation of sparingly soluble calcium oxalate solids (HUMMEL & VAN LOON 1999). Therefore, hydrolysis is much stronger and dominates speciation. Because $A \gg \sum_n \beta_n \cdot [L]^n$, the sorption reduction factor given by Eq. 5 equals 1 for oxalate/bitumen.

Cellulose is known to degrade relatively quickly in an alkaline environment (VAN LOON et al. 1999a). The main degradation product is ISA (GLAUS et al. 1999). It is known that ISA forms stable complexes, especially with tri- and tetravalent nuclides (VERCAMMEN et al. 1999; VERCAMMEN 2000) and can exert a large effect on the sorption of radionuclides (WIELAND et al. 1998; VAN LOON et al. 1999b; WIELAND et al. 2002). The extent of the effect, however, depends on the ISA concentration in solution, which is determined by the amount of cellulose in the repository, the extent of degradation, the stability of ISA, the formation of sparingly soluble solids and the sorption of ISA onto HCP. The extent of degradation is discussed in VAN LOON & GLAUS (1997). Based on the actual knowledge of cellulose degradation it is anticipated that only up to 10 % of the cellulose inventory will degrade to ISA in the first 10^5 years after repository closure. A complete degradation would take 10^6 years (at 25°C). Since there is still some uncertainty involved as to what extent cellulose degradation occurs, a

full degradation of cellulose will be assumed for further calculations⁷. Moreover, ISA is assumed to be stable under alkaline conditions. Owing to the formation of sparingly soluble calcium isosaccharinate solids, the concentration of ISA cannot be higher than 0.1 M (VAN LOON et al. 1999c). However, the main process in regulating the concentration of ISA in CPW is the sorption of ISA on HCP. Recent studies have shown that ISA sorbs strongly on HCP (VAN LOON et al. 1997).

The average concentration of ISA expected in the porewater of the ILW repository can be calculated as follows:

$$[\text{ISA}]_{\text{max}} = \frac{W_{\text{cellulose}}}{\text{MW} \cdot V} \quad [\text{M}] \quad (9)$$

$W_{\text{cellulose}}$ is the weight of cellulose, V is the pore volume, and MW is the molecular weight of the monomeric unit in cellulose (molecular weight of ISA: $\text{MW} = 162$).

The total amount of cellulose, $W_{\text{cellulose}}$, in the ILW repository is estimated to be about 500 kg using the material inventories reported by MCGINNIS (2002). The pore volume, V , amounts to 3'000 m³ with the volume of the repository to be about 10'000 m³ based on the present design given in NAGRA (2002a) and a porosity of 30 %. Assuming that all the cellulose degrades to ISA and, in addition, neglecting ISA sorption on HCP, the maximum (average) concentration of ISA amounts to 10⁻³ M. However, the concentration in the porewater is much lower taking into account ISA sorption on HCP. The aqueous ISA concentration amounts to $\sim 3 \cdot 10^{-6}$ M using the sorption isotherm reported by VAN LOON et al. (1997) at a S/L ratio of 2 kg L⁻¹. The ISA concentration in the porewater is expected to be $\sim 3 \cdot 10^{-7}$ M for a more realistic case, where only 10 % of the cellulose degrades and ISA is allowed to sorb onto HCP. No effect of ISA on the uptake of the safety-relevant radionuclides by HCP has been reported at this concentration level (WIELAND et al. 1998; VAN LOON et al. 1999b; WIELAND et al. 2002). Thus, because $A \gg \sum_n \beta_n \cdot [L]^n$, the sorption reduction factor given in Eq. 5 equals 1 for ISA.

⁷ Note that discrepancies in the interpretation of degradation kinetics have been reported (VAN LOON & GLAUS 1997 and 1998; PAVASARS 1999). Nevertheless, the assumption of a full degradation of cellulose appears to be conservative, but unrealistic, on the basis of our current understanding. An experimental programme to resolve open questions concerning cellulose degradation is ongoing.

4.2 Concrete admixtures

Compounds such as naphthalenesulphonate, melamine formaldehyde, sodium ligninsulphonate, polycarboxylates and sodium gluconate are commonly added to cement mixtures as plasticizers and water content reducers. The effect of such organic compounds on the sorption of radionuclides depends strongly on the molecular structure of the compounds and on their concentration in the porewater. The effect of concrete admixtures on sorption has been investigated for trivalent metal cations, e.g., Eu(III). For example, studies published by SAWYER (1964) and TITS et al. (2002) show that trivalent metal cations tend to form stable complexes with gluconic acid under alkaline conditions, and thus, their sorption behaviour is sensitive to the presence of complexing ligands. GLAUS & VAN LOON (2003) found that naphthalenesulphonate and melamine formaldehyde hardly affect Eu binding onto HCP. By contrast, ligninsulphonate and gluconate (GLU) were found to exert a great effect on Eu uptake by HCP. Furthermore, the study demonstrates that concrete admixtures cannot be treated on the whole, but their effect on sorption has to be investigated individually from case to case.

Like in the case of ISA, the main process in regulating the concentration of concrete admixtures in CPW is sorption on HCP (GLAUS & VAN LOON 2003). For example, the concentration of GLU expected in the porewater of the ILW repository can be estimated as follows: Concretes are manufactured by adding admixtures to cement at typically 0.1 wt %. For the ILW near field, the amount of HCP in contact with porewater is estimated at 2 kg L⁻¹. With this, the maximum GLU concentration to be potentially released into the porewater amounts to 10⁻² M. Nevertheless, due to the strong interaction of GLU with HCP, the organic will predominantly be associated with the solid. Uptake of GLU by HCP significantly reduces the aqueous GLU concentration. Thus, the porewater concentration is estimated to be typically < 10⁻⁷ M using the GLU sorption isotherms determined by GLAUS & VAN LOON (2003). Moreover, recent studies by TITS (2002) show that GLU at [GLU]_{aq} = 10⁻⁷ M has no measurable effect on Eu and Th uptake by CSH phases at pH = 13.3.

The main problem with concrete admixtures stems from the fact that it is presently not known which concrete admixtures will be used for the construction of the repository. Nevertheless, within the Swiss waste management programme, GLU-based concrete admixtures are currently employed for the cement-based conditioning of waste materials, and therefore, GLU is considered to be a constituent of the waste matrix. The new information available on the influence of GLU on radionuclide sorption supports

the approach applied in CEM-97 to estimate the impact of concrete admixtures based on GLU as a representative of organic concrete admixtures. Thus, the sorption reduction factors reported in CEM-97 are still valid and recommended for use in the PA study.

4.3 Sorption reduction due to the presence of colloids

Colloid-facilitated transport may be of importance in the backfill of the ILW repository. A highly permeable "Monokorn" mortar, designation by Nagra as mortar M1, is currently favoured as backfill material for the ILW repository. The backfill was specially designed to allow the release of gas, which could be generated in the repository due to corrosion, and to ensure mechanical stability through the filling of voids between the waste containers. The material consists of about 80 wt % quartz and has a porosity of about 27 % (JACOBS et al. 1994). Due to the presence of quartz, which is unstable in high pH solutions, and the high porosity, the material is considered to be a chemical environment with some potential for colloid formation.

Colloid-facilitated radionuclide migration has been considered in the transport model used for the PA studies of a L/ILW repository (SMITH 1993; SMITH & DEGUELDRE 1993). In this model two colloid parameters are included: 1) the concentration of dispersed colloids, and 2) the distribution ratio of a radionuclide between the colloidal and aqueous phase. Thus, assessment and quantification of the two parameters for a specific near-field environment were the key issues to be addressed in the experimental studies reported by WIELAND (2001).

4.3.1 Colloid mass concentrations in the backfill porewater

Colloid concentrations have been determined in the porewater of the highly permeable mortar. Porewater samples were collected from a column filled with the backfill mortar and used for large-scale flow experiments (WIELAND & SPIELER 2001). Measurements of colloid concentrations were carried out using an in-house developed particle counting system, which was designed to allow detection of colloids at very low concentrations (WIELAND 2001).

To illustrate the influence of the water composition on colloid inventories, the colloid mass concentration determined in CPW can be compared with colloid concentrations determined in water samples collected from various groundwater systems (Fig. 5).

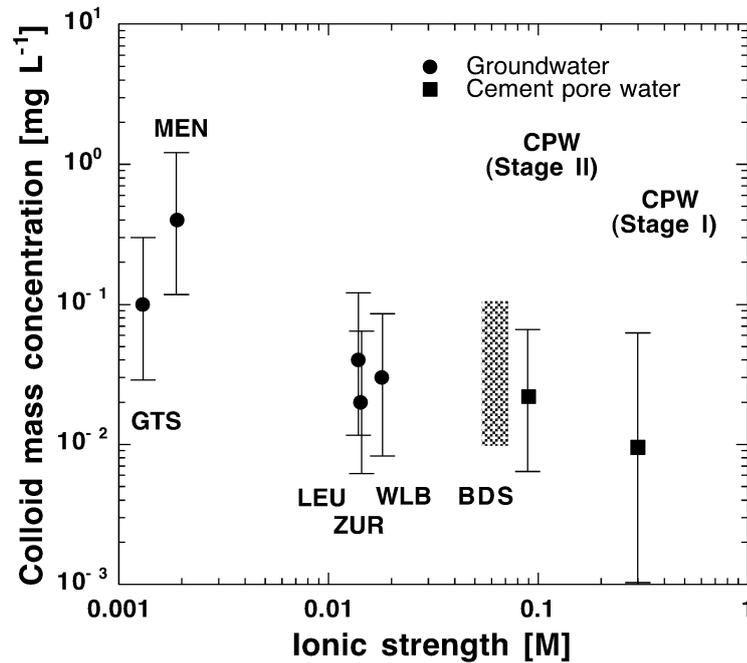


FIGURE 5: Colloid mass concentrations of groundwater and CPW samples shown as a function of the ionic strength of the fluids. The values given for the granitic systems with quasi-stagnant groundwater aquifers (Groundwaters: BDS = Bad Säckingen, MEN = Menzenschwand, LEU = Leuggern, ZUR = Zurzach, GTS = Grimsel Test Site) were published by DEGUELDRE et al. (1996). Data for the Wellenberg site (WLB) were taken from DEGUELDRE (1997). CPW measurements were reported by WIELAND (2001) for a stage I CPW and WIELAND & SPIELER (2001) for a stage II CPW. For the BDS groundwater, the colloid concentration range was estimated based on the experimental data reported by DEGUELDRE et al. (1996). The uncertainty in the data is estimated to be one order of magnitude.

Colloid analysis was conducted on groundwater samples collected from various alpine and pre-alpine subsurface systems (DEGUELDRE 1994; DEGUELDRE et al. 1996; DEGUELDRE 1997). Fig. 5 reveals a trend to lower colloid concentrations with increasing ionic strength in spite of the large differences in the chemical composition of the fluids⁸. The use of ionic strength as master variable is based on the finding that the salt concentration exhibits an influence on colloid inventories in groundwater systems (e.g., DEGUELDRE et al. 1996). Because the ionic strength of CPW is high compared to groundwaters, low colloid concentrations are expected in the water-saturated mortar backfill. Indeed, the colloid concentrations were found to be typically below $\sim 0.1 \text{ mg L}^{-1}$

⁸ Note that the colloid mass concentrations given in Fig. 5 correspond to quasi-stagnant flow regimes, which are anticipated both for the groundwater aquifers and the laboratory settings.

(WIELAND & SPIELER 2001). Moreover, consistently low colloid concentrations were observed when backfill mortar was in contact with ACW of pH 13.3 in batch-type systems (WIELAND 2001). Based on the available data an upper bound on the colloid mass concentration for the backfill is estimated to be $\sim 0.1 \text{ mg L}^{-1}$. It is to be noted that the results obtained from the laboratory studies are in excellent agreement with measurements of colloid concentrations in groundwater samples collected from the highly alkaline aquifer system at the Maqarin site (WETTON et al. 1998). There, colloid mass concentrations were found to range in value between 0.06 mg L^{-1} and 0.19 mg L^{-1} .

The potential impact of organics on colloid stability is discussed in WIELAND (2001). In there it is argued that the potential effect of organics on colloid stability may be negligible due to the low concentrations of natural (e.g., humic acids) and near-field derived organics (e.g., ISA, concrete admixtures) expected for the ILW porewater. Therefore, at low concentrations of organics, the long-term colloid concentration of the near-field CPW is expected to be less than about 0.1 mg L^{-1} .

4.3.2 R_c values

The affinity of a radioelement for HCP (expressed by R_d) and for the colloidal material (expressed by R_c) are tentatively related by a scaling factor, S_c (WIELAND 2001):

$$R_c = S_c \cdot R_d \quad (10)$$

The scaling factor depends on 1) the sorption capacity, i.e., the total site concentration, and 2) the binding constants (surface complexation constant) of a radioelement for the bulk and the colloidal phases. The total number of surface sites (expressed in moles per gram) is assumed to be proportional to the specific surface area of the near-field materials, whereas the binding constant of a radioelement only depends on the chemical nature of the surface sites of the bulk and colloidal materials. In this study it is assumed that the chemical nature of the surface sites exposed both on HCP and cement-derived colloids are similar (WIELAND 2001). On this assumption, differences in the binding constants can be ignored. Differences in the capacities of HCP and cement-derived colloids can be taken to be proportional to differences in the specific surface areas. The specific surface area of intact HCP was estimated to be $\sim 50 \text{ m}^2 \text{ g}^{-1}$ (ROWAN et al. 1988). The specific surface area of the colloidal material was estimated to range in value between $240 \text{ m}^2 \text{ g}^{-1}$ and $770 \text{ m}^2 \text{ g}^{-1}$ (WIELAND & SPIELER 2001). With this, a realistic upper limit for the scaling factor, S_c , is estimated to be $S_c \sim 20$ (range ~ 5 to ~ 16).

4.3.3 Sorption reduction in the presence of near-field colloids

The effect of colloids on radionuclide mobilisation can be estimated using Eq. 8. WIELAND (2001) assessed sorption reduction effects caused by the presence of cement-derived near-field colloids, assuming a realistic and a pessimistic upper limit for the scaling factor, i.e., $S_c = 20$ (realistic) and $S_c = 100$ (upper bound value). For both cases, the R_d values are assumed to range in value between $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ (very weakly sorbing radionuclides) and $100 \text{ m}^3 \text{ kg}^{-1}$ (strongly sorbing radionuclides). Fig. 6 shows the dependence of the sorption reduction factor, F_{red} , on the colloid mass concentration for the realistic case. An increase in F_{red} indicates increased mobilisation of radionuclides in CPW. Fig. 6 reveals no colloid-derived effect on the retardation of weakly to moderately sorbing radionuclides ($R_d \leq 1 \text{ m}^3 \text{ kg}^{-1}$) up to colloid concentrations of about $10^{-3} \text{ kg m}^{-3}$ (1 ppm). Some effect on sorption is predicted for the strongly sorbing radionuclides with $R_d > 1 \text{ m}^3 \text{ kg}^{-1}$. However, this effect is almost insignificant up to a colloid concentration of about $10^{-4} \text{ kg m}^{-3}$ (0.1 ppm) ($F_{\text{red}} = 1.2$). Using the upper bound value $S_c = 100$, the sorption reduction factor for the strongly sorbing radionuclides ($R_d = 100 \text{ m}^3 \text{ kg}^{-1}$) amounts to $F_{\text{red}} = 2$ at a colloid concentration of $10^{-4} \text{ kg m}^{-3}$. Note that the sorption reduction factors are larger for a colloid concentration of 1 ppm, i.e., $F_{\text{red}} \sim 3$ ($S_c = 20$) and $F_{\text{red}} \sim 10$ ($S_c = 100$), respectively.

In Table 6, sorption reduction factors are listed for both cases (realistic and upper bound), assuming a colloid mass concentration of $10^{-4} \text{ kg m}^{-3}$ (0.1 ppm). Effective sorption values, $R_{d,\text{eff}}$, can be calculated from Eq. 8 using the sorption values, R_d , given in Table 5 and the reduction factors, F_{red} , listed in Table 6.

It is worth re-emphasising here that the above assessment of the effect of near-field colloids on sorption is based on two assumptions: first, the scaling factor only accounts for differences in the specific surface areas of the bulk and colloidal materials. Secondly, it is assumed that the kinetics of the interaction processes with both bulk and colloidal materials are reversible. Note that the transport models used in PA studies also account for irreversible sorption processes. An irreversible binding mechanism is expected when colloid formation and radionuclide sorption coincide, resulting in an “encapsulation” effect. Therefore, future studies focussing on the mode of radionuclide-surface interactions, i.e., the extent of reversibility of the uptake process, are required to assess possible implications for PA studies.

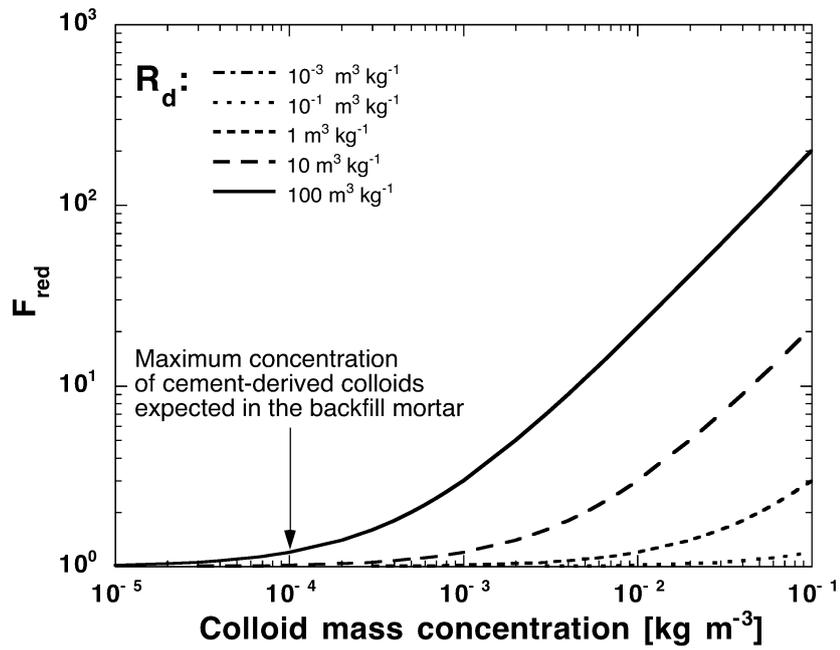


FIGURE 6: Effect of colloids on the retardation of radionuclides for the realistic case. F_{red} denotes the sorption reduction factor in the presence of colloids (Eq. 8). R_d and R_c values are related by a scaling factor, S_c , of 20.

5 SUMMARY

This report describes how sorption values for the cementitious near field of a repository for long-lived intermediate-level radioactive wastes (ILW) have been selected taking into account previous cement sorption data bases (SDB) compiled for the cementitious near field of the repository for low- and intermediate-level radioactive wastes (L/ILW) (BRADBURY & SAROTT 1995; BRADBURY & VAN LOON 1998).

Model calculations reported by NEALL (1994) and SCHWYN et al. (2003) show that the chemical compositions of L/ILW and ILW cement porewaters (CPW) are similar. Differences in results for the high and low saline near-field conditions as reported in these studies reflect the large differences in ionic strength of the input groundwaters. We anticipate that variations in the L/ILW and ILW CPW compositions, i.e., differences in pH and the concentrations of complexing anions such as CO_3^{2-} , SO_4^{2-} , F^- , Cl^- and $\text{H}_2\text{SiO}_4^{2-}$ are too small to exert any significant effect on radionuclide speciation and uptake processes.

Selection of the sorption values (R_d values) is based on in-house sorption measurements and a critical survey of the literature. Changes to, or re-appraisals of, the sorption values recommended in the L/ILW SDBs (BRADBURY & SAROTT 1995; BRADBURY & VAN LOON 1998) were only made if new information and/or data were available. Otherwise, the sorption values were taken as given in the previous SDBs. The selection of sorption values in the L/ILW SDBs was based on a CPW composition corresponding with the L/ILW case. Thus, due to similarities of the CPW compositions of the cementitious L/ILW and ILW near fields, the R_d values selected for the L/ILW near field can also be used for the ILW repository. The sorption values recommended for the safety-relevant radionuclides of an ILW repository are summarised in Table 5 (units of m^3 per kg hardened cement paste (HCP)). In this study uncertainty ranges have been assigned to sorption values taking into account estimates for the uncertainties on the experimental data.

For some key radio-elements, i.e., Cs(I), Sr(II), Ni(II), Eu(III), Th(IV) and Sn(IV), new information was also available from in-house measurements. In these studies, the dependence of the sorption values on the HCP to porewater ratio (S/L ratio) of the cement systems was investigated for the elements mentioned above. The sorption values of Cs(I), Sr(II), Eu(III), Th(IV) and Sn(IV) are found to be constant irrespective of the S/L ratio as expected for a sorption-type uptake process. This is not the case for Ni(II), where a solubility-controlled limitation of the Ni concentration in cement systems is

indicated based on measurements of stable Ni inventories. The determination of stable element inventories enables us to assess the use of batch-type sorption values under repository conditions in more detail and, above all, to distinguish sorption-controlled from solubility-controlled uptake in cement systems. Finally, a first attempt has been made to prove consistency in the sorption data determined for the key radioelements by correlating the sorption values with important chemical characteristics of the metal centres, i.e., the ratio of the effective charge of the metal centre to the distance of the metal oxygen bond.

The effects of bitumen, cellulose degradation products, concrete admixtures as well as cement-derived colloids, on radionuclide uptake by HCP are assessed within the framework of this study. Bitumen and cellulose are the most important groups of organic materials in ILW. Their influence on radionuclide sorption was quantified based on the current knowledge of the degradation processes and the sorption properties of the degradation products. The concentrations of the main degradation products in the porewater of an ILW near field, i.e., oxalate in the case of bitumen and isosaccharinic acid (ISA) in the case of cellulose, are found to be too low to exert any significant effect on radionuclide sorption.

Recent studies indicate that concrete admixtures cannot be treated in general, but their effect on sorption has to be considered individually from case to case (GLAUS & VAN LOON 2003). In this study, the effect of concrete admixtures is assessed using gluconate as a representative, mainly for two reasons. First, gluconate has the largest effect on the uptake of tri- and tetravalent radioelements by HCP. Secondly, gluconate-based concrete admixtures are used for the cement-based conditioning of waste matrices. Thus, the approach proposed by BRADBURY & VAN LOON (1998) to estimate sorption reduction by concrete admixtures based on gluconate is still valid.

A sorption reduction factor has been used to account for the potential effect of colloids on radionuclide mobilisation. Realistic and upper bound values for this factor can be estimated assuming different values for the scaling factor, S_c , which interrelates the sorption value on HCP (R_d) and the colloidal phase (R_c). For the realistic case ($S_c = 20$), sorption reduction is expected to be almost insignificant up to a colloid concentration in CPW of 0.1 mg L^{-1} and for the safety-relevant radionuclides with $R_d \leq 10 \text{ m}^3 \text{ kg}^{-1}$. A minor effect is expected only in the case of strongly sorbing radionuclides ($R_d = 100 \text{ m}^3 \text{ kg}^{-1}$). Using the upper bound value ($S_c = 100$) results in a sorption reduction by less than a factor of two for $R_d \leq 100 \text{ m}^3 \text{ kg}^{-1}$.

6 SUMMARY OF SORPTION VALUES AND REDUCTION FACTORS

TABLE 5: Selected sorption values for HCP ($\text{m}^3 \text{kg}^{-1}$).

Element	Region of cement degradation ¹				f_E ³	Ref.
	Stage I		Stage II			
	Oxid.	Red.	Oxid.	Red.		
H (HTO)	10^{-4}	10^{-4}	10^{-4}	10^{-4}	1.4	this work
Be	0	0	0	0		this work
CO_3^{2-}	See section 5.27 in CEM-94					CEM-94
Cl	$5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	1.4	CEM-97
Ca, Fe, Co, Ni ²	Solubility limitation					this work
Se	10^{-3}	$3 \cdot 10^{-2}$	10^{-3}	$3 \cdot 10^{-2}$	1.4	this work
Sr	10^{-1}	10^{-1}	10^{-3}	10^{-3}	1.4	this work
Zr	10	10	10	10	3.3	this work
Nb	1	1	1	1	1.4	CEM-97
Mo	0	0	0	0		CEM-97
Tc	10^{-3}	1	10^{-3}	1	1.4	CEM-97
Ru	0	0	0	0		this work
Pd	10^{-1}	10^{-1}	10^{-1}	10^{-1}	1.4	CEM-97
Ag	0	0	0	0		CEM-97
Sn	10	10	10	10	3.3	this work
Sb	10^{-3}	10^{-1}	10^{-3}	10^{-1}	1.4	this work
I	10^{-3}	10^{-3}	10^{-3}	10^{-3}	1.4	this work
Cs	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$5 \cdot 10^{-3}$	$5 \cdot 10^{-3}$	1.4	this work
Pm	100	100	100	100	3.3	this work
Sm	100	100	100	100	3.3	this work
Eu	100	100	100	100	3.3	this work
Pb	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	$5 \cdot 10^{-1}$	1.4	CEM-97
Po	0	0	0	0		CEM-97
Ra	10^{-1}	10^{-1}	$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	1.4	this work
Ac	100	100	100	100	3.3	this work
Th	100	100	100	100	3.3	this work
Pa	10^{-1}	100	10^{-1}	100	1.4/3.3	this work
U	2	100	2	100	1.4/3.3	this work
Np	10^{-1}	100	10^{-1}	100	1.4/3.3	this work
Pu	10^{-1}	100	10^{-1}	100	1.4/3.3	this work
Am	100	100	100	100	3.3	this work
Cm	100	100	100	100	3.3	this work

¹ Definitions of the regions of the cement degradation are given in CEM-94.

² Solubility limits are given in BERNER (1999) and in Sections 3.2 and 3.4.1.

³ Experimental uncertainty limits are given according to Eq. 4 (Section 3.6).

TABLE 6: Sorption reduction factors (realistic and upper bound (pessimistic) values), F_{red} , for sorption on HCP in the presence of cement-derived near-field colloids assuming a typical colloid concentration of $10^{-4} \text{ kg m}^{-3}$. Sorption reduction factors are listed for the elements with sorption values different from zero. F_{red} is calculated from Eq. 8, using the R_d values listed in Table 5. R_d and R_c values are related by a scaling factor, S_c , which is set to $S_c = 20$ (realistic case) and $S_c = 100$ (upper bound value).

Element	Region of cement degradation			
	Stage I		Stage II	
	Oxid. real./pess.	Red. real./pess.	Oxid. real./pess.	Red. real./pess.
H (HTO)	1/1	1/1	1/1	1/1
Cl	1/1	1/1	1/1	1/1
Se	1/1	1/1	1/1	1/1
Sr	1/1	1/1	1/1	1/1
Zr	1.02/1.1	1.02/1.1	1.02/1.1	1.02/1.1
Nb	1/1.01	1/1.01	1/1.01	1/1.01
Tc	1/1	1/1.01	1/1.01	1/1
Pd	1/1	1/1	1/1	1/1
Sn	1.02/1.1	1.02/1.1	1.02/1.1	1.02/1.1
Sb	1/1	1/1	1/1	1/1
I	1/1	1/1	1/1	1/1
Cs	1/1	1/1	1/1	1/1
Pm	1.2/2	1.2/2	1.2/2	1.2/2
Sm	1.2/2	1.2/2	1.2/2	1.2/2
Eu	1.2/2	1.2/2	1.2/2	1.2/2
Pb	1/1	1/1	1/1	1/1
Ra	1/1	1/1	1/1	1/1
Ac	1.2/2	1.2/2	1.2/2	1.2/2
Th	1.2/2	1.2/2	1.2/2	1.2/2
Pa	1/1	1.2/2	1/1	1.2/2
U	1/1.01	1.2/2	1/1.01	1.2/2
Np	1/1	1.2/2	1/1	1.2/2
Pu	1/1	1.2/2	1/1	1.2/2
Am	1.2/2	1.2/2	1.2/2	1.2/2
Cm	1.2/2	1.2/2	1.2/2	1.2/2

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8 ACKNOWLEDGEMENTS

The careful reviews from and many valuable comments made by Drs. D. Pellegrini and F. Besnus (IRSN), Dr. A. Johnson (EAWAG), and Drs. M. Bradbury (PSI), U. Berner (PSI) and J. Hadermann (PSI) are gratefully acknowledged. Thanks are extended to Dr. J. Tits (PSI) for allowing us to use some of his unpublished sorption data. We wish to thank Dr. I. Hagenlocher (Nagra) for a translation of the abstract, Drs. I. Hagenlocher (Nagra), B. Schwyn (Nagra) and P. Wersin (Nagra) for their constructive comments on the manuscript and continuous support of this study, and B. Gschwend (PSI) for the final layout work. Partial financial support by the National Cooperative for the Disposal of Radioactive Waste (Nagra) is kindly acknowledged.

APPENDIX I

E. WIELAND

DISTRIBUTION RATIOS FOR SAFETY-RELEVANT RADIONUCLIDES IN THE CEMENTITIOUS NEAR FIELD OF THE ILW REPOSITORY

PREFACE

Appendix I of this report provides a set of distribution ratios (R_d values) for use in predicting the partitioning of safety-relevant radioelements between hardened cement paste (HCP) and cement porewater (CPW) in the near field of the planned Swiss repository for long-lived intermediate-level radioactive waste (ILW). In the main part of this report (Chapters 1 to 7), the sorption values for safety-relevant radionuclides of both their reduced and oxidised forms have been deduced according to the chemical conditions anticipated for a cementitious near field without specifying reference redox potentials. In this appendix, the sorption values are selected from the main part of this report, taking into account the reference redox conditions in the ILW repository. For this, speciation of the safety-relevant radionuclides is considered in view of assigning the dominant oxidation state to the radioelements under the given CPW conditions, that is for an initial stage of cement degradation ($E_h = -430$ mV, $pH = 13.44$), for the reference case ($E_h = -230$ mV, $pH = 12.55$), and under oxidising conditions ($E_h = +350$ mV) expected for specific waste forms.

From the main part of this report (Chapter 3) it emerges that the uptake of C (CO_3^{2-}), Ca, Fe, Co and Ni by HCP cannot be described in terms of an adsorption-type process. Thus, for these elements, an approach is developed in this appendix, which allows upper bounds for the concentration of the corresponding radioisotopes to be estimated based on solubility limits and isotopic exchange as potential retention mechanism.

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1 INTRODUCTION

This report provides a set of distribution ratios (R_d values) recommended for use in the disposal feasibility study for a repository for long-lived intermediate-level radioactive waste (ILW) in the Opalinus clay (OPA) host rock. The R_d values account for the immobilization of safety-relevant radioelements in the cementitious near field of the ILW repository. The values reported here are taken from a larger set of R_d values previously compiled in sorption data bases (SDBs), taking into account recently reported assessments of the chemical conditions in the cementitious near field of the ILW repository by WERSIN et al. (2003) and SCHWYN et al. (2003). The selection procedures and detailed discussions of the individual R_d values are given in the SDBs published by BRADBURY & SAROTT (1995), BRADBURY & VAN LOON (1998) and WIELAND & VAN LOON (2003).

For some of the safety-relevant radionuclides, that is ^{14}C , ^{41}Ca , ^{55}Fe , ^{60}Co and $^{59/63}\text{Ni}$, retention in the cementitious near field is assessed based on solubility limits and on the assumption that isotopic exchange is the uptake-controlling process. This approach accounts for the notion that the retention of these elements in a cementitious environment is controlled by solubility limits rather than sorption-type processes.

2 BACKGROUND

2.1 Oxidation states

The oxidation states of the redox-sensitive radioelements present in the intermediate-level radioactive waste and to be taken into account for the present study are listed in Table AI-1. The list is a compilation of two tables published earlier by BRADBURY & SAROTT (1995) and WIELAND & VAN LOON (2003). It is noted that, in general, solubility limits and the extent of sorption are strongly influenced by the oxidation state of a radioelement, which is determined by the Eh of the cementitious near field, and the speciation of an element in solution under alkaline conditions. Compilation of operational “reference” porewaters for the cementitious near field of the ILW repository, which includes estimates for Eh and pH, thus was a prerequisite for assigning R_d values to the redox-sensitive radioelements.

2.2 The reference porewater

The expected compositions of the reference cement porewaters (CPW) can be found in SCHWYN et al. (2003), whereas the development of redox conditions in the cementitious near field is described by WERSIN et al. (2003). The pH of the CPW for the reference case is 12.55 corresponding to the pH of a CPW in the stage II of cement degradation (SCHWYN et al. 2003). Note that, in this stage, the chemical composition of the alkali-depleted CPW is controlled by the solubility of portlandite, which fixes the total Ca concentration at about 20 mM and the pH at about 12.5. The reference redox potential was estimated to be about -230 mV based on speciation calculations assuming magnetite as the dominant Fe bearing phase and an upper limit of 10^{-7} M for dissolved Fe(II,III) in CPW (WERSIN et al. 2003). In the initial stage, i.e., the stage I of cement degradation, the composition of CPW is determined by the release of alkali hydroxides (NaOH and KOH), which fixes the pH at about 13.4 and Eh at about -430 mV (SCHWYN et al. 2003). Oxidising conditions (Eh = +350 mV), however, may prevail, at least temporary, in specific waste streams containing large inventories of nitrates (WERSIN et al. 2003).

For this study the recommendations made by WERSIN et al. (2003) and SCHWYN et al. (2003) concerning the reference redox potentials and compositions of the porewaters for both stages of the cement degradation are accepted, and pH and Eh are taken as given above. R_d values are reported for the reference case, i.e., for chemical conditions corresponding to the reference porewater (Table AI-2) and, in addition, for the initial phase of cement degradation (Table AI-3). Redox-specific R_d values are listed for those redox-sensitive radionuclides where changes in the oxidation state are expected upon an increase of Eh to +350 mV (Table AI-4).

TABLE AI-1: Oxidation states of the redox-sensitive ILW-specific radioelements.

Element	Oxidised state	Reduced state
Fe	+III	+II
Se	+VI	+IV/-II
Nb	+V	+III
Mo	+VI	+IV
Tc	+VII	+IV/+II
Ru	+VI	+IV/0
Pd	+II	0
Sn	+IV	+II
Sb	+V	+III
Po	+IV	+II
Pu	+V	+IV/+III
U	+VI	+IV
Np	+V	+IV/+III
Pa	+V	+IV

2.3 Thermodynamic calculations

Speciation calculations for the safety-relevant radionuclides under CPW conditions can be found in BERNER (2003). These calculations were performed using the updated Nagra/PSI thermochemical data base (HUMMEL et al. 2002). The dominant redox states were assigned on the basis of the compilations reported by BERNER (2003) or unpublished speciation calculations (BERNER, pers. comm.).

2.4 Sorption data bases

SDBs for a cementitious near field have been published by BRADBURY & SAROTT (1995) and BRADBURY & VAN LOON (1998) and more recently by WIELAND & VAN LOON (2003). These SDBs are the main data sources for the selection process described in this study. The SDBs have been developed using similar procedures concerning data evaluation and the selection process to ensure continuity in the methodology. Thus, the procedures applied here to select representative sorption values for the stages I and II of cement degradation are described in detail in the above SDBs. Furthermore, possible effects of organic ligands and colloids present in the near field have been addressed in these SDBs.

3 ILW - RECOMMENDED SORPTION VALUES

3.1 Distribution ratios for the redox-sensitive radionuclides

The following considerations apply to the redox-sensitive radioelements listed in Table AI-1 except Fe. The partitioning of the latter element will be estimated in Section 3.2, taking into account solubility limits and isotopic exchange. The distribution ratios summarized in Tables AI-2, AI-3 and AI-4 account for the partitioning of the redox-sensitive radioelements between HCP and CPW under the conditions relevant to the near field of an ILW repository in OPA (reference case, initial phase, oxidising conditions). The tables further include upper and lower bound values using estimates for the uncertainties on the experimental data (WIELAND & VAN LOON 2003).

Selenium:

Se(-II) and Se(IV) are the dominant redox states under the given redox and pH conditions, and HSe^- and SeO_3^{2-} are the dominant species (BERNER 2003). Note that SeO_3^{2-} is the dominant species under moderately reducing conditions, whereas Se(-II) dominates under strongly reducing conditions. The distribution ratios given in Tables AI-2 and AI-3 are selected on the assumption that Se(IV) is the relevant oxidation state under the conditions prevailing in the near field and based on in-house sorption data for SeO_3^{2-} (WIELAND & VAN LOON 2003). It is to be noted that, to date, no sorption data exist for the Se(-II)/HCP system, and therefore, the same R_d value is assigned to Se(IV) and Se(-II) species. SeO_4^{2-} (Se(VI)) is the dominant species under oxidising conditions. The R_d value of $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ as listed in Table AI-4 was reported by BRADBURY & VAN LOON (1998).

Niob, Molybdenum:

In the Nb system NbO_3^- (or $\text{Nb}(\text{OH})_6^-$) is found to be the dominant complex in solution under the conditions prevailing in the ILW repository (BERNER 2003). The distribution ratios listed in Tables AI-2 and AI-3 were reported by BRADBURY & VAN LOON (1998).

Speciation calculations reveal that MoO_4^{2-} is the dominant complex in the Mo system (BERNER 2003). No sorption data are available for Mo(VI) to the best of our knowledge. Although weak uptake by HCP is anticipated as, for example, observed in the case of Se(VI), the distribution ratio is set to zero due to lack of back-up from experimental data.

Technetium:

TcO_4^- (Tc(VII)) and $\text{TcO}(\text{OH})_3^-$ (Tc(IV)) are the dominant species at $E_h < -230$ mV and $\text{pH} \geq 12.55$ (BERNER 2003). BRADBURY & SAROTT (1995) selected a distribution ratio of $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ for Tc(VII), which is the value accepted for this study (Tables AI-2 and AI-3). The same value is assigned to $\text{TcO}(\text{OH})_3^-$ as no sorption data are available for Tc(IV).

Ruthenium:

Almost no thermodynamic data are known for Ru and, therefore, no speciation calculations are available (BERNER, pers. comm.). In addition, no sorption data have been reported to the best of our knowledge. WIELAND & VAN LOON (2003) set the distribution ratios to zero due to conflicting information available on the relevant oxidation states and lack of knowledge on the speciation in aqueous solution.

Palladium:

Dissolved Pd exists only in the oxidation state +II (BERNER 2003). The distribution ratios given in Tables AI-2 and AI-3 for Pd(II) are taken from BRADBURY & VAN LOON (1998).

Tin:

Speciation calculations reveal that Sn(II) is not stable in the E_h range between -790 mV and -230 mV at $\text{pH} \geq 12.55$ (BERNER 2003). Thus, the Sn system is dominated by Sn(IV), and $\text{Sn}(\text{OH})_6^{2-}$ is the dominant complex. The distribution ratios recommended in Tables AI-2 and AI-3 are selected based on back-up from in-house sorption studies (WIELAND & VAN LOON 2003).

Antimony:

The speciation calculations reported by BERNER (2003) show that the Sb system is determined by Sb(V) at redox potentials above -600 mV. WIELAND & VAN LOON (2003) assigned a distribution ratio of $10^{-3} \text{ m}^3 \text{ kg}^{-1}$ to Sb(V) (Tables AI-2 and AI-3).

Polonium:

No speciation calculations are available due to lack of thermodynamic data. Moreover, no sorption data are available to the best of our knowledge. BRADBURY & VAN LOON (1998) set the distribution ratio to zero (Tables AI-2 and AI-3).

Plutonium, Neptunium:

At $E_h < -230$ mV the Pu and Np systems are determined by the oxidation state +IV, and $\text{Pu}(\text{OH})_4(\text{aq})$ and $\text{Np}(\text{OH})_4(\text{aq})$ are the dominant complexes (BERNER 2003). Note that Np(III) and Pu(III) exist only under extremely reducing conditions (BERNER, pers. comm.), and therefore, the oxidation state +III is ignored in this study.

Th(IV) is considered to be an appropriate chemical analogue for the tetravalent actinides (BRADBURY & SAROTT 1995). Thus, the high distribution ratio selected for Th(IV) by WIELAND & VAN LOON (2003) ($R_d = 100 \text{ m}^3 \text{ kg}^{-1}$) is also assigned to Pu(IV) and Np(IV) due to similarities in speciation under alkaline conditions.

Under oxidising conditions pentavalent NpO_2^+ and PuO_2^+ are considered to be the dominant complexes (BERNER 2003). Because no sorption data have been reported for these species to date, WIELAND & VAN LOON (2003) use a nominal sorption value ($R_d = 0.1 \text{ m}^3 \text{ kg}^{-1}$) for both Np(V) and Pu(V). This value is accepted for the present study (Table AI-4).

Uranium, Protactinium:

Speciation calculations indicate that U(VI) is the stable redox state at $E_h > -430$ mV and $\text{pH} \geq 12.55$ (BERNER 2003). The uranyl cation, UO_2^{2+} , hydrolyses under strongly alkaline conditions to form $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$ complexes. A sorption value of $R_d = 2 \text{ m}^3 \text{ kg}^{-1}$ was selected by BRADBURY & VAN LOON (1998). The value is retained for this study (Tables AI-2 and AI-3).

The Nagra/PSI thermochemical data bases do not include data for Pa (PEARSON et al. 1991; HUMMEL et al. 2002) and, therefore, no speciation calculations for Pa under CPW conditions are available. BERNER (2003) suggests the use of U as an appropriate chemical analogue for Pa. However, in contrast to U, +IV and +V are the only possible oxidation states of Pa. In this study, the Pa system is considered to be determined by Pa(V) under the conditions relevant to a cementitious near field. With this and by analogy with Np(V), a nominal sorption value of $R_d = 0.1 \text{ m}^3 \text{ kg}^{-1}$ is assigned to Pa(V).

3.2 Distribution ratios for the redox-stable radionuclides

The distribution ratios for the redox-stable radioelements listed in Tables AI-2 and AI-3, i.e., H(HTO), Be(II), Cl(-I), Sr(II), Zr(IV), Ag(I), I(-I), Cs(I), Pm(III), Sm(III), Eu(III), Pb(II), Ra(II), Th(IV), Ac(III), Am(III) and Cm(III), correspond to values previously published by BRADBURY & VAN LOON (1998) and WIELAND & VAN LOON (2003).

3.3 The partitioning of ^{14}C , ^{41}Ca , ^{55}Fe , ^{60}Co and $^{59/63}\text{Ni}$

BRADBURY & SAROTT (1995) discuss possible modes of the immobilization of ^{14}C in cementitious near fields. Isotopic exchange between dissolved $^{14}\text{CO}_3^{2-}$ and CaCO_3 of the near field is regarded as being the dominant process controlling the retention of ^{14}C . The approach presented by these authors is adopted for this study.

The data reported by WIELAND & VAN LOON (2003) indicate that the concentrations of Ca, Fe, Co and Ni in the cementitious near field of an ILW repository are determined by solubility-limiting rather than sorption-type processes. For example, experimental and modelling studies show that the Ca concentration in CPW is controlled by portlandite solubility at $\text{pH} = 12.55$ (e.g., BERNER 1992). Furthermore, the concentration of dissolved Fe is expected to be controlled by sparingly soluble calcium-aluminium-ferrite phases present in the cement matrix (TAYLOR 1997). In the case of Ni, however, EXAFS studies indicate the formation of mixed Ni-Al layered double hydroxides (LDH) which are considered to be the solubility-limiting phases in cementitious systems (SCHEIDEGGER et al. 2000). This may also be true for Co due to chemical similarity of Ni and Co. It is noted here that robust thermodynamic data for some of these phases are still lacking.

In this study the partitioning of the above-mentioned radioelements is tentatively described in terms of isotopic exchange and on the assumption that a solubility-limiting process may effectively control the aqueous concentrations of the elements. Isotopic exchange accounts for a process by which the radiosotopes of an element present in CPW replace stable isotopes of the same element associated with the cement matrix.

TABLE AI-2: Reference case: Distribution ratios for the stage II of cement degradation.

Element	R _d value (m ³ kg ⁻¹)			Ref.
	recomm- ended	Estimated lower limit	Estimated upper limit	
H (HTO)	10⁻⁴	7.1·10 ⁻⁵	1.4·10 ⁻⁴	W&VL 03
Be(II)	0			W&VL 03
CO ₃ ²⁻ (C-14)	Section 5.27 in B&S 95 and next section			
Cl(-I)	5·10⁻³	3.6·10 ⁻³	7·10 ⁻³	W&VL 03
Ca, Fe, Co, Ni	Next section			
Se(IV)	3·10⁻²	2.1·10 ⁻²	4.2·10 ⁻²	W&VL 03
Sr(II)	10⁻³	7.1·10 ⁻⁴	1.4·10 ⁻³	W&VL 03
Zr(IV)	<i>10</i>	<i>3</i>	<i>33</i>	W&VL 03
Nb(V)	1	0.7	1.4	B&VL 98
Mo(VI)	0			B&VL 98
Tc(VII)	10⁻³	7.1·10 ⁻⁴	1.4·10 ⁻³	B&VL 98
Ru	0			W&VL 03
Pd(II)	<i>10⁻¹</i>	<i>7.1·10⁻²</i>	<i>1.4·10⁻¹</i>	B&VL 98
Ag(I)	0			B&VL 98
Sn(IV)	10	3	33	W&VL 03
Sb(V)	<i>10⁻³</i>	<i>7.1·10⁻⁴</i>	<i>1.4·10⁻³</i>	W&VL 03
I(-I)	10⁻³	7.1·10 ⁻⁴	1.4·10 ⁻³	W&VL 03
Cs(I)	5·10⁻³	3.6·10 ⁻³	7·10 ⁻³	W&VL 03
Pm(III)	<i>100</i>	<i>30</i>	<i>330</i>	W&VL 03
Sm(III)	<i>100</i>	<i>30</i>	<i>330</i>	W&VL 03
Eu(III)	100	30	330	W&VL 03
Pb(II)	5·10⁻¹	3.6·10 ⁻¹	7·10 ⁻¹	B&VL 98
Po	0			B&VL 98
Ra(II)	<i>5·10⁻²</i>	<i>3.6·10⁻²</i>	<i>7·10⁻²</i>	B&VL 98
Ac(III)	<i>100</i>	<i>30</i>	<i>330</i>	W&VL 03
Th(IV)	100	30	330	W&VL 03
Pa(V)	<i>10⁻¹</i>	<i>7.1·10⁻²</i>	<i>1.4·10⁻¹</i>	W&VL 03
U(VI)	2	1.4	2.8	W&VL 03
Np(IV)	<i>100</i>	<i>30</i>	<i>330</i>	W&VL 03
Pu(IV)	<i>100</i>	<i>30</i>	<i>330</i>	W&VL 03
Am(III)	<i>100</i>	<i>30</i>	<i>330</i>	W&VL 03
Cm(III)	<i>100</i>	<i>30</i>	<i>330</i>	W&VL 03

Bold type: Sorption values are selected based on experimental data including estimates for the uncertainties.

Italic type: Sorption values are selected based on chemical analogy including expected uncertainty limits.

References: B&S 95: BRADBURY & SAROTT (1995)
 B&VL 98: BRADBURY & VAN LOON (1998)
 W&VL 03: WIELAND & VAN LOON (2003)

TABLE AI-3: Initial phase: Distribution ratios for the stage I of cement degradation.

Element	R_d value ($m^3 kg^{-1}$)			Ref.
	recomm- ended	Estimated lower limit	Estimated upper limit	
H (HTO)	10^{-4}	$7.1 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	W&VL 03
Be(II)	0			W&VL 03
CO ₃ ²⁻ (C-14)	Section 5.27 in B&S 95 and next section			
Cl(-I)	$5 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$	$7 \cdot 10^{-3}$	W&VL 03
Ca, Fe, Co, Ni	Next section			
Se(IV)	$3 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$	W&VL 03
Sr(II)	10^{-1}	$7.1 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$	W&VL 03
Zr(IV)	<i>10</i>	3	33	W&VL 03
Nb(V)	1	0.7	1.4	B&VL 98
Mo(VI)	0			B&VL 98
Tc(VII)	10^{-3}	$7.1 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	B&VL 98
Ru	0			W&VL 03
Pd(II)	<i>10^{-1}</i>	<i>$7.1 \cdot 10^{-2}$</i>	<i>$1.4 \cdot 10^{-1}$</i>	B&VL 98
Ag(I)	0			B&VL 98
Sn(IV)	10	3	33	W&VL 03
Sb(V)	<i>10^{-3}</i>	<i>$7.1 \cdot 10^{-4}$</i>	<i>$1.4 \cdot 10^{-3}$</i>	W&VL 03
I(-I)	10^{-3}	$7.1 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	W&VL 03
Cs(I)	$5 \cdot 10^{-4}$	$3.6 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	W&VL 03
Pm(III)	<i>100</i>	30	330	W&VL 03
Sm(III)	<i>100</i>	30	330	W&VL 03
Eu(III)	100	30	330	W&VL 03
Pb(II)	$5 \cdot 10^{-1}$	$3.6 \cdot 10^{-1}$	$7 \cdot 10^{-1}$	B&VL 98
Po	0			B&VL 98
Ra(II)	<i>10^{-1}</i>	<i>$7.1 \cdot 10^{-2}$</i>	<i>$1.4 \cdot 10^{-1}$</i>	B&VL 98
Ac(III)	<i>100</i>	30	330	W&VL 03
Th(IV)	100	30	330	W&VL 03
Pa(V)	<i>10^{-1}</i>	<i>$7.1 \cdot 10^{-2}$</i>	<i>$1.4 \cdot 10^{-1}$</i>	W&VL 03
U(VI)	2	1.4	2.8	W&VL 03
Np(IV)	<i>100</i>	30	330	W&VL 03
Pu(IV)	<i>100</i>	30	330	W&VL 03
Am(III)	<i>100</i>	30	330	W&VL 03
Cm(III)	<i>100</i>	30	330	W&VL 03

Bold type: Sorption values are selected based on experimental data sets including estimates for the uncertainties

Italic type: Sorption values are selected based on chemical analogy including suggested uncertainty limits.

References: B&S 95: BRADBURY & SAROTT (1995)
B&VL 98: BRADBURY & VAN LOON (1998)
W&VL 03: WIELAND & VAN LOON (2003)

TABLE AI-4: Distribution ratios for selected redox-sensitive radionuclides under oxidising conditions.

Element	R_d value ($m^3 kg^{-1}$)			Ref.
	recomm- ended	Estimated lower limit	Estimated upper limit	
Se(VI)	10^{-3}	$7.1 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	B&VL 98
Np(V)	10^{-1}	$7.1 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$	W&VL 03
Pu(V)	10^{-1}	$7.1 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$	W&VL 03

Italic type: Sorption values are selected based on chemical analogy including suggested uncertainty limits.

References: B&VL 98: BRADBURY & VAN LOON (1998)
W&VL 03: WIELAND & VAN LOON (2003)

The following calculations are based on assumptions concerning the extent of isotopic exchange: First, it is assumed that the total inventory of a stable isotope in the cement matrix is accessible to isotopic exchange. This suggests that the exchange of the corresponding radionuclides with HCP is complete, i.e., the total inventory of an element associated with the cement matrix is accessible in the course of the exchange process. Nevertheless, incomplete exchange will be taken into account by assuming that only a small proportion of the total inventory is accessible to isotopic exchange. For this study it is assumed that these proportions amount to 10% or 1% of the HCP inventory of an element. Note that these proportions are chosen arbitrarily, and there is no information available to the best of our knowledge, which currently allows a thorough justification of these assumptions. On the above assumptions, the partitioning of radionuclides is given by:

$$\frac{m_c \cdot f}{m_c^*} = \frac{m_{aq}}{m_{aq}^*} \quad (1)$$

where:

m_c : number of moles of an element M (stable isotope) in the repository associated with HCP [mol],

m_c^* : number of moles of the corresponding radionuclides in the repository associated with HCP [mol],

m_{aq} : number of moles of the element M (stable isotope) in CPW [mol],

m_{aq}^* : number of moles of the corresponding radionuclides in CPW [mol],

f: proportion of the stable isotope inventory accessible to isotopic exchange [-].

The factor f is set to 1 (complete exchange with the solid phase), 0.1 (10% of the solid accessible to exchange) and 0.01 (1% of the solid accessible to exchange).

The maximum concentrations of the radionuclides in CPW can be calculated from Eq. 1 provided that the waste inventories of the radionuclides and the inventories of the corresponding stable isotopes in HCP and CPW are known. It is noted that this approach is based on parameters, which are specific for the system under consideration, e.g., the inventories of the radionuclides in the waste matrix and the stable isotopes associated with HCP as well as the maximum concentrations of the elements in CPW. The input data used for further calculations are summarized in Tables AI-5 and AI-6, and include ILW-specific and element-specific parameters.

TABLE AI-5: Characteristic parameters of the ILW repository.

Parameter	Notation	Value ¹
Total volume of cavern [m ³]	V_{tot}	9512
Average porosity [-]	ϵ	0.32
Mass of HCP [kg]	m_{cem}	$3.96 \cdot 10^6$
Volume of CPW [m ³]	V_{CPW}	3044

¹ Uncertainties on the values are estimated to be ± 5 %.

TABLE AI-6: Element-specific parameters.

Element	Ca	Fe	Ni	Co	C
<u>Radionuclides</u>					
Radionuclides present in the waste matrix ¹	⁴¹ Ca	⁵⁵ Fe	^{59/63} Ni	⁶⁰ Co	¹⁴ C
BE: Waste inventory (m_i^*) ¹ [mol]	0.2	0.9	1073	5.3	22.5
BC: Waste inventory (m_i^*) ¹ [mol]	0	1.4	820	8.5	10
<u>Stable isotopes</u>					
Concentration in HCP ² [mol kg ⁻¹]	9.8	0.29	$3.4 \cdot 10^{-4}$	$5.9 \cdot 10^{-5}$	$4.0 \cdot 10^{-2}$
Concentration in CPW ³ [mol L ⁻¹]	$2 \cdot 10^{-2}$	10^{-7}	$3 \cdot 10^{-7}$	$7 \cdot 10^{-7}$	$9.7 \cdot 10^{-6}$

¹ Nuclide inventories as given for the "best estimate (BE)" and "base case (BC)" (Nagra, unpublished data).

² Concentrations of Ca, Fe and C as published by NEALL (1994); Ni and Co data are based on unpublished in-house measurements.

³ BERNER (2003) (radionuclide concentration limits at pH = 12.5).

The following constraints apply to mass balance for the waste and CPW inventories, m_t^* and $m_{t,aq}$, respectively:

$$m_t^* = m_c^* + m_{aq}^* \quad [\text{mol}] \quad (2)$$

$$m_{t,aq} = m_{aq} + m_{aq}^* \quad [\text{mol}] \quad (3)$$

where:

m_t^* : total number of moles of a radionuclide in the repository (waste matrix) [mol],

$m_{t,aq}$: total number of moles of an element (stable + radionuclide) in CPW [mol].

The waste inventories of the safety-relevant radionuclides, m_t^* , are listed in Table AI-6. The total inventory of an element in CPW, $m_{t,aq}$, can be estimated from the volume of CPW in the near field and the maximum CPW concentrations reported by BERNER (2003).

Combining Eqs. 1, 2 and 3 results in a quadratic equation for the CPW inventory of a nuclide, m_{aq}^* :

$$\left(m_{aq}^*\right)^2 - \left(m_t^* + m_{t,aq} + f \cdot m_c\right) m_{aq}^* + m_{t,aq} \cdot m_t^* = 0 \quad (4)$$

CPW inventories calculated from Eq. 4 and the corresponding concentrations are listed in Table AI-8 together with apparent distribution ratios, R_d , for the radionuclides of interest, which were calculated as follows:

$$R_d = \frac{m_c \cdot f}{m_{aq}} \cdot \left(\frac{V_{CPW}}{m_{cem}}\right) = \frac{m_c^*}{m_{aq}^*} \cdot \left(\frac{V_{CPW}}{m_{cem}}\right) = \frac{m_t^* - m_{aq}^*}{m_{aq}^*} \cdot \left(\frac{V_{CPW}}{m_{cem}}\right) \quad [\text{m}^3 \text{kg}^{-1}] \quad (5)$$

It is worth re-emphasizing that R_d values deduced in this manner are based on system parameters and, therefore, are not regarded as being equivalent to R_d values constraint by the mass action law. Note further that uncertainties are associated with the parameters used for calculating the R_d value. For example, uncertainties are associated with the elemental composition of HCP, and even larger uncertainties were assigned to the solubility limits of some of the above-mentioned elements (BERNER 2003). Thus, uncertainties on the radionuclide concentrations in CPW and the apparent R_d values can be estimated taking into account the corresponding uncertainties on the ILW-specific parameters ($\pm 5\%$) and the element-specific parameters as listed in Table AI-7. Estimates for the upper bound values of the CPW concentrations and the lower bound values of the corresponding R_d values given in Table AI-8 are based on the maximum

inventories of radionuclides in the repository for the “best estimate“ or “base case“, respectively, the maximum total CPW inventories, the minimum amount of HCP in the repository and the minimum volume of CPW in contact with HCP.

TABLE AI-7: Element-specific parameters: Uncertainty ranges (L = lower limit, U = upper limit).

Element	Ca	Fe	Ni	Co	C
Concentration in HCP ¹ [mol kg ⁻¹]: L	9.3	0.27	3.2·10 ⁻⁴	4.5·10 ⁻⁵	3.6·10 ⁻²
U	10.3	0.30	3.6·10 ⁻⁴	7.4·10 ⁻⁵	4.4·10 ⁻²
Concentration in CPW ² [mol L ⁻¹]: L	1.8·10 ⁻²	5.0·10 ⁻⁸	10 ⁻⁸	7.0·10 ⁻⁸	8.7·10 ⁻⁶
U	2.2·10 ⁻²	1.2·10 ⁻⁶	8.0·10 ⁻⁶	7.0·10 ⁻⁶	1.1·10 ⁻⁵

¹ Uncertainties are assumed to be ± 5 % for Ca and Fe, ± 6.5 % for Ni, ± 26 % for Co and ± 10 % for C based on analytical errors. Note that the uncertainties do not account for the variability among different cements, which are expected to be larger than the analytical errors. Nevertheless, there are no reliable data available, which would allow a systematic comparison of the elemental compositions of different cement types to be made.

² Uncertainties are estimated based on the solubility limits given in BERNER (2003).

TABLE AI-8: Estimates for the maximum concentrations of the radionuclides in CPW and the corresponding apparent R_d values taking into account complete (f = 1) and incomplete (f < 1) isotopic exchange.

Radionuclides	⁴¹ Ca	⁵⁵ Fe	⁵⁹ Ni, ⁶³ Ni	⁶⁰ Co	¹⁴ C
<u>f = 1</u>					
CPW inventory [mol]	3.2·10 ⁻⁴	2.5·10 ⁻⁷	0.41	4.7·10 ⁻²	4.2·10 ⁻³
Concentration in CPW [mol L ⁻¹]	1.0·10 ⁻¹⁰	8.0·10 ⁻¹⁴	1.3·10 ⁻⁷	1.5·10 ⁻⁸	1.4·10 ⁻⁹
<i>Upper bound value [mol L⁻¹]</i>	<i>1.2·10⁻¹⁰</i>	<i>1.7·10⁻¹²</i>	<i>3.8·10⁻⁶</i>	<i>3.0·10⁻⁷</i>	<i>1.8·10⁻⁹</i>
Apparent R _d value [m ³ kg ⁻¹]	0.5	2900	2.0	8.7·10 ⁻²	4.1
<i>Lower bound value [m³ kg⁻¹]</i>	<i>0.4</i>	<i>230</i>	<i>7.5·10⁻²</i>	<i>6.7·10⁻³</i>	<i>3.3</i>
<u>f = 0.1</u>					
CPW inventory [mol]	3.1·10 ⁻³	2.5·10 ⁻⁶	0.8	0.4	4.2·10 ⁻²
Concentration in CPW [mol L ⁻¹]	1.0·10 ⁻⁹	7.9·10 ⁻¹³	2.7·10 ⁻⁷	1.2·10 ⁻⁷	1.4·10 ⁻⁸
<i>Upper bound value [mol L⁻¹]</i>	<i>1.2·10⁻⁹</i>	<i>1.7·10⁻¹¹</i>	<i>7.2·10⁻⁶</i>	<i>1.4·10⁻⁶</i>	<i>1.8·10⁻⁸</i>
Apparent R _d value [m ³ kg ⁻¹]	4.9·10 ⁻²	290	1.0	1.0·10 ⁻²	0.4
<i>Lower bound value [m³ kg⁻¹]</i>	<i>4.2·10⁻²</i>	<i>23</i>	<i>3.9·10⁻²</i>	<i>8.0·10⁻⁴</i>	<i>0.3</i>
<u>f = 0.01</u>					
CPW inventory [mol]	2.7·10 ⁻²	2.4·10 ⁻⁵	0.91	1.35	0.4
Concentration in CPW [mol L ⁻¹]	8.9·10 ⁻⁹	7.8·10 ⁻¹²	3.0·10 ⁻⁷	4.4·10 ⁻⁷	1.3·10 ⁻⁷
<i>Upper bound value [mol L⁻¹]</i>	<i>1.1·10⁻⁸</i>	<i>1.7·10⁻¹⁰</i>	<i>7.9·10⁻⁶</i>	<i>2.6·10⁻⁶</i>	<i>1.8·10⁻⁷</i>
Apparent R _d value [m ³ kg ⁻¹]	4.9·10 ⁻³	29	0.91	2.3·10 ⁻³	4.2·10 ⁻²
<i>Lower bound value [m³ kg⁻¹]</i>	<i>4.2·10⁻³</i>	<i>2.3</i>	<i>3.5·10⁻²</i>	<i>1.0·10⁻⁴</i>	<i>3.3·10⁻²</i>

SUMMARY

The R_d values listed in Tables AI-2, AI-3 and AI-4 are recommended for use in the ongoing disposal feasibility study for an ILW repository in the Opalinus clay. The values have been selected by taking into account the specific redox conditions and porewater compositions of the cementitious near field of the ILW repository and the dominant oxidation states of the radioelements under these conditions. The values were chosen from a larger set of recommended sorption values previously reported in SDBs for cementitious near fields (BRADBURY & SAROTT 1995; BRADBURY & VAN LOON 1998; WIELAND & VAN LOON 2003).

The R_d values reported in the above-mentioned SDBs account for sorption-type processes. Nevertheless, it is suggested, and partly supported by new experimental data, that the partitioning of some radioelements, e.g., C (CO_3^{2-}), Ca, Fe, Co and Ni, is controlled by solubility limitation in cement systems. In all these cases, the CPW concentrations appear to be fixed by solubility limits. The solubility-limiting phases of CO_3^{2-} and Ca in cement systems are well known (CaCO_3 and Ca(OH)_2). Nevertheless, the solubility-limiting solid phases of Fe, Co and Ni are poorly known and robust thermodynamic data are still lacking. Evidence for solubility limitation of Ni and Co was provided based on the finding that the CPW concentrations of these elements are constant in cement systems (WIELAND & VAN LOON 2003). In the case of Ni, mixed Ni-Al LDHs were suggested to be the solubility-limiting solid phases. A similar type of compounds is expected to be responsible for limiting the Co concentration in the cement matrix. In addition, it was suggested that calcium-aluminium-ferrite phases may control the Fe concentration in cement systems (TAYLOR 1997).

In this study an approach is presented which enables us to quantify the source term for ^{14}C , ^{41}Ca , ^{55}Fe , ^{60}Co and $^{59/63}\text{Ni}$. The approach is based on the assumption that the aqueous concentrations of the radioelements in CPW are fixed by solubility limits and that, in the cement matrix, isotopic exchange between radionuclides and stable isotopes takes place. With this, maximum concentrations for the above-mentioned radionuclides in CPW can be deduced. Maximum concentrations are calculated for different extents of isotopic exchange, i.e., increasing proportions of the stable isotope inventories of HCP accessible to isotopic exchange. These proportions are set to 100 %, 10 % and 1 % for all elements.

Apparent R_d values are estimated based on the proposed conceptual approach. It is noted that R_d values deduced in this manner are regarded as being bound by characteristic

parameters of the near field, i.e., the inventory of a radionuclide in the waste matrix and the corresponding stable isotope associated with HCP as well as the maximum concentration of an element in CPW (solubility). These parameters are characteristic for a specific repository system, and therefore, the R_d values deduced in this manner represent system-bound sorption values rather than sorption values constraint by the mass action law.

Upper bound values for the radionuclide concentrations in CPW and, accordingly, lower bound values for the apparent R_d values can be deduced by taking into account uncertainties on the ILW-specific parameters, i.e., the mass of HCP and the volume of CPW, as well as the element-specific parameters, i.e., the nuclide inventories, the solubility of an element in CPW and the stable isotope inventories of HCP.

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APPENDIX II

B. SCHWYN (NAGRA)

K_d VALUES FOR THE CEMENTITIOUS NEAR FIELD OF AN ILW REPOSITORY USED IN SAFETY ASSESSMENT CALCULATIONS WITHIN THE PROJECT OPALINUS CLAY (ENTSORGUNGSNACHWEIS)

The sorption data base for a cementitious ILW repository used for safety assessment calculations was derived using a stepwise procedure.

In the main part of this report (Chapter 6, Table 5) sorption values for cement degradation stages I and II are listed. For redox-sensitive elements values of both their reduced and oxidised forms are given without specifying reference redox potentials. Uncertainty factors and the potential influence of colloids are also reported.

In Appendix I values for the reference redox conditions were selected from the main part of this report. Reducing conditions (Eh = -230 mV to -430 mV, depending on pH) for the waste group ILW-1 and oxidising conditions (+350 mV) for the waste group ILW-2 are assumed. In addition, Appendix I gives maximum concentrations for some radionuclides (e.g. ¹⁴C, ⁶⁰Co and ^{59/63}Ni) which were derived assuming shared solubilities with the corresponding stable isotopes present in the cement (Table AI-8). This information is not considered in Table AII-1 (see below), but is included in the data base for solubility limits in a cementitious ILW repository (Addendum in BERNER 2003).

From the information mentioned above, values to be used for safety assessment calculations were carefully selected and listed in Table AII-1. Plausibility checks were carried out by using independent information, in particular by comparing the data set presented here with the ones used in other recent performance assessments. This work will be presented in a separate report (SCHWYN & WERSIN 2003).

All the values in Table AII-1 were derived from the Tables AI-2, AI-3 and AI-4 (see Appendix I of this report) considering the comments below:

- In the main part and in Appendix I of this report the symbol R_d is used for the distribution ratio between hardened cement paste and cement porewater. For safety assessment purposes R_d is renamed to K_d indicating that equilibrium conditions are assumed in transport calculations.

- Cement degradation stage II was fixed as reference case. The appropriate sorption values were therefore taken from Table AI-2. As an exception, the value for cesium was conservatively taken from Table AI-3 (cement degradation phase I). Due to the relatively small K_d value, this nuclide will probably have diffused out of the near field before cement degradation stage II will start.
- The evaluation of the performed nickel sorption studies revealed that the element concentration was solubility-controlled under the given experimental conditions. (Section 3.2.2.3 in the main part of this report). An independent sorption value was not available and K_d had to be conservatively set to zero. By analogy, a K_d value of zero was used for cobalt. As for C_{inorg} , the retention of Ni and Co in the cementitious near field is considered in the data base for solubility limits assuming shared solubilities of the concerned radionuclides with the corresponding stable isotopes present in the cement (see Appendix I, Chapter 3.3 and Addendum in BERNER 2003).
- Due to a high content of nitrate in the ILW-2 waste, oxidising conditions may prevail in the corresponding tunnel. This would affect the K_d values of selenium, neptunium and plutonium. The corresponding values for ILW-2 were taken from Table AI-4. For all other elements K_d values for ILW-2 equal ILW-1 values.
- Since iodine is an important safety-relevant element a "What if?"¹ case with $K_d = 0$ was also included in the safety assessment calculations. It is, however, very unlikely, that iodine does not sorb in cement (see Section 3.4.2.3 in the main part of this report).
- Colloids may reduce sorption of strongly sorbing elements as pointed out in Chapter 4 in the main part of this report. The following table considers this potential sorption reduction using Eqns. 8 and 10 from the above mentioned Chapter 4. For the reference case K_d values, a surface scaling factor S_c of 20 was used and for the lower limit K_d values a scaling factor S_c of 100 (see Section 4.3.3 in the main part of this report). Affected values are underlined in Table AII-1. No impact of colloids was assumed for the upper limit K_d values.
- If necessary, values were truncated (reference case and lower limit) or rounded (upper limit) to one significant figure.

¹ Defined in Appendix 5 of NAGRA (2002a).

- The list of nuclides discussed in this report is larger than the list of safety-relevant nuclides considered in the safety assessment calculations. This is because the simple screening analysis for the derivation of the list of safety-relevant nuclides described in Appendix 5 of NAGRA (2002b) was modified at a later stage in Project Opalinus Clay, i.e., after the bulk of the work described in this report was undertaken. Therefore, some elements were dropped in Table AII-1.

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Table AII-1: Sorption values (K_d) in cement for the waste groups ILW-1 and ILW-2: reference cases and corresponding lower (pessimistic) and upper (optimistic) limits. Values are expressed in terms of m^3 per kg hardened cement paste.

This table corresponds to Table A2.7 of Nagra (2002a).

Element	K_d ILW-1			K_d ILW-2 ¹		
	Ref. case [$\text{m}^3 \text{ kg}^{-1}$]	Lower limit (pessimistic) [$\text{m}^3 \text{ kg}^{-1}$]	Upper limit (optimistic) [$\text{m}^3 \text{ kg}^{-1}$]	Ref. case [$\text{m}^3 \text{ kg}^{-1}$]	Lower limit (pessimistic) [$\text{m}^3 \text{ kg}^{-1}$]	Upper limit (optimistic) [$\text{m}^3 \text{ kg}^{-1}$]
H	$1 \cdot 10^{-4}$	$7 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$7 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
C _{inorg} ²	0	0	0	0	0	0
C _{org}	0	0	0	0	0	0
Cl	0.005	0.003	0.007	0.005	0.003	0.007
Co ²	0	0	0	0	0	0
Ni ²	0	0	0	0	0	0
Se	0.03	0.02	0.04	0.001	$7 \cdot 10^{-4}$	0.001
Sr	0.001	$7 \cdot 10^{-4}$	0.001	0.001	$7 \cdot 10^{-4}$	0.001
Zr	10	<u>2</u>	30	10	<u>2</u>	30
Nb	1	0.7	1	1	0.7	1
Mo	0	0	0	0	0	0
Tc	0.001	$7 \cdot 10^{-4}$	1	0.001	$7 \cdot 10^{-4}$	0.001
Sn	10	<u>2</u>	30	10	<u>2</u>	30
I ³	0.001	$7 \cdot 10^{-4}$	0.001	0.001	$7 \cdot 10^{-4}$	0.001
Cs ⁴	$5 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$7 \cdot 10^{-4}$
Sm	<u>80</u>	<u>20</u>	300	<u>80</u>	<u>20</u>	300
Eu	<u>80</u>	<u>20</u>	300	<u>80</u>	<u>20</u>	300
Pb	0.5	0.3	0.7	0.5	0.3	0.7
Po	0	0	0	0	0	0
Ra	0.05	0.03	0.07	0.05	0.03	0.07
Ac	<u>80</u>	<u>20</u>	300	<u>80</u>	<u>20</u>	300
Th	<u>80</u>	<u>20</u>	300	<u>80</u>	<u>20</u>	300
Pa	0.1	0.07	0.1	0.1	0.07	0.1
U	2	1	2	2	1	2
Np	<u>80</u>	<u>20</u>	300	0.1	0.07	0.1
Pu	<u>80</u>	<u>20</u>	300	0.1	0.07	0.1
Am	<u>80</u>	<u>20</u>	300	<u>80</u>	<u>20</u>	300
Cm	<u>80</u>	<u>20</u>	300	<u>80</u>	<u>20</u>	300

¹ The derived ILW-2 values may also be used as conservative estimates for a "what if?" case that assumes oxidising conditions in ILW-1.

² Shared solubility assumed (see Appendix 1, Chapter 3.3 and BERNER 2003), no independent sorption values available

³ Also a "what if?" case for $K_d = 0 \text{ m}^3 \text{ kg}^{-1}$

⁴ Cement degradation phase I (Table AI-3)

Underlined: Reduction of sorption assumed due to colloids