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Sorption Data Base for the Cementitious Near Field of L/ILW and ILW Repositories for Provisional Safety Analyses for SGT-E2

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Summary

The near field of the planned Swiss repositories for low- and intermediate-level waste (L/ILW) and long-lived intermediate-level waste (ILW) consists of large quantities of cementitious materials. Hardened cement paste (HCP) is considered to be the most important sorbing material present in the near field of L/ILW and ILW repositories. Interaction of radionuclides with HCP represents the most important mechanism retarding their migration from the near field into the host rock.

This report describes a cement sorption data base (SDB) for the safety-relevant radionuclides in the waste that will be disposed of in the L/ILW and ILW repositories. The current update on sorption values for radionuclides should be read in conjunction with the earlier SDBs CEM-94 (Bradbury & Sarott 1994), CEM-97 (Bradbury & Van Loon 1997) and CEM-02 (Wieland & Van Loon 2002). Sorption values have been selected based on procedures reported in these earlier SDBs. The values are revised if corresponding new information and/or data are available. The basic information results from a survey of sorption studies published between 2002 and 2013. The sorption values recommended in this report have either been selected from in-house experimental studies or from literature data, and they were further assessed with a view to the sorption values recently published in the framework of the safety analysis for the planned near surface disposal facility in Belgium.

The report summarizes the sorption properties of HCP and compiles sorption values for safety-relevant radionuclides and low-molecular weight organic molecules on undisturbed ("fresh") and degraded HCP.

A list of the safety-relevant radionuclides is provided based on the currently available information on radionuclide inventories. The radionuclide inventories are determined by the waste streams to be disposed of in the L/ILW and ILW repositories. Information on the elemental and mineral composition of HCP was obtained from hydration studies (Lothenbach & Wieland 2006). The concentrations of the most important impurity elements in cement were obtained from dissolution studies on HCP. In this report, particular emphasis is placed on summarizing our current knowledge of the uptake mechanisms of safety-relevant radionuclides and the role of the uptake-controlling cement minerals.

In the disposal caverns, HCP is influenced by internal geochemical processes, such as carbonation due to the generation of CO₂ in the course of the degradation of organic waste materials or due to the dissolution of metallic waste materials, and by externally induced geochemical processes, such as degradation due to interaction of inflowing saline and non-saline groundwater from the host rock. These processes can change the mineral composition of HCP and/or the composition of the pore solution, which could have an effect on radionuclide uptake. The effect of these time-dependent changes on radionuclide uptake has been assessed for three characteristic stages of the degradation of HCP by the interaction with inflowing groundwater. The stages are differentiated based on results from reactive transport calculations, which allow the composition of HCP and the corresponding pore water to be determined (Kosakowski et al. 2014). The presently available mechanistic understanding of radionuclide uptake by cementitious materials (HCP, cement phases) in combination with the results from reactive transport modelling allows well-supported appraisal of sorption values for radionuclides in an evolving cementitious near field to be made.
Important organic and inorganic ligands, such as EDTA, CN⁻, and degradation products of spent basic anion-exchange resins (e.g. ammonia) and cellulose (i.e. isosaccharinic acid), as well as concrete admixtures (e.g. gluconic acid) and cement-derived near-field colloids are taken into account as potential perturbations which could reduce radionuclide uptake in the near field. Possible impacts of these perturbing factors on radionuclide mobility are considered and quantified in terms of sorption reduction factors.

This report further includes a preliminary appraisal of the diffusion parameters of cementitious materials for use in safety analysis in the framework of stage 2 of the Sectoral Plan for Deep Geological Repositories (SGT-E2). The parameters are selected on the basis of a survey of literature data. The parameters are consistent with those used in earlier national and international performance assessment-related studies and, furthermore, with the parameters used in reactive transport calculations carried out in the framework of SGT-E2 (Kosakowski et al. 2014).
Zusammenfassung


Im vorliegenden Bericht werden Sorptionseigenschaften von Zementstein beschrieben und Sorptionswerte für sicherheitsrelevante Radionuklide und niedermolekulare organische Moleküle an ungestörtem ("frischem") und degradiertem Zementstein aufgelistet.


mit den Ergebnissen aus den reaktiven Transportmodellierungen erlaubt es, eine gut fundierte Beurteilung der Sorptionswerte für Radionuklide in einem sich entwickelnden zementhaltigen Nahfeld durchzuführen.

Als mögliche Störeinflüsse auf die Aufnahme von Radionukliden durch Zementstein werden wichtige organische und anorganische Liganden wie EDTA, CN⁻, Abbauprodukte von basischen Ionenaustauscherharzen (z.B. Ammoniak) und Zellulose (d.h. Isosaccharinsäure) sowie Betonzusatzmittel (z.B. Glukonsäure) und zementartige Nahfeldkolloide berücksichtigt. Diese Störfaktoren können die Radionuklidsorption in einem Nahfeld reduzieren. Mögliche Auswirkungen dieser Störfaktoren auf die Radionuklidmobilität werden mittels Sorptionsreduktionsfaktoren berücksichtigt und quantifiziert.

Résumé

Le champ proche des dépôts géologiques pour déchets radioactifs de faible et moyenne activité (DFMA) et de moyenne activité à vie longue (DMAL), tel qu'il sont prévus en Suisse, est constitué pour une grande part de matériaux à base de ciment. Dans les analyses de sûreté pour ce type de dépôt, on considère la pâte de ciment comme le principal matériau sorbant du champ proche. L'interaction avec la pâte de ciment constitue ainsi le principal mécanisme retardant la migration des radionucléides du champ proche vers la roche d'accueil.

Ce rapport décrit une base de données de sorption pour le ciment pour les radionucléides importants pour la sûreté des dépôts géologiques de DFMA et DMAL. Il est fait référence à plusieurs bases de données compilées précédemment, à savoir CEM-94 (Bradbury et Sarott 1994), CEM-97 (Bradbury et Van Loon 1997) et CEM-02 (Wieland et Van Loon 2002). Les coefficients de sorption ont été sélectionnés selon les procédures décrites dans ces bases de données. Dans les cas où de nouvelles informations et/ou données étaient disponibles, les valeurs ont été modifiées en conséquence. Les informations contenues dans ce rapport sont basées sur des études publiées entre 2002 et 2013. Les coefficients de sorption recommandés ont été sélectionnés, soit parmi des données obtenues lors d'expériences dans notre laboratoire, soit dans les publications. Une comparaison a par ailleurs été effectuée avec des coefficients de sorption récemment publiés dans l'analyse de sûreté d'un dépôt de surface destiné aux déchets radioactifs de faible activité en Belgique.

Le présent rapport résume les propriétés de sorption de la pâte de ciment et présente les coefficients de sorption pour les radionucléides importants pour la sûreté du dépôt et les molécules organiques de faible poids, tant pour la pâte de ciment intacte («fraîche») que pour la pâte dégradée.

La liste des radionucléides importants pour la sûreté a été dressée sur la base des informations actuellement disponibles sur les inventaires de déchets. Les inventaires de radionucléides sont déterminés par les types de déchets destinés à être stockés dans les dépôts géologiques pour DFMA et DMAL. Les informations sur la composition élémentaire et minérale de la pâte de ciment proviennent d'études d'hydratation (Lothenbach et Wieland 2006). Les valeurs utilisées pour la concentration des impuretés dans le ciment sont issues d'expériences de dissolution de la pâte de ciment. Dans ce rapport, un accent particulier a été mis sur la synthèse des connaissances disponibles actuellement sur les mécanismes de sorption des radionucléides importants pour la sûreté, ainsi que sur le rôle des minéraux du ciment dans le contrôle des phénomènes de sorption.

Dans les cavernes de stockage, la pâte de ciment sera affectée par des processus géochimiques internes, tels que la carbonatation due au CO₂ généré par la dégradation des déchets organiques ou la dissolution des déchets métalliques. Elle sera aussi exposée à des processus géochimiques externes, par exemple une dégradation consécutive à un afflux d’eaux salines et non salines provenant de la roche d'accueil. Ces processus évoluent en fonction du temps et peuvent modifier la composition minérale de la pâte de ciment et/ou la composition de la solution interstitielle, ce qui pourrait influer sur les capacités de sorption. L’impact potentiel de ces modifications sur la sorption des radionucléides a été étudié pour trois étapes caractéristiques de la dégradation de la pâte de ciment, intervenant à la suite d’un afflux d’eau souterraine non saline. Ces étapes ont été déterminées sur la base de résultats de modélisations de transport réactif, permettant de déterminer la composition de la pâte de ciment et de l'eau interstitielle correspondante (Kosakowski et al. 2014). Les connaissances actuelles relatives aux mécanismes de sorption des radionucléides dans les matériaux cimentaires (pâte de ciment, phases...
cimentaires), combinées avec les résultats de la modélisation du transport réactif, constituent une base solide pour déterminer les coefficients de sorption des radionucléides dans un champ proche cimentaire évoluant en fonction du temps.

La sorption des radionucléides dans le champ proche pourrait être perturbée par une série de facteurs, qu’il s’agisse de liants organiques et inorganiques importants, tels que EDTA, CN⁻, de produits de dégradation de résines échangeuses d'ions (p.ex. ammoniaque) et de la cellulose (c’est-à-dire l'acide isosaccharinique), ou encore d’additifs du béton (p.ex. l'acide gluconique) et de colloïdes dérivés du ciment. Les impacts possibles de ces éléments perturbateurs sur la mobilité des radionucléides ont été examinés, puis quantifiés sous la forme de facteurs de réduction de la sorption.

Dans la perspective des analyses de sûreté prévues à l'étape 2 du plan sectoriel "Dépôts en couches géologiques profondes" (SGT-E2), le présent rapport comprend en outre une évaluation préliminaire des paramètres de diffusion des matériaux cimentaires. Ces paramètres ont été sélectionnés sur la base des publications existantes. Ils sont compatibles avec ceux qui ont été utilisés dans des études de sûreté effectuées précédemment au niveau national et international, de même qu’avec les paramètres utilisés dans les calculs de transport réactif effectués au cours de SGT-E2 (Kosakowski et al. 2014).
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1 Introduction

1.1 Deep geological repositories for cement-stabilized radioactive waste

In the framework of the Swiss disposal programme it is foreseen to dispose of nuclear waste in deep geological repositories for spent fuel (SF), vitrified high-level waste (HLW) and long-lived intermediate-level waste (ILW) and separately for low- and intermediate-level waste (L/ILW).

As part of Stage 1 of the Sectoral Plan for Deep Geological Repositories, Nagra has proposed six regions which are suitable for hosting a repository for L/ILW waste and three regions for HLW waste (Nagra 2008). In the current Stage 2 of the Sectoral Plan, Nagra will propose at least two siting regions each for the L/ILW repository and for the HLW repository for further consideration. Provisional safety analyses for all siting regions are part of the procedure and support the evaluation and selection process. The host rocks to be considered are Opalinus Clay, 'Brauner Dogger', Effingen Member and Helvetic Marls. All host rocks can all be classified as argillaceous rocks (clay rock and marl).

Mainly cement has been used to stabilize ILW (LMA in Swiss terminology) and L/ILW (SMA in Swiss terminology), which is a common practice to also immobilize industrial and civil waste. Furthermore, cement will be used to construct the engineered barrier systems (container, backfill and liner materials). The ILW and L/ILW repository concepts, therefore, imply the presence of large amounts of cementitious materials, which will be emplaced in a manner to function as the major physical and chemical barriers to the release of radionuclides from the cementitious near field into the host rock.

In the ILW and L/ILW repositories hydrated cement – or hardened cement paste (HCP) – is considered to be the main sorbing material retarding the release of radionuclides from the near field. Sorption of aggregates is neglected. Therefore, sorption values for the safety-relevant radionuclides are key input data as uptake by HCP determines the mobile portion of a radionuclide in the near field. In this study the general terms "uptake", "retention" or "partitioning" will be preferentially used owing to the diversity of possible binding mechanisms in cementitious systems. The retention potential of HCP for radionuclides (anionic and cationic species) is very high due to the diversity of sorption sites available in the different cement minerals constituting the cement matrix. Furthermore, the high pH conditions ensure low aqueous solubility for many radionuclides. Hence, the mobility of radionuclides with high inventory will be limited by solubility.

1.2 Objective of this report

The aim of this report is to establish a sorption database through a survey of the open literature and on the basis of results from in-house sorption studies. This report documents the procedures whereby sorption values for the cementitious ILW and L/ILW near fields have been chosen, taking into account the presently known waste inventories and current design of the repositories.

The present report should be read in conjunction with the published cement sorption databases (SDBs) compiled in connection with earlier Nagra PAs for ILW and L/ILW. These reports will be referred to as CEM-94 (Bradbury & Sarott 1994), CEM-97 (Bradbury & Van Loon 1997) and CEM-02 (Wieland & Van Loon 2002). Thus, the current SDB is regarded as an update on the previous ones with emphasis on application in the framework of the Sectoral Plan for Deep Geological Repositories (Sachplan Geologische Tiefenlager SGT). Furthermore, the present SDB has further been developed with a view to the comprehensive compilations of sorption values recently published in the framework of the PA for the planned near surface disposal facility in Belgium (Wang et al. 2009, Ochs et al. 2010).
The procedures outlined in CEM-94, CEM-97 and CEM-02 have been applied in this report to ensure continuity in the methodology and transparency concerning the selection of sorption values. Additional aspects have only been addressed if they were required for clarity or owing to new requirements in the framework of the SGT. For example, a new set of sorption data was required to consider retention of radionuclides in a cementitious near field at lower pH (stage III of the cement degradation) and in contact with saline groundwater. The development of such cement SDB requires knowledge of the chemical conditions of the near field and information on the uptake process of the radionuclides of interest by hydrated cement. Therefore, in line with the previous cement SDBs CEM-94, CEM-97 and CEM-02, the current update was prepared on the basis of the following information:

- A list of the safety-relevant radionuclides was drawn up using available information on waste inventories (Nagra 2008a).
- Model predictions of the geochemical evolution of a cementitious near field provided information on the composition of the cement pore waters and hydrated cement for different stages of the cement degradation (Kosakowski et al. 2014).
- Sorption data for the safety-relevant radionuclides in the planned L/ILW and ILW repositories were compiled in view of the earlier SDBs for three characteristic stages of the cement degradation. The sorption values of the radionuclides compiled in the previous SDBs were revised if new information and/or data were available that allowed well-justified changes to or re-appraisals of the data. Otherwise, the sorption values were taken as given in the previously published SDBs. 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.
- Upper and lower bounds of the recommended sorption values were assigned with a view to previously published data compilations of sorption values for a cementitious near field. Selection of these data was based on an elicitation process.
- Degradation products of spent basic anion-exchange resins (e.g. ammonia) and cellulose (i.e. isosaccharinic acid), concrete admixtures and cement-derived near-field colloids were considered to be the main sources affecting radionuclide uptake by HCP. Their influence on radionuclide uptake was quantified in terms of sorption reduction factors by taking into account expected concentration ranges of near-field colloids and the respective complexing ligands in the two main groups of waste types. The influence on radionuclide uptake by HCP was assessed on the basis of literature data and in-house sorption measurements.
- The influence of increased chloride concentrations on radionuclide uptake by hydrated cement was assessed on the basis of a literature survey, new in-house sorption data and thermodynamic speciation calculations.

The main objectives of the SDB development are to select and document the sources of sorption data used and the procedure upon which the selection process is based, and further to demonstrate that the "best available" laboratory sorption values have been selected. The guiding principles in the development of SDBs are "transparency" and "traceability", implying that the documentation of the selection process should allow any third party to make an independent judgement of the quality of the selected data (Wieland et al. 2003). In addition it has been realised that a thorough justification of the values chosen can only be achieved when the underlying uptake mechanism(s) and the uptake-controlling phase are known, and the process can be expressed in terms of a thermodynamically-based model (Bradbury & Sarott 1994). The latter description allows proposed mechanism(s) and models to be verified over the range of conditions, which represent the real system. In this regard, the situation for cementitious systems has slightly improved compared to previous SDBs because a great number of sorption studies have
been carried out since 2002 with the aim of developing a mechanistic understanding of sorption processes. The development of the current update still has to be based on selecting representative sorption values by "expert judgement" from the large pool of available data. The selection process, however, is guided by our current knowledge of uptake mechanisms and is thoroughly documented in this report.

The term "uptake" is preferentially used in this report instead of "sorption", except in connection with well-established terms such as "sorption database" and "sorption value". Uptake of radionuclides by HCP will be quantified in terms of a distribution ratio, $R_d$. 
2 Geochemical Evolution of the Disposal System

2.1 Repository

Possible layouts for the deep geological L/ILW and ILW repositories were reported in detail elsewhere (Nagra 2002a,b, Kosakowski et al. 2014). The waste is emplaced in steel drums and usually conditioned with cement or concrete. The containments facilitate interim storage, handling and transport prior to final storage. The drums will be emplaced in disposal containers made of concrete. The voids between the drums in the disposal containers will be backfilled with a porous free-flowing mortar (Mayer & Wittmann 1996). The void space between the waste containers and the cavern lining, the top heading, as well as transfer- and unloading areas will also be backfilled with a porous, yet not free-flowing mortar composed of mono-grained aggregate material covered by hydrated cement (Jacobs et al. 1994). The backfill mortar was designed to contain accessible volume for gas formed in the emplacement cavern and to ensure mechanical stability through filling of voids between the waste containers.

The waste shows large variability and heterogeneity. More than 200 materials (substances, chemical compounds, etc.) present in the different waste sorts have been inventoried in the framework of the Swiss disposal programme. Nagra's disposal concept foresees that the waste sorts will be divided into two groups, SMA-1/LMA-1 and SMA-2/LMA-2 (Nagra 2008a,b). SMA-1/LMA-1 waste has only limited inventories of materials showing detrimental effects on the integrity of the cement barrier and radionuclide mobility. In contrast, SMA-2/LMA-2 waste has larger inventories of such materials, which requires particular consideration of their long-term fate in conjunction with performance assessment.

Estimates of the material inventories of L/ILW and ILW repositories suggest that the main materials are HCP, aggregate materials, such as quartz, as well as steel. In particular about 20 weight (wt.) % of the cementitious near field consists of HCP. For dose calculations in current PA studies HCP is assumed to be the only material in the cementitious near field sorbing radionuclides. The radionuclide release into the host rock is thus determined by the uptake by HCP and by the solubility of a radionuclide in case of large radionuclide inventories. In this study, uptake by HCP, i.e. the distribution of a radionuclide between the solid phase (HCP) and the highly alkaline aqueous phase is quantified in terms of a distribution ratio (Ra value).

2.2 Cement

2.2.1 Compositions of ordinary Portland cement

A sulphate-resisting Portland cement CEM I 52.5 N HTS (Haute Teneur en Silice) (Lafarge, France) is currently in use for the conditioning of radioactive waste in Switzerland. This cement, along with other ordinary Portland cements (OPC) presumably employed for the construction of the engineered barrier, are considered to be the main material controlling radionuclide immobilization in the cementitious near field of the Swiss L/ILW and ILW repositories. For dose calculations in current PA studies HCP is assumed to be the only material in the cementitious near field sorbing radionuclides; sorption on aggregates is thus neglected. The chemical composition of modern, calcite-containing HTS cement is listed in Tab. 2.1 (Lothenbach & Wieland 2006) and compared with the chemical composition of another typical OPC (Lothenbach & Winnefeld 2006).
Tab. 2.1: Comparison of the composition of the sulphate-resisting OPC CEM I 52.5 N HTS (Blaine surface area: 354 m²/kg) with that of OPC CEM I 42.5 N (Blaine surface area: 300 m²/kg).

<table>
<thead>
<tr>
<th>Chemical analysis</th>
<th>Normative phase composition *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CEM I 52.5 ** [g/100g]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>22.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.9</td>
</tr>
<tr>
<td>CaO</td>
<td>65.7</td>
</tr>
<tr>
<td>MgO</td>
<td>0.85</td>
</tr>
<tr>
<td>SrO</td>
<td>0.16</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.22</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.13</td>
</tr>
<tr>
<td>CaO (free)</td>
<td>0.45</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.6</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.2</td>
</tr>
<tr>
<td>Readily soluble alkalis ***</td>
<td>MgO *****</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* Calculated from chemical analysis
** Data for CEM I 52.5 N HTS taken from Lothenbach & Wieland (2006) Data for CEM I 42.5 N taken from Lothenbach & Winnefeld (2006)
*** Readily soluble alkalis were calculated from the concentrations of alkalis determined in solution after 5 min agitation at water/cement (w/c) ratio of 10; present as alkali sulphates.
**** CEM I 52.5 N HTS: anhydrite (1.5 g/100 g), hemihydrate (1.1 g/100 g), gypsum (1.3 g/100 g) CEM I 42.5 N: anhydrite (2.5 g/100 g), hemihydrate (0.5 g/100 g), gypsum (1.5 g/100 g)
***** Present as solid solution in the clinker phases alite, belite, aluminate and ferrite

CEM I 52.5 N HTS is a sulphate-resisting OPC, which has a lower Al content (about a factor of 2) than normal OPCs while the Fe content is comparable (Tab. 2.1). The lower Al content ensures that the formation of ettringite, and consequently destructive expansion of HCP, due to reaction of Al with sulphate from sulphate-rich water is reduced. Otherwise, the chemical compositions of the two cements are very similar. For example, the difference in the CaO content is less than ~ 5 wt.-% while the difference in the SiO₂ contents is less than ~ 10 wt.-%. Therefore, it is expected that the mineral composition of the hydrate assemblage of the two cements is similar upon hydration. On the basis of differences in CaO, SiO₂, Al₂O₃ and Fe₂O₃ contents, however, it is expected that hydrated CEM I 52.5 N HTS has a slightly higher content of calcium silicate hydrates (C-S-H phases) while the higher Al and Fe contents of CEM I 42.5 N give rise to larger proportions of calcium aluminates formed, i.e. AFm (Al₂O₃-Fe₂O₃-mono phases) and AFt (Al₂O₃-Fe₂O₃-tri phases), in the course of cement hydration.
2.2.2 Mineral composition of hydrated cement

The hydration process of the two cements was studied in detail and reported elsewhere (Lothenbach & Wieland 2006, Lothenbach & Winnefeld 2006). Thermodynamic modelling allowed the composition of the hydrate assemblages to be predicted as a function of time. The mineral compositions of the two cements after 28 days hydration, which were prepared at slightly different water-to-cement (w/c) ratios (CEM I 52.5 N HTS: w/c = 0.4; CEM I 42.5 N: w/c = 0.5), are listed in Tab. 2.2. The model predictions confirm that the portion of C-S-H phases is higher in CEM I 52.5 N HTS compared to CEM I 42.5 N while the opposite is true for the calcium aluminate phases, i.e. AFt and AFm. Differences in mineral compositions of the two hydrated pastes could have an influence on radionuclide uptake since the latter process is mineral-specific. For example, AFt and AFm phases mainly control anion binding in HCP while the uptake of metal cations is predominantly controlled by C-S-H phases (see Chapter 3). Note, however, that the differences in the mineral composition of OPC cements which are less than 50 % for all cement minerals (e.g. ~ 25 % for C-S-H, ~ 34 % for AFt, ~ 24 % for AFm) are expected to have only a limited effect on the measured distribution ratios ($R_d$ values). Therefore, sorption measurements on different OPC's should result in $R_d$ values, which lie within the estimated uncertainty range associated with the experiments (factor 2 to 10; see Chapter 4). The latter consideration further implies that $R_d$ values determined on cement CEM I 52.5 N HTS can be regarded as good estimates for other OPCs with slightly different mineral compositions.

Tab. 2.2: Estimated portions of the main minerals in the hydrate assemblage of sulphate-resisting OPC CEM I 52.5 N HTS (w/c = 1.3) and OPC CEM I 42.5 N (w/c = 0.5) after about 3 years of hydration.

<table>
<thead>
<tr>
<th>Cement phase *</th>
<th>Portion in CEM I 52.5 N [wt.-%]</th>
<th>Portion in CEM I 42.5 N [wt.-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-S-H</td>
<td>51</td>
<td>40</td>
</tr>
<tr>
<td>Portlandite</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>AFt phases (ettringite)</td>
<td>8.9</td>
<td>13.5</td>
</tr>
<tr>
<td>AFm phases (i.e. monocarbonate)</td>
<td>9.7</td>
<td>12.7</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>1.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Non-hydrated clinker minerals</td>
<td>7.7</td>
<td>11</td>
</tr>
</tbody>
</table>

* Estimates are based on the data reported in Lothenbach & Wieland (2006) and Lothenbach & Winnefeld (2006).

The above consideration further implies that only sorption data determined on OPC should be considered for the selection process. In contrast, sorption values determined on blended cements or cements manufactured in presence of large amounts of supplementary materials, such as silica, should not be taken into consideration since the mineral composition of the hydrate assemblage of these cements may be very different from that of OPCs (Lothenbach 2010).
2.2.3 Impurities

Portland cements are ordinarily manufactured by heating raw mixes including limestone and clay, or materials with similar bulk composition and reactivity, ultimately to a temperature of about 1450 °C (Taylor 1997). Portland cement clinker forms due to partial fusion of the raw materials along with the release of CO₂. This material is mixed with few per cent of calcium sulphate and, in modern cements, calcium carbonate, and finely ground. Non-volatile impurity elements inherently associated with the raw materials are therefore accommodated in the clinker minerals after heat treatment and are then released and distributed among liquid and solid phase during hydration. Hence, the impurity elements inherently associated with unhydrated cements determine the background inventory of these elements in the aqueous and solid phase of hydrated cements.

The concentration of the most important impurity elements was determined in a calcite-free CEM I 52.5 N HTS cement (Lothenbach & Wieland 2006) by acid dissolution of the cement paste according to a method developed earlier for silicate rocks and minerals (Ayranci 1977). Note that, in contrast to the modern calcite-containing CEM I 52.5 N HTS cement (Tab. 2.1), the same cement type manufactured 15 years ago did not contain calcium carbonate filler. Apart from that, the chemical composition of the calcite-free cement was found to be similar to that of the calcite-containing CEM I 52.5 N HTS (Lothenbach & Wieland 2006). The single sample solution prepared upon acid dissolution of HCP was analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES), atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS). The concentrations are related to the amount of unhydrated cement used for the preparation of the paste (Tab. 2.3).

Tab. 2.3 shows that the impurity elements are present at different concentration levels in unhydrated cement. For example, concentrations above 100 ppm (µg/g) were determined for few elements such as Mn, P, Sr (Sr = 1'580 ppm estimated from the SrO content in Tab. 2.1), Ti, and Zn. Most elements are present at concentrations ranging between 1 – 100 ppm while the concentration of a few elements is below 1 ppm (Be, Cd, Eu, Ho, Lu, Tb, Tm, Yb), in particular the concentration of the rare earth elements. Furthermore, it was found that I and Se concentrations in cement are ~ 0.

The impurity elements, preferentially associated with the clinker minerals alite, belite, aluminate and ferrite in unhydrated cement, are redistributed among the minerals of the hydrate assemblage during the hydration process. The elements may be taken up by the structure of the latter minerals or may adsorb onto the surface. In contact with large volumes of aqueous solution, such as in batch-type sorption experiments carried out in dilute systems, these elements are released to solution as a result of desorption from the surface of cement phases or as a result of the dissolution of small portions of these phases under initially non-equilibrium conditions. Hence, an aqueous solution in contact with hydrated cement can contain concentrations of the impurity elements in accordance with the partitioning of the element between the liquid and solid phase. For example, the partitioning of the stable fraction of Sr and Ni between HCP and solution was demonstrated in previous studies (Wieland et al. 2006, Wieland et al. 2008).

The above considerations further imply that the uptake of a radiotracer by HCP in batch-type sorption experiments can only be investigated against the background concentration of competing impurity elements present in solution. Hence, all sorption measurements on HCP implicitly account for the sorption competition of radiotracers added with all impurity elements present in unhydrated cement and released upon immersion in aqueous solution. Furthermore, hydrated cement is considered to be an important, maybe even the main source of most impurity...
elements in the cementitious near field of ILW and L/ILW repositories, except for a few elements, such as Mn, Mo, Ni, and Cr, for which steel might be the main source due to the high concentrations of these elements in steel.

Tab. 2.3: Concentrations of the most important impurity elements in unhydrated CEM I 52.5 N HTS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration * [ppm]</th>
<th>Element</th>
<th>Concentration * [ppm]</th>
<th>Element</th>
<th>Concentration * [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>37.4</td>
<td>Ho</td>
<td>0.35</td>
<td>Rb</td>
<td>13.4</td>
</tr>
<tr>
<td>Ba</td>
<td>87.7</td>
<td>La</td>
<td>10.9</td>
<td>Sm</td>
<td>2.10</td>
</tr>
<tr>
<td>Be</td>
<td>0.75</td>
<td>Li</td>
<td>16.0</td>
<td>Sn</td>
<td>3.47</td>
</tr>
<tr>
<td>Cd</td>
<td>0.29</td>
<td>Lu</td>
<td>0.13</td>
<td>Sr</td>
<td>1576.0</td>
</tr>
<tr>
<td>Ce</td>
<td>19.8</td>
<td>Mn</td>
<td>208.9</td>
<td>Tb</td>
<td>0.32</td>
</tr>
<tr>
<td>Cl</td>
<td>80.0</td>
<td>Mo</td>
<td>2.58</td>
<td>Th</td>
<td>3.34</td>
</tr>
<tr>
<td>Co</td>
<td>4.28</td>
<td>Nb</td>
<td>3.19</td>
<td>Ti</td>
<td>684.2</td>
</tr>
<tr>
<td>Cr</td>
<td>58.4</td>
<td>Nd</td>
<td>10.1</td>
<td>Tm</td>
<td>0.13</td>
</tr>
<tr>
<td>Cs</td>
<td>1.23</td>
<td>Ni</td>
<td>24.3</td>
<td>U</td>
<td>3.84</td>
</tr>
<tr>
<td>Cu</td>
<td>42.2</td>
<td>P</td>
<td>336.0</td>
<td>V</td>
<td>37.9</td>
</tr>
<tr>
<td>Dy</td>
<td>1.80</td>
<td>Pb</td>
<td>47.0</td>
<td>Yb</td>
<td>0.92</td>
</tr>
<tr>
<td>Er</td>
<td>1.08</td>
<td>Pd</td>
<td>1.36</td>
<td>Zn</td>
<td>140.5</td>
</tr>
<tr>
<td>Eu</td>
<td>0.40</td>
<td>Pd</td>
<td>1.36</td>
<td>Zr</td>
<td>46.8</td>
</tr>
<tr>
<td>Gd</td>
<td>2.31</td>
<td>Pr</td>
<td>2.59</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Estimated uncertainty: ± 10 %

2.3 Nuclide inventories

The safety-relevant radionuclides present in ILW and L/ILW include all actinides and their daughters with long half-lives as well as activation and fission products. The list of radioelements considered in this study is shown in Tab. 2.4. The radionuclides have been selected on the basis of an analysis of the waste streams (Nagra 2008a, Tab. A3.1-2). Most of the radionuclides were classified as being safety-relevant in the previous stages of the Swiss waste management programme for which several databases were developed i.e. CEM-94, CEM-97 and CEM-02 (Bradbury & Sarott 1994, Bradbury & Van Loon 1997, Wieland & Van Loon 2002).

Tab. 2.4: Safety-relevant radioelements* (Nagra 2008a).

Some radioelements, i.e. H(HTO), Ca, Fe, Ho, Mn, Na, Pd, Pm, Ru, Sb included in previous SDBs are not discussed in this study due to their lower priority in the current stage of PA.

<table>
<thead>
<tr>
<th>Group I and II elements</th>
<th>K, Cs, Be, Sr, Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition elements (first and second series)</td>
<td>Co, Ni, Zr, Nb, Mo, Tc, Ag</td>
</tr>
<tr>
<td>Group IV, V, VI and VII elements</td>
<td>Sn, Pb, Se, Po, Cl, I</td>
</tr>
<tr>
<td>Lanthanides and actinides</td>
<td>Sm, Eu, Ac, Th, Pa, U, Np, Pu, Am, Cm</td>
</tr>
</tbody>
</table>
The sorption behaviour of a radioelement is influenced by the redox state of the dominant aqueous species. In this study, sorption values are given for reduced and oxidized species of a radioelement to account for possible variability of the redox potential in the cementitious near field of a repository. Note that oxidizing conditions prevail in the early phase of a repository while reducing conditions are expected to establish after repository closure due to the presence of large quantities of steel in the near field, which bind oxygen by oxic steel corrosion (Wersin et al. 2003). In the latter study, the reference $E_h$ potential was estimated to be $-230 \text{ mV}$. Kosakowski et al. (2014) indicate an $E_h$ range varying between $\sim -180 \text{ mV}$ and $\sim -530 \text{ mV}$ depending on the stage of the cement degradation. Tab. 2.5 shows the expected valence states of the redox-sensitive radioelements under the oxidizing and reducing conditions of L/ILW and ILW repositories in relation to the reference potential. Knowledge of the dominant redox state of a radionuclide under these conditions is important because the different redox species behave differently with respect to sorption and speciation.

Tab. 2.5: Redox states of redox-sensitive radioelements in aqueous media under highly alkaline conditions considered in this study.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidizing conditions</th>
<th>Reducing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>+VI</td>
<td>+IV/−II</td>
</tr>
<tr>
<td>Mo</td>
<td>+VI</td>
<td>+VI</td>
</tr>
<tr>
<td>Tc</td>
<td>+VII</td>
<td>+IV</td>
</tr>
<tr>
<td>Sn</td>
<td>+IV</td>
<td>+IV</td>
</tr>
<tr>
<td>Po</td>
<td>+IV</td>
<td>+II</td>
</tr>
<tr>
<td>Pa</td>
<td>+V</td>
<td>+IV</td>
</tr>
<tr>
<td>U</td>
<td>+VI</td>
<td>+IV</td>
</tr>
<tr>
<td>Np</td>
<td>+VI/+V</td>
<td>+IV/+III</td>
</tr>
<tr>
<td>Pu</td>
<td>+VI/+V</td>
<td>+IV/+III</td>
</tr>
</tbody>
</table>

2.4 Geochemical evolution of the cementitious near field

The geochemical evolution of the cementitious near field is controlled by internal chemical processes, such as steel corrosion, decomposition of organic materials, interaction between hydrated cement and aggregates, and processes driven by the interaction with the surrounding host rock, such as ingress of pore water from the host rock into the near field, interaction of the hyper alkaline near-field pore water with the surrounding host rock (pH plume). As mentioned in Kosakowski et al. (2014) the geochemical evolution may not proceed in terms of a linear sequence of single processes but rather by coupling of different processes. Furthermore, the availability of water is a prerequisite for chemical reactions, such as steel corrosion or the decomposition of organic materials, which is potentially mediated by microbial activity.
The following geochemical information should be available to ensure traceability of the selection process for sorption values:

- Chemical composition of the pore water in HCP as a function of the geochemical evolution of cementitious materials
- Mineral composition of the cementitious material in the course of its geochemical evolution

Geochemical evolution of the near field (cement degradation) is driven by the interaction of cement paste with infiltrating groundwater on the one hand, and/or waste materials on the other hand. Both pathways of geochemical evolution have an effect on the pore water composition and mineral composition of the cement matrix over time.

### 2.4.1 Cement degradation by groundwater ingress

In the absence of any degradation by waste materials, cement is subject to chemical degradation caused by groundwater ingress. Cement alteration occurs because groundwater from the host rock is not in equilibrium with hydrated cement. In general, three stages of the cement degradation are distinguished (Atkinson et al. 1989, Berner 1992, Kosakowski et al. 2014). The cement pore water composition is dominated by the release of alkali hydroxides (NaOH and KOH) from cement in the first stage of cement degradation (stage I) which results in a pH of about 13.3 or higher. In stage II, the chemical composition of the alkali-depleted pore water is controlled by the solubility of portlandite, which fixes \([\text{Ca}^{\text{tot}}]\) at \(\sim 2 \times 10^{-2}\) M and the pH at \(\sim 12.5\). 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 C-S-H phases and other cement phases determines the pH buffering capacity. When thermodynamic equilibrium between the cement minerals and the pore water is assumed, the time scale of the different stages depends on the rate of pore water exchange in the near field.

Models of cement degradation have been developed and used to predict the evolution of the cement material and pore water compositions in the near field of the planned Swiss ILW and L/ILW repositories (Berner 1988, Berner 1990, Neall 1994, Pfingsten & Shiotoku 1998, Pfingsten 2002, Schwyn et al. 2003). In these earlier studies the cement degradation model as proposed by Berner (1990) was used to estimate the pore water composition of the L/ILW near field in contact with inflowing groundwater of different compositions, i.e., a NaHCO₃ and a NaCl-containing groundwater (Neall 1994). The modelling approach proposed by Neall (1994) was further adopted for the prediction of the pore water composition of the ILW near field in Opalinus Clay (OPA) (Schwyn et al. 2003). A comparison of the pore water data obtained in the two latter studies revealed that the chemical conditions prevailing in the L/ILW and ILW near fields are similar for the same type of inflowing groundwater that is NaHCO₃ or NaCl-containing groundwater, respectively. While differences in the concentrations of some elements were recognized (e.g. Al, SO₄²⁻), variations in the two main parameters, that is pH and the concentrations of important radionuclide-complexing, inorganic ligands (e.g. CO₃²⁻, Cl⁻, F⁻) were found to be small. The latter finding allowed the simplification to be made that no significant effect on radionuclide speciation and uptake processes is anticipated in the two repository systems for L/ILW and ILW (Wieland & Van Loon 2002).

Recent predictions of the geochemical evolution of the near field of a cement-based repository were based on reactive transport calculations assuming diffusive exchange across the host rock/concrete interface or advective water flow in a fractured host rock (Kosakowski et al. 2014). In the former case, concrete degradation is not expected to take place in a sharp geochemical front where all cement minerals are dissolved simultaneously. Instead, several sub-
sequent mineral transformation zones are expected to develop, which are spatially distributed in the system. In the case of fracture flow, however, a sharp degradation front is anticipated since the dissolution zones of the cement minerals do not widen over time (Kosakowski et al. 2014). Furthermore, the propagation of the degradation front will directly depend on the water flux and the composition of the inflowing groundwater. For example, ingress of highly saline groundwater (e.g. from Effingen Member) is expected to accelerate cement degradation. The compositions of pore waters for the three stages of the cement degradation were determined from reactive transport modelling (Kosakowski et al. 2014). They are listed in Tab. 2.6 and further discussed in Section 2.5.

2.4.2 Cement Degradation by interaction with waste materials

Cement degradation may further occur as a consequence of metal corrosion, the decomposition of organic materials, and/or the interaction of hydrated cement with silicate aggregates (Kosakowski et al. 2014). This process can be largely ignored for SMA-1/LMA-1-type waste sorts because the inventories of metals and organic materials will not exceed the critical limit that could cause any adverse effect on the engineered cement barrier. In SMA-2/LMA-2-type waste, however, the inventories of the latter materials could exceed the critical limit, which could give rise to significant cement degradation (for details see Sections 4.5 and 4.6).

Metallic materials will be subject to anoxic corrosion, which produces H₂. The most important reactive metals in the waste matrix are Mg, Al and Fe (Kosakowski et al. 2014). These elements are constituents of cement minerals and therefore, their release during corrosion into solution may have an impact on the mineral composition of hydrated cement. A literature survey, supported by thermodynamic scoping calculations, allowed potential impacts to be assessed (Kosakowski et al. 2014). For example, a large portion of Mg generated during corrosion was found to precipitate as brucite (Mg(OH)₂), while only a small amount of Mg was bound as hydroxide. The large Mg inventories of some waste forms are not expected to significantly alter the mineral composition of HCP by forming new Mg-rich cement phases because Mg mainly precipitates as brucite. Therefore, no effect on radionuclide retention is expected. High Al loadings give rise to the conversion of portlandite and ettringite into hydrogarnet, calcium hemicarboaluminate and calcium hemisulphoaluminate. Similarly, under the reducing conditions of the near field, increasing Fe(II) loadings were predicted to cause the conversion of ettringite into hydromagnetite and pyrite, along with the simultaneous precipitation of excess Ca as portlandite and calcite. Therefore, high loadings of metallic Al and Fe, as found in the SMA-2/LMA-2-type waste compartments, may give rise to significant cement alteration under these conditions, which may have an effect on radionuclide retention.

Decomposition of low-molecular-weight (LMW) and high-molecular-weight (HMW) organic materials can take place via biotic, abiotic or radiolytic processes (Kosakowski et al. 2014). Cellulose was reported to degrade via an abiotic decomposition process under alkaline conditions while radiolytic decomposition of bitumen was observed, which generates LMW organic compounds. In general, hydrolysis or abiotic degradation of HMW organics is regarded as the first step for microbial degradation of HMW organic compounds, which is an important degradation process of organics under repository conditions. The near field will not be sterile and microbial activity has to be considered as possible route of the degradation of organic materials in a cementitious near field. However, it should be noted that biotic degradation is expected to be very slow under the hyper alkaline conditions of the cementitious near field as microbial processes will be largely decelerated. Microbial degradation of organic materials is expected to take place predominantly via methanogenesis forming CO₂ and CH₄, while anaerobic degradation due to respiration, which consumes Fe³⁺ and SO₄²⁻ as electron acceptors,
is considered to be a possible, alternative pathway of less importance due to their limited availability. Production of \( \text{CO}_2 \) gives rise to \( \text{CaCO}_3 \) precipitation in the near field, which consumes the main Ca sources portlandite and C-S-H phases:

\[
\text{Ca(OH)}_2(s) + \text{CO}_2 \ (g) \leftrightarrow \text{CaCO}_3(s) + \text{H}_2\text{O} \quad (1)
\]

\[
x\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}(s) + x\text{CO}_2(g) \leftrightarrow x\text{CaCO}_3(s) + \text{Si(OH)}_4 + (n-2) \text{H}_2\text{O} \quad (2)
\]

Consumption of portlandite and C-S-H phases will allow pH to drop below pH 12.5 i.e. the pH controlled by portandite solubility. Nagra's PA is based on the safety criterion that the amount of portlandite allowed to transform into calcite by the degradation of organic matter (Eq. 1) should not exceed 2/3 of the initial portlandite inventory in HCP in the SMA-1/LMA-1-type waste compartments. This ensures that the retention-controlling cement minerals are present in the cement matrix although partial conversion of portlandite into calcite occurs. This ensures that the barrier function will be maintained during the evolution of the cementitious near field. In the SMA-2/LMA-2-type waste compartments, however, portlandite conversion may well exceed the above limit, thus giving rise to substantial cement alteration caused by the microbial degradation of organic materials. There, cement alteration may have a significant effect on radionuclide retention.

Cement degradation could further be initiated by the reaction of hydrated cement with silicate aggregates (e.g. quartz, feldspars). The latter materials are thermodynamically unstable at high pH and therefore act as a Si source. Si released from the aggregate material could react with portlandite, the main Ca source of hydrated cement, to form C-S-H phases. Hence, presence of the thermodynamically unstable aggregates could promote cement degradation by converting portlandite-containing HCP into a strongly degraded material, which is depleted of portlandite and contains C-S-H phases with a significantly lower calcium-to-silica (C/S) ratio. It should be noted that kinetic constraints, in particular the dissolution of aggregate material, could become important and determine the extent of internal cement degradation over time. Information on the dissolution rates of silicate aggregates in concrete is scarce (Kosakowski et al. 2014). The development of reaction rims on the surface of aggregates may change the transport characteristics of solutes and therefore limit the progress of silica-induced cement degradation. Eventually, availability of water may be a limiting factor as the conversion reaction consumes water that needs to be transported to the reaction front, either in liquid or in gaseous form (water vapour). As noticed in Kosakowski et al. (2014) the temporal evolution of internal cement degradation is determined by parameters that are presently ill defined. Nevertheless, the considerations reported in Kosakowski et al. (2014) reveal that in the presence of silicate aggregates the stage of cement degradation determined by portlandite saturation (pH \( \sim 12.5 \)) could cover a much shorter period of time than anticipated from degradation scenarios solely based on groundwater ingress from the host rock.

For the development of the present SDB three characteristic stages of the cement degradation are taken into consideration (see Chapter 4) associated with the ingress of groundwater from the host rock. The effect of internal cement degradation on radionuclide retention in the near field is briefly discussed in connection with radionuclide retention in SMA-2/LMA-2 waste compartments (Section 4.6).

### 2.5 Composition of cement paste and pore water for SDB development

The composition of the pore water in the cementitious near field was estimated on the basis of results from the reactive transport calculations, which were carried out to predict the geo-chemical evolution of cement-based repositories using state-of-the-art modelling tools.
(Kosakowski et al. 2014). The pore water compositions were selected according to three characteristic stages of the cement degradation: 1) A "fresh" HCP system with high concentrations of alkalis and pH > 13, 2) HCP depleted from alkalis and pH controlled by portlandite solubility, and 3) a HCP system controlled by incongruent dissolution of C-S-H and other cement phases, which determines the pH buffering capacity ("low-pH" stage of HCP).

All major cement phases are expected to be present in the first two stages of the cement degradation that is portlandite, ettringite, AFm (e.g. calcium monocarboaluminate) and C-S-H phases, calcite and hydrotalcite (Tab. 2.6). A cement paste altered to stage III of the cement degradation, however, will be depleted from portlandite and AFm phases while the other cement phases are expected to persist to this last stage of the cement degradation. Note that C-S-H phases with C/S ratio > 1.5 were found to prevail in cement paste in stage I and II of the cement degradation while the C/S ratio of C-S-H phases in stage III of the cement degradation will be significantly lower (C/S < 1).

Tab. 2.6: Geochemical conditions (solids, pore water composition) for the three characteristic stages of the cement degradation (Kosakowski et al. 2014).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Stage I</th>
<th>Stage II</th>
<th>Stage III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity [%]</td>
<td>20</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>pH</td>
<td>13.1</td>
<td>12.54</td>
<td>11.07</td>
</tr>
<tr>
<td>Eh [mV]</td>
<td>-529.9</td>
<td>-498.1</td>
<td>-180.7</td>
</tr>
<tr>
<td>Ionic strength [m]</td>
<td>0.168</td>
<td>9.83 × 10^-2</td>
<td>0.150</td>
</tr>
<tr>
<td>Solutes [mol/L]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>9.68 × 10^-2</td>
<td>4.21 × 10^-2</td>
<td>0.104</td>
</tr>
<tr>
<td>K</td>
<td>7.27 × 10^-2</td>
<td>3.30 × 10^-3</td>
<td>2.55 × 10^-2</td>
</tr>
<tr>
<td>Ca</td>
<td>2.43 × 10^-3</td>
<td>1.80 × 10^-2</td>
<td>5.35 × 10^-3</td>
</tr>
<tr>
<td>Sulfate</td>
<td>6.24 × 10^-4</td>
<td>4.70 × 10^-5</td>
<td>7.81 × 10^-3</td>
</tr>
<tr>
<td>Chloride</td>
<td>2.46 × 10^-4</td>
<td>3.74 × 10^-2</td>
<td>0.123</td>
</tr>
<tr>
<td>Carbonate</td>
<td>4.46 × 10^-5</td>
<td>8.04 × 10^-6</td>
<td>1.67 × 10^-5</td>
</tr>
<tr>
<td>Si</td>
<td>4.34 × 10^-5</td>
<td>3.42 × 10^-5</td>
<td>3.45 × 10^-4</td>
</tr>
<tr>
<td>Al</td>
<td>2.61 × 10^-5</td>
<td>6.89 × 10^-6</td>
<td>1.15 × 10^-4</td>
</tr>
<tr>
<td>Fe</td>
<td>2.11 × 10^-7</td>
<td>5.58 × 10^-8</td>
<td>3.86 × 10^-8</td>
</tr>
<tr>
<td>Major solids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-S-H</td>
<td>Portlandite</td>
<td>Portlandite</td>
<td>C-S-H</td>
</tr>
<tr>
<td>Ettringite</td>
<td>Ettringite</td>
<td>Ettringite</td>
<td></td>
</tr>
<tr>
<td>Monocarbonate</td>
<td>Monocarbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>Calcite</td>
<td>Calcite</td>
<td></td>
</tr>
<tr>
<td>OH-hydrotalcite</td>
<td>OH-hydrotalcite</td>
<td>OH-hydrotalcite</td>
<td></td>
</tr>
</tbody>
</table>
Tab. 2.7: Predicted composition of the cement pore waters in stages I and II of the cement degradation for a repository in OPA host rock (Schwyn et al. 2003, Table 4-3).

<table>
<thead>
<tr>
<th>Component</th>
<th>Stage I Early pore water [mmol/L]</th>
<th>Stage II OPA [mmol/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>101</td>
<td>169</td>
</tr>
<tr>
<td>K</td>
<td>303</td>
<td>5.7</td>
</tr>
<tr>
<td>Ca</td>
<td>0.84</td>
<td>20.1</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt; 10^{-4}</td>
<td>&lt; 10^{-4}</td>
</tr>
<tr>
<td>Al</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>0.20</td>
<td>0.01</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>0.75</td>
<td>0.1</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>160</td>
</tr>
<tr>
<td>F</td>
<td>0.76</td>
<td>0.10</td>
</tr>
<tr>
<td>Si</td>
<td>0.05</td>
<td>0.016</td>
</tr>
<tr>
<td>pH</td>
<td>13.44</td>
<td>12.55</td>
</tr>
<tr>
<td>Eh [mV]</td>
<td>-790 to -430</td>
<td>-750 to -230</td>
</tr>
</tbody>
</table>

Tab. 2.6 further shows the chemical compositions of the pore waters as obtained from reactive transport modelling (Kosakowski et al. 2014). The concentrations of solutes can be compared with those determined on the basis of earlier modelling approaches as listed in Tab. 2.7 (Berner 1990, Neall 1994). Both modelling approaches were carried out for a cement-based repository in OPA. The results were reported by Schwyn et al. (2003) along with the modelling approach and further discussed in connection with the development of the CEM-02 SDB (Wieland & Van Loon 2002). The compositions of the pore waters are consistent in the different stages of the cement degradation. For example, differences in the solute concentrations of stage I pore water are smaller than a factor of 5. Minor differences result for Na, S and Si concentrations while differences are within a factor of 3 – 4 for Ca, Al and OH$^-$ concentrations as well as Eh. This is further true for stage II pore water: minor differences appear in pH, and the concentrations of Ca, carbonate and Al while differences are within a factor of 2 – 5 for Na, K, S, Cl and Si concentrations. Deviations in the concentrations of the major elements, such as Ca, S, carbonate, Si and Al, are caused by the different sets of thermodynamic data used for modelling the solubility of the main cement minerals in the different studies. Differences in Na, K and Cl concentrations can be attributed to differences in the composition of the host rock groundwater.

The differences in the main parameters (pH, Eh) and the elemental concentrations are small and therefore, they are ignored in connection with the selection process of sorption values. The differences in the concentrations of Na, K, Ca, S, Si and Al only have a negligibly small effect on the mineral composition of HCP. Furthermore, the differences in the concentrations of Cl and carbonate only have a minor effect on radionuclide complexation.
3 Uptake Process in Hydrated Cement

3.1 Macroscopic data and process understanding

The large pool of cement sorption data available to date originates from single-point sorption measurements with radionuclides on cementitious systems i.e. hydrated cement, individual cement minerals. At best, the data sets consist of sorption kinetic and isotherm measurements as well as sorption studies conducted at varying pH in the alkaline pH range (pH $\geq 11$). As often no specific information on the uptake mechanisms is available, it is warranted to express the partitioning of a radionuclide between cement pore water and the cementitious material in terms of a distribution ratio, $R_d$, given by:

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

The above expression represents the depletion of the radionuclide from solution due to uptake by the solid. The amount of a radionuclide sorbed is determined by the difference between the initial radionuclide activity and the final activity in solution. The experimental approach to determine the partitioning does not provide any specific information on the uptake mechanism. The latter information can only be obtained on the basis of additional parameter variations in wet chemistry investigations, such as measurements at increasing solute concentrations (isotherms) and reversibility tests, or spectroscopic investigations on the coordination environment of the sorbate. The majority of published sorption studies, however, do not provide any specific information on the uptake mechanisms in cementitious systems. Thus, the mechanisms are often poorly known and for some radionuclides, several mechanism have been proposed to explain their uptake by HCP (see review by Evans 2008). This illustrates that the uptake mechanisms in cementitious systems are diverse and intricate, and in particular, it means that available information on uptake mechanisms is rather limited. As a consequence of the above and in the framework of this study, all sorption data reported in the literature from sorption studies on cementitious systems are primarily considered to represent radionuclide partitioning (expressed in terms of an $R_d$ value). Furthermore, any additional information published on the partitioning of a radionuclide of interest has been critically assessed with the aim of proving whether or not this information allows a specific mechanism of the uptake process to be proposed, further underpinning the selected $R_d$ value. This approach allows the distribution ratios of a radionuclide on HCP to be related to a specific uptake mechanism controlled by a specific cement phase. An understanding of the uptake mechanisms on cementitious materials is essential for long-term predictions of the safe disposal of radioactive waste because it allows sorption values to be assigned which are consistent with the different stages of the cement degradation in a repository (see Section 2.4). A mechanistic understanding of uptake processes enables us to justify the use of sorption values, which were determined from laboratory experiments, and enables their use in PA studies, which consider much longer time scales.


- Precipitation or surface precipitation, i.e., the formation of a pure solid phase
- Co-precipitation or surface precipitation with other phases, i.e. the formation of a solid phase with mixed composition without forming a solid solution
• Solid-solution formation, i.e., lattice incorporation into a cement mineral by re-crystallization, precipitation with, or diffusion into an existing solid phase
• Adsorption onto hydrous surfaces (adsorption, chemisorption)

Adsorption of radionuclides and formation of solid solutions can reduce their concentration below saturation with respect to a pure solid phase, thus circumventing precipitation. Adsorption is either specific (e.g. surface complexation) or non-specific (e.g. electrostatic interaction) while the formation of a solid solution depends on ion parameters such as size, charge, local geometry, and therefore is regarded as specific sorption process. Uptake mechanisms are species-specific and several cement minerals, such as calcium aluminates (AFm- and AFt-phases) and C-S-H phases, are prime candidates for cation and anion binding in the cement matrix because of their abundance and appropriate surface and structural sites available for sorption. Furthermore, the mechanisms often cannot be absolutely delimited, and the aforementioned categories represent limiting cases of radionuclide binding.

Uptake of radionuclides is quantified in terms of a distribution ratio, \( R_d \) (or \( R_\theta \)). "Sorption" is used in the narrower sense (except in connection with well-established terms such as "sorption database" and "sorption value"), hence implying uptake of a component due to adsorption, ion exchange, solid solution formation, and isotopic exchange. The distribution ratio, \( R_d \), thus corresponds to a distribution coefficient, \( K_d \) (or \( K_\theta \)), if precipitation can be excluded to be the uptake process. "Adsorption" refers to a net accumulation of matter at the interface between solid phase and an aqueous phase (Sposito 1984, Sposito 1989), which is a two-dimensional process and therefore different from absorption (structural incorporation) or precipitation (three-dimensional molecular structure). Three fundamental adsorption modes are distinguished in case of organics: hydrophobic expulsion, electrostatic attraction, and surface complexation. Adsorption of metal cations is due to electrostatic attraction (or "outer sphere" surface complex formation) or surface complexation (or "inner sphere" surface complex formation) (Schindler 1990, Stumm 1992).

At the present time only very few thermodynamic models exist which allow radionuclide uptake by cementitious materials to be predicted for a wide range of conditions (Wieland et al. 2008; Gaona et al. 2012a). As a consequence, the extent of radionuclide interaction with HCP still has to be expressed in terms of conditional distribution constants (e.g. \( R_d \) or \( K_d \) values). While the pool of sorption data available in literature is substantial (e.g. reviews in Wang et al. 2009 and Oechs et al. 2010), the current understanding of uptake mechanisms on the atomistic scale is still limited because mechanistic sorption studies only exist for very few safety-relevant radionuclides on the basis of spectroscopic investigations (e.g. Scheidegger et al. 2000, Pointeau et al. 2001, Tits et al. 2003a, Schlegel et al. 2004, Stumpf et al. 2004, Bonhoure et al. 2006, Vespa et al. 2006a,b, Vespa et al. 2007a,b, Wieland et al. 2008, Gaona et al. 2011, Tits et al. 2011b, Gaona et al. 2013). Molecular-level studies on uptake mechanisms are indispensable with the aim of developing thermodynamic models of radionuclide uptake by cementitious materials. Implementation of sorption processes in thermodynamic cement models will enable us to predict the interaction of radionuclides with cementitious materials over the wide range of conditions that represent the real system (e.g. radionuclide retention in a degrading cementitious near field). To date, only very few studies report a consistent thermodynamic modelling approach that allows radionuclide uptake by hydrated cement to be predicted under varying conditions (e.g. Gaona et al. 2012a). Remarkable progress has been made over the last years in the thermodynamic modelling of the evolution of the phase composition during the hydration process (e.g. Lothenbach & Winnefeld 2006, Lothenbach et al. 2008, Balonis et al. 2010). As stated earlier in CEM-94 (Bradbury & Sarott 1994), availability of such models will be important to fully justify the sorption values recommended for use in PA. Therefore, due to the lack of
currently existing thermodynamic sorption models in cementitious systems, the selection process for the current update of the cement SDB strongly relies on "expert judgement" with the aim of developing a consistent set of sorption values for HCP.

### 3.2 In-house sorption measurements

Over the last decade in-house investigations on the uptake of safety-relevant radionuclides, such as Cs(I), Sr(II), Ra(II), Ni(II), Eu(III), Am(III), Sn(IV), Th(IV), U(VI), Np(IV/V/VI), Se(IV) and I(-I) on sulphate-resisting Portland cement (CEM I 52.5 N HTS) and cement minerals (C-S-H phases, AFm-phases) have been carried out under conditions relevant to the near field of a repository for radioactive waste. HTS cement has been used for many years to solidify and stabilise low- and intermediate-level waste in Switzerland. The above radionuclides were selected as representatives of important groups of elements, i.e., Cs(I) and Sr(II) for the alkali and earth-alkali metals, including Ra(II), Ni(II) for the bivalent transition metals, Eu(III) for the trivalent lanthanides and actinides, Th(IV) and Np(IV) for the tetravalent actinides, Np(V) for the pentavalent actinides, and U(VI) and Np(VI) for the hexavalent actinides. Furthermore, Sn(IV) represents the strongly hydrolysing tetravalent metal cations. Through-diffusion experiments have been carried out in-house and are complementary to batch-type sorption studies with the aim of assessing the retention of selected radioelements (Cs(I), Ni(II), Cl(-I) and I(-I)) in compact cement paste. The large number of in-house sorption measurements carried out under well-defined conditions enables us to use these data as guidance in this study.

Uptake studies on HTS cement were conducted as described in detail elsewhere (Wieland et al. 1998, Wieland et al. 2000, Wieland et al. 2002, Wieland et al. 2006, Wieland et al. 2008). The measurements were carried out using crushed HCP material (size fraction ≤ 70 µm; N 2-BET (Brunauer-Emmett-Teller) surface area = 46 ± 4 m²/g) prepared from HTS cement. Preparation of the paste was described earlier (Sarott et al. 1992). For the sorption measurements, appropriate amounts of crushed HCP material were added to artificial cement pore water (ACW) in 40 mL polyallomere centrifuge tubes to achieve the appropriate solid-to-liquid (S/L) ratio. To ensure equilibrium conditions ACW had the composition of a pore water in equilibrium with fresh HCP in stage I of the cement degradation with respect to the main cement-derived cations at pH 13.3, i.e., Na, K, Ca, and the most important minor elements, i.e. Al, S and Si. Stability tests carried out by immersing crushed HCP in ACW allowed the equilibrium concentrations of the aforementioned elements to be determined (Wieland et al. 2006). To simulate conditions in stage II of the cement degradation crushed HCP material was immersed in Milli-Q water which was replaced twice to remove the alkalis (e.g. Tits et al. 2006a,b). The pH of the solution was fixed at ~ 12.5 by the solubility of portlandite present in HCP, thus indicating that stage II of the cement degradation was reached.

In addition to sorption studies on HCP, sorption measurements on C-S-H phases were carried out as described in detail elsewhere (Tits et al. 2003a, Tits et al. 2004, Tits et al. 2006a, Tits et al. 2006b, Tits et al. 2008). In brief, AEROSIL 300 (SiO₂) (Degussa-Huls AG, Baar Switzerland) was mixed with CaO (obtained by firing CaCO₃ (Merck AG, Dietikon, Switzerland) at 1'000°C) in polyallomere centrifuge tubes to give target C/S ratios between 0.6 and 1.82. To this, ACW or Milli-Q water was added to achieve the appropriate target S/L ratios of the suspensions. After an ageing period of at least 2 weeks, the C-S-H suspensions were used for sorption studies. Test experiments showed that the composition of the supernatant solution was constant after 2 weeks, suggesting that ageing of the C-S-H phases was complete within this period of time.
The partitioning of a radioelement between HCP or C-S-H and the equilibrium solution were determined by adding small aliquots of tracer solutions of the selected radionuclide to the suspensions (total volume of 40 mL). Radiotracers were added at concentrations well below the solubility with respect to potentially solubility-limiting phases under the given conditions (typical concentration range $10^{-11} - 10^{-8}$ M). The suspensions were equilibrated end-over-end for appropriate periods of time. For each radioelement, the time period was selected based on the results from preceding kinetic tests. The time required to reach equilibrium typically ranged from 7 to 30 days. After equilibration, the solid and liquid phases were separated by centrifugation (95'000 g for 60 min). Aliquots were withdrawn from the supernatant solution for activity measurements ($\beta/\gamma$ counting). All preparation and equilibration steps were carried out in a glove box under a N$_2$ atmosphere (O$_2$ and CO$_2$ < 2 ppm).

The distribution ratio ($R_d$) of the radionuclide of interest was determined with Eq. (3), i.e. as the ratio of the activity of the radionuclides bound onto the solid and the measured radionuclide activity in solution. The amount of sorbed tracer is given as the difference between the initial radionuclide activity in the sample and the measured activity in solution at equilibrium. It should be noted that, in case of strongly sorbing tracers such as trivalent lanthanides and actinides as well as tetravalent actinides, determination of the $R_d$ value is strongly influenced by the experimental window on the one hand, that is the S/L ratio used in combination with the total activity or concentration, respectively, of a radiotracer added to the system, and the technique used for solid-liquid phase separation on the other hand. The S/L ratio in combination with the total activity (or concentration) of the sorbing tracer are the main factors that determine the experimental window for which statistically meaningful sorption values can be obtained (Tits et al. 2002). It is conceivable that some sorption measurements with strongly sorbing radionuclides published in the open literature were performed outside the acceptable experimental window, in particular in all those cases where high S/L ratios along with low initial tracer activities were used. Under these conditions the tracer activity (or concentration) in solution may be close to the detection limit of the analytical technique. Sorption values determined close to or at the detection limit correspond to maximum sorption values that can be measured for the given experimental set-up rather than "true" sorption values. Hence, the "true" sorption values are greater than the measured ones in all these cases (Tits et al. 2002).

The separation technique used for the experiments determines the efficiency of phase separation, in particular the degree to which colloidal matter is removed from solution. The protocol used in sorption experiments to separate solid and liquid phase, which is usually based on filtration or centrifugation, determines the boundary between a "truly" dissolved species and a colloid-borne species. This boundary is particularly important in the case of the strongly sorbing radiotracers where the applied separation technique operationally distinguishes between measurable activity in solution, either as true solution species or colloid-borne species, and the activity associated with the solid phase. For example, Cowper et al. (2006) showed that the sorption value for Am on HCP was lower when centrifugation was carried out at low acceleration (e.g., bench-top centrifuge for 30 min at 4'500 rpm). Thus, increasing concentrations of colloids in solution onto which Am sorbed gave rise to an apparent increase in the aqueous Am concentration. As a consequence, low sorption values were determined for Am after centrifugation at low acceleration. On the other hand, filtration is the technique widely used for solid-liquid phase separation. This technique has deficiencies, which could have a strong impact on measured sorption values. For example, in addition to the colloid-borne species, which are retained according to the cut-off of the filter membrane, also "truly" dissolved species could sorb onto the filter cake and/or the filter device, due to the large surface area exposed by these media. Such artefacts could invalidate the measured sorption values.
In this study the $R_d$ values determined for the strongly sorbing radionuclides, as reported in the literature and obtained from in-house sorption measurements, are regarded as "operational" values deduced on the basis of specific protocols applied for solid-liquid phase separation in the experiments. It is believed that centrifugation for 60 min at 95,000 g which was applied in the course of the in-house sorption studies, was insufficient to remove all colloid-borne species from solution. Strongly sorbing radionuclides bound to colloids with size < 20 nm remained dispersed in solution, thus contributing to the measured activity inventory in solution. Hence, "true" sorption values for the strongly sorbing radionuclides could be even higher than those determined from in-house sorption experiments.

In Chapter 3, results from in-house sorption measurements with safety-relevant radionuclides are discussed along with the corresponding values reported in the open literature.

### 3.3 Uptake-controlling cement phases

It has been recognized that uptake processes in cementitious systems are species sensitive and often require particular involvement of a specific cement phase (e.g. reviews in Gougar et al. 1996, Cornelis et al. 2008, Evans 2008). The mineral composition of the hydrate assemblage of the HTS cement used for the stabilization of radioactive waste in the framework of the Swiss disposal programme is known (Section 2.2.2). Relevance of single cement phases can be assessed with a view to their potential for radionuclide immobilization.

#### 3.3.1 Calcium silicate hydrates (C-S-H)

C-S-H phases comprise ~ 46 wt.-% of the cement paste of HTS cement. C-S-H phases are predominantly amorphous in nature with a high surface area (~ 150 m²/g; Tits et al. 2014) while presence of microcrystalline domains cannot be excluded. The initially amorphous C-S-H gel may gradually convert to a more crystalline phase over time. C-S-H phases are among the thermodynamically most stable cement phases and they are found to persist over a very long time scale in an evolving cementitious near field (Atkinson et al. 1989, Berner 1992, Wang et al. 2009, Kosakowski et al. 2014). The current view of cement degradation as revealed from model predictions are supported by the limited number of currently available experimental studies (Faucon et al. 1997).

Ca$^{2+}$ is the most important cation controlling the C-S-H surface charge (Viallis-Terrisse et al. 2001, Jönsson et al. 2004). Hence, the surface charge of C-S-H phases under alkaline conditions depends on the Ca$^{2+}$ concentration in solution. The zero point of charge (molar C/S ratio = 0.66 and 1.5) was found to be reached at an aqueous Ca concentration of about 2 mM (Viallis-Terrisse et al. 2001, Labbez et al. 2007). Note that the aqueous Ca concentration in equilibrium with fresh, intact HCP ranges between ~ 1 and ~ 2 mM (pH >13). The aqueous Ca concentration is dependent on pH in degrading systems i.e. ranging from ~ 0.1 mM at pH ~ 11.5 to ~ 20 mM at pH = 12.5 (Pointeau et al. 2006b). The surface charge is expected to exert only a minor effect on the uptake of metal cations while an influence on anion retention by C-S-H phases cannot be disregarded.

The adsorption capacity of C-S-H phases for metal cations is well documented (reviews by Gougar et al. 1996, Cornelis et al. 2008, Evans 2008). Adsorption may often be the first intermediate step in the uptake of metal cations by C-S-H phases and it was proposed in earlier studies that metal cations could be taken up into the structure of C-S-H phases (Cocke & Mollah 1993, Glasser 1992). For more than a decade modern synchrotron-based spectroscopic techniques allow the local coordination environment of sorbed species to be directly determined.
in cementitious systems (Scheidegger et al. 2006, Vespa et al. 2007a). This further allows adsorption and absorption processes to be distinguished from each other on the basis of the number of neighbouring atoms of a central metal cation or an anion. Recent studies provide experimental evidence that the initial adsorption step of a metal cation bound onto C-S-H phases is followed by subsequent structural incorporation (Mandaliev et al. 2009, Mandaliev et al. 2011, Gaona et al. 2011, Tits et al. 2011). The latter process then determines long-term immobilization of radionuclides. Hence, structural information on the local arrangement of radionuclides (cations, anions) is considered to be essential for the determination of uptake mechanisms and the development of thermodynamic models of radionuclide immobilization in cementitious materials (Gaona et al. 2012a).

Uptake of anions into the C-S-H structure seems to be less important though some evidence exists that silicate substitution in C-S-H phases by chromate and arsenate could occur (see Cornelis et al. 2008 and references therein). AFt and AFm phases are believed to have a stronger tendency to bind anions. For example, arsenate, arsenite, selenite and to some extent also chromate are considered to be taken up by C-S-H phases due to action of surface charge (see review by Cornelis et al. 2008). Furthermore, chloride was reported to be taken up by C-S-H phases with high C/S ratios while chloride had no influence on the C-S-H structure (Beaudoin et al. 1990). This suggests that Cl⁻ binding occurs onto the surface of C-S-H phases.

Re-crystallization could be an important process governing incorporation of radionuclides into C-S-H phases. In dispersed cementitious systems, the dynamic of solid phase re-crystallization operates on a time scale comparable to that of the kinetics of uptake processes. For example, ⁴⁵Ca exchange experiments revealed that a significant portion of the structures of crystalline C-S-H phases, i.e. 11 Å tobermorite and xonotlite, are accessible to Nd(III) uptake due to re-crystallization (Mandaliev et al. 2010b). The re-crystallization rate was found to continuously decrease over time. Fast ⁴⁵Ca uptake within the first day (~ 5 %) was attributed to a reversible exchange process with surface-bound Ca while the significantly lower re-crystallization rate between 1 day and about 150 days was attributed to the replacement of stable Ca by ⁴⁵Ca in the structure of C-S-H phases. Within this period of time, large portions of the two C-S-H structures had been re-crystallized. The different re-crystallization rates of the two crystalline C-S-H phases could be attributed to differences in the specific surface areas.

From the information available it is concluded that re-crystallization of C-S-H phases has positive consequences on radionuclide uptake as radionuclides could be taken up into the re-crystallized structure. In fact, spectroscopic investigations recently provided clear evidence for the incorporation of tri- and tetravalent actinides (Mandaliev et al. 2011, Gaona et al. 2011).

### 3.3.2 Ettringite (AFt)

Ettringite, a calcium aluminate mineral, is the common AFt phase of hydrated cement (Taylor 1997). AFt (Al₂O₃-Fe₂O₃-tri) phases (e.g. ettringite) are represented by the general formula (tricalcium)-Aluminate-Ferrite•tri(sulphate, hydroxide, etc.)•(hydrate), which implies the commonly used acronym. They contain three molecules of CaX₂n⁻ per molecule of aluminate (C₃A), where Xⁿ⁻ is the anionic species present in the interlayer, as opposed to AFm (Al₂O₃-Fe₂O₃-mono) phases, which contain stoichiometrically one molecule of CaX₂n⁻ per molecule of C₃A.

Ettringite forms hexagonal prismatic or acicular crystals. Columns consisting of Al(OH)₃ octahedra alternating with triangular groups of edge-sharing CaO₈ polyhedra and columns occupied by SO₄²⁻ and H₂O molecules account for the main structural features. Incorporation of oxyanions, such as arsenate, chromate, selenate, selenite etc., owing to partial or even full
replacement of $SO_4^{2-}$, is considered to be the dominant retention process. However, adsorption of anions is less likely due to the net negative surface charge of ettringite (Cornelis et al. 2008 and references therein). Uptake of oxyanions by ettringite can, in principle, be described thermodynamically in terms of solid solution formation (Perkins & Palmer 2000, Ochs et al. 2002). It should be noted, however, that very few modelling studies have been published to date due to lacking or incomplete thermodynamic data.

No evidence was found that indicates strong interaction of monovalent anions, such as chloride and iodide, with ettringite. Anion binding onto ettringite is expected to be negligibly small as the surface is negatively charged. Incorporation of monovalent anions is further believed to be limited by the coordinative constraints imposed by the column structure.

While ample evidence for the uptake of oxyanions by ettringite has been provided, few studies report metal cation substitution at the $Ca^{2+}$ and $Al^{3+}$ sites of the ettringite structure (Gougar et al. 1996 and references therein). Substitution of $Al^{3+}$ by $Fe^{3+}$ was observed (Möschner et al. 2008) while possible substitution with other trivalent cations, e.g. $Co^{3+}$, and bivalent cations, e.g. $Ni^{2+}$ etc., is only poorly known (Gougar et al. 1996 and references therein).

Ettringite is expected to be present in cement paste in all stages of the cement degradation (see Tab. 2.6). Upon complete dissolution of portlandite in stage II of degrading paste, further degradation is controlled by the dissolution of calcium aluminate phases, such as AFm and C-S-H phases. According to thermodynamic modelling, ettringite is expected to dissolve in the final phase of the last stage of the cement degradation (Kosakowski et al. 2014).

### 3.3.3 AFm phases

AFm phases readily form when the ions they contain are brought together in appropriate stoichiometric amounts. AFm phases form in nature under hydrothermal conditions where they are called hydrocalumites. They belong to the family of layered double hydroxides (LDH). The minerals form platey, hexagonal crystals in hydrated cement. However, they are often poorly crystalline and intermixed with C-S-H phases. The AFm structure consists of positively-charged structural units with the composition $[Ca_2(Al,Fe)(OH)_6\cdot2H_2O]^+$. The overall positive structural charge of the octahedral layers is compensated by anions, which are bound in the interlayer space between two adjacent layers. Hence, the cavities formed in the interlayer space allow anionic contaminants to be accommodated. These cavities are often surrounded by three water molecules.

AFm phases exhibit a significant sorption potential for anions. For example, high uptake of oxyanions such as selenate, chromate, molybdate and borate was observed (Zhang & Reardon 2003). Note, however, that selenite is believed to bind via a surface adsorption mechanism (Baur & Johnson 2003). Chloride was found to readily displace OH$, SO_4^{2-}$ and $CO_3^{2-}$ anions in the AFm phases (Birnin-Yauri & Glasser 1998, Glasser & Kindness 1999, Balonis et al. 2010). Chloride binding predominantly occurs by the formation of a solid solution between calcium monocarboaluminate ($3CaO\cdotAl_2O_3\cdotCaCO_3\cdot11H_2O$) and Friedel's salt ($3CaO\cdotAl_2O_3\cdotCaCl_2\cdot10H_2O$) (Nielsen et al. 2005, Balonis et al. 2010). Furthermore, AFm phases seem to be capable of immobilizing iodide (Aimoz et al. 2012b). Iodide binding occurs due to the formation of a solid solution between calcium monosulphoaluminate and calcium monoiodoaluminate (Aimoz et al. 2012b).

Uptake of cations by AFm phases is possible. For example, it was demonstrated that $Fe^{3+}$ substitutes $Al^{3+}$ sites in the AFm structure (Dilnesa et al. 2011). Therefore, it is conceivable that $Al^{3+}$ substitution by other trivalent cations, such as $Co^{3+}$, could occur. However, experimental evidence for $Al^{3+}$ substitution by cations other than $Fe^{3+}$ is presently lacking.
AFm phases are expected to be present in hydrated cement in the first and second stage of the cement degradation (see Tab. 2.6) while the dissolution of AFm phases is expected to take place in the early phase of the last stage of the cement degradation.

3.3.4 Portlandite

Portlandite plays an important role as a pH buffer in the cement matrix. Nevertheless, the mineral seems to have only a minor effect on cation and anion retention. Some studies indicate that arsenate, molybdate and antimonate could show some affinity for portlandite (see Cornelis et al. 2008 and references therein). However, any evidence is lacking that portlandite could outbalance the effectiveness of C-S-H phases for cation retention or that of calcium aluminates (AFt, AFm) for anion retention, respectively, in cement paste. A low sorption capacity is plausible as portlandite forms relatively large crystals, which have a relatively low specific surface area compared to that of nanosize C-S-H, AFt and AFm phases. Thus, on the assumption that adsorption is the dominant sorption mechanism, the portion of anions or cations bound onto portlandite is expected to be much lower than that bound onto C-S-H, AFt or AFm phases. Furthermore, no evidence has been found that incorporation into the structure of portlandite could be an important retention process.

3.3.5 Hydrotalcite

Alike the AFm phases, the naturally occurring mineral hydrotalcite Mg₆Al₂(OH)₁₆CO₃·₄H₂O belongs to the LDH family. The hydroxide layers have a brucite-like crystal structure with a permanent positive charge due to partial replacement of Al³⁺ by Mg²⁺. The net positive charge of the octahedral layers is compensated by anions, such as carbonate, located in the interlayer space along with water molecules.

Hydrotalcite is structurally similar to the AFm phases formed in cement paste and therefore it could act as sorbent for anions by uptake into the interlayer space. Nevertheless, the sorption capacity of hydrotalcite in cement paste is limited because of the small proportion of hydrotalcite compared to AFt and AFm (see Tab. 2.2). Furthermore, some evidence was given that the presence of carbonate might stabilize carbonate-containing hydrotalcite against hydrotalcite bearing other bivalent anions in the interlayer (Dousova et al. 2003). In contrast, replacement of Mg²⁺ and Al³⁺ by the other bi- and trivalent cations is a well-documented process of cation retention (Lehmann et al. 1999, Khan & O'Hare 2002, Rozov et al. 2011).

3.3.6 Calcite

Ca²⁺ and CO₃²⁻ are the potential determining ions at the calcite surface (Stipp 1999). Carbonate is the coordinative counterpart for inner sphere coordination of metal cations at the calcite surface contrary to metal oxides and hydroxides where hydroxyl groups act as surface bound ligands. In addition to surface complex formation co-precipitation with calcite is a common way of metal cation retention in calcite (Curti 1999). Thereby, size and charge of the metal cation control the uptake by the calcite structure.

The surface charge of calcite does depend on the Ca concentration (Stipp 1999). A net positive charge was observed above 4 × 10⁻⁵ M Ca²⁺. Particular affinity of arsenite and selenite for the calcite surface was reported due to the trigonal pyramidal structure of these oxyanions similar to that of carbonate (Cornelis et al. 2008 and references therein). In contrast, lower uptake was observed for molybdate and selenate because the latter oxyanions don't exhibit a trigonal
structure. The latter finding shows that anions may only be marginally retained by adsorption onto the positively charged calcite surface. Uptake into the structure may be the dominant mode of anion interaction with calcite.

Retention of $^{14}$CO$_3^{2-}$ by calcite can be treated in terms of an isotopic exchange between $^{14}$CO$_3^{2-}$ and $^{14}$CO$_3^{2-}$ bound in CaCO$_3$. This process is considered with the aim of estimating a sorption value for $^{14}$CO$_3^{2-}$ in the cementitious near field (see Appendix 1).

The amount of pristine calcite is very low in cement paste (see Tab. 2.2). However, the amount of calcite may increase during the course of the evolution of the repository due to precipitation of secondary calcite caused by the diffusion-controlled mixing of carbonate-rich groundwater intruding from the host rock with the calcium-rich cement-type pore water of the cementitious near field.

### 3.3.7 Iron (oxy)hydroxides

Amorphous Fe(III) oxides, also denoted as hydrous ferric oxides (HFO), were observed in cement mixes containing fly ash as supplementary material (Cornelis et al. 2008 and references therein). Hydrous ferric oxides were also observed as an intermediate phase, which rapidly formed in cement paste during the first day of the hydration process (Dilnesa et al. 2014). In the long-term, however, HFO was found to convert to Fe/Al-siliceous hydrogarnet. The main Fe(III) bearing phases in oxidized cement paste are ferrite and Fe/Al-siliceous hydrogarnet while HFO is expected to be only a minor phase. Hence, it is further expected that HFO plays only a minor role in radionuclide retention by hydrated cement, unless large amounts of HFO form during the course of steel corrosion. It should be noted that the sorption capacity of the two main Fe(III)-bearing phases in cement paste, i.e. ferrite and Fe/Al-siliceous hydrogarnet, are not considered in the present assessment of anion and cation retention.

### 3.3.8 Aluminium oxides

In hydrated cement amorphous aluminium (hydr)oxides are thermodynamically unstable as Al is preferentially bound by calcium aluminates (Aft, AFm) and partially in C-(A)-S-H phases and Fe/Al-siliceous hydrogarnet. However, amorphous aluminium oxide might form upon release of large amounts of Al from corroding aluminium metal (Setiadi et al. 2006). Thermodynamic scoping calculations further support the presence of aluminium oxide under these conditions (Wieland & Berner 2011). Thus, presence of amorphous aluminium (hydr)oxides in cement paste can be excluded for all stages of the cement degradation unless the waste matrix acts as an additional Al source.
4 Sorption Values for Cement Paste

4.1 Recommended values for SMA-1/LMA-1 waste groups

The main characteristics of SMA-1/LMA-1 waste group are as follows (Schwyn et al. 2003):

- The degradation of organic and inorganic waste materials has no deleterious effect on the cement barrier. In particular, phase transformation processes have no adverse effect on the retention properties of hydrated cement;
- The concentration of complexing ligands in the cement pore water, such as ISA, GLU etc., is below the critical limit (Section 4.6) that could enhance radionuclide mobility.

Further characterisation of this waste group is given elsewhere (Nagra 2008a). In case of the SMA-1/LMA-1 waste group the degradation of the hydrate cement due to ingress of ground-water from the host rock formation is the only process that may have an influence on the retention of radionuclides in the near field. In Section 2.5 cement degradation is described in terms of three characteristic geochemical stages with respect to the pore water composition and the mineral composition of hydrated cement (Tab. 2.6). In the following, the uptake of safety-relevant radionuclides by cement paste in the different stages of the cement degradation is discussed with emphasis on possible uptake mechanisms and, in the light of mechanistic arguments, an appraisal of the distribution ratio (Rd).

4.1.1 $^{14}$CO$_3^{2-}$, Ni, Co

The partitioning of carbonate, Ni and Co can be tentatively described in terms of isotopic exchange and on the assumption that a solubility-limiting process may effectively control the aqueous concentrations of the respective species (denoted as "shared solubility"). Isotopic exchange accounts for a process by which the radioisotopes of an element present in the pore solution replace stable isotopes of the same element associated with the cement matrix.

In the case of $^{14}$CO$_3^{2-}$ isotopic exchange with solid CaCO$_3$ in cement paste is considered to control $^{14}$CO$_3^{2-}$ retention in the near field (Bradbury & Sarott 1994). It should be noted that CaCO$_3$ precipitation also occurs at the interface between the cementitious near field and the host rock due to diffusion-controlled mixing of Ca rich pore water emanating from the alkaline near field and CO$_3^{2-}$ rich pore water intruding from the host rock formation (Pfingsten 2002). Isotopic exchange of $^{14}$CO$_3^{2-}$ on finely divided calcite in cement paste was found to be a slow process (Allard et al. 1981, Bayliss et al. 1988). Pointeau et al. (2003) studied isotopic exchange of $^{14}$CO$_3^{2-}$ on calcite, hence providing further experimental evidence for the robustness of the proposed "shared solubility" approach on the basis of an isotopic exchange reaction of $^{14}$CO$_3^{2-}$ and the CO$_3^{2-}$ concentration being controlled by calcite solubility. Pointeau and co-workers presented an empirical relationship, which allows the fraction of calcite available for isotopic exchange to be estimated as a function of the particle size of calcareous aggregates (Wang et al. 2009).

Isotopic exchange is further expected to control $^{59,63}$Ni and $^{60}$Co retention in cement paste. Note that, in this study, Ni is considered to be an appropriate chemical analogue for Co and therefore, both elements are treated in the same way. Experimental evidence was provided that $^{63}$Ni uptake by HCP has to be interpreted in terms of an isotopic exchange process rather than an adsorption process on HCP (Wieland et al. 2000, Wieland & Van Loon 2002, Wieland et al. 2006). Determination of sorption isotherms showed that Ni binding to HCP cannot be interpreted in terms of a Langmuir or Freundlich-type isotherm. Recent sorption studies with Ni on cement-
based materials, such as the Nirex reference vault backfill (NRVB), support this finding (Felipe-Sotelo et al. 2012). Furthermore, sorption studies with $^{60}$Ni revealed a strong decrease of the $R_d$ value with increasing S/L ratio (Wieland & Van Loon 2002). Both findings contradict the notion of an adsorption-type uptake process. It should be noted that evidence for a solubility-controlled uptake process was previously given in Hietanen et al. (1984), Pilkington & Stone (1990) and Ochs et al. (1998).

Wieland et al. (2006) further showed that only a small portion of the inventory of stable Ni in the cement matrix is accessible to the isotopic exchange reaction with $^{60}$Ni (range ~ 2 – 5 %). Attempts were made to identify the Ni bearing phase (Scheidegger et al. 2000, Vespa et al. 2006a/b). The latter studies suggest that a mixed Ni-Al LDH phase may form in cement systems. Therefore, Ni-Al LDHs are regarded as solid phases being potentially present in the waste matrix and governing Ni uptake. It should be noted that the study by Johnson & Glasser (2003) predicts a solubility of Ni-Al LDH phase which corresponds to that of Ni(OH)$_2$ under alkaline conditions. On the basis of the solubility data reported for Ni$_4$Al$_2$(OH)$_6$CO$_3$·2H$_2$O in the latter study the aqueous Ni concentration is expected to be higher (~ 3 × 10$^{-6}$ M at pH 12.5; Berner 2014) than experimentally observed (range: ~ 2 × 10$^{-8}$ M ~ 10$^{-7}$ M; Wieland et al. 2006, Engelsen et al. 2010). This indicates that the chemical nature of the Ni-Al LDH phase formed in cement paste, which controls Ni solubility and the retention of radionickel in cementitious systems, is still poorly known. Therefore, Wieland & Van Loon (2002) recommended the use of concentration limits for radionickel in PA calculations, which are based on solubility limits for stable Ni and isotopic exchange of $^{59,60}$Ni ("shared solubility").

Chemical analogy was suggested between Co and Ni with regards to their retention in cement paste (Wieland & Van Loon 2002). Similarities in the chemical behaviour of Ni and Co in cementitious systems emerged from measurements of the aqueous concentration of stable Ni and Co as a function of the S/L ratio of HCP suspensions. It was observed that, similarly to Ni, the partitioning of stable Co between cement paste and pore solution cannot be interpreted in terms of an adsorption-type process using reported sorption values (Idemitsu et al. 1991). The latter finding rather suggests that a solubility-limiting process in combination with isotopic exchange controls $^{60}$Co retention in cementitious systems. Note that Vespa et al. (2007b) provided evidence for the presence of a solubility-limiting Co phase in cement paste. The authors further showed that Co(III) may form in cementitious systems in the presence of O$_2$. In the absence of O$_2$, however, Co(II) is considered to be the dominant oxidation state, such as under the reducing conditions of a cement-based repository established in the long term.

The data reported in CEM-94 (Bradbury & Sarott 1994) and CEM-02 (Wieland & Van Loon 2002) indicate that the retention of $^{14}$CO$_3^{2-}$, $^{59,60}$Ni and $^{60}$Co in the cementitious near field of a cement-based repository is determined by solubility-limiting rather than adsorption-type processes. The partitioning of the radiotracers can therefore be described in terms of an isotopic exchange process with the CO$_3^{2-}$. Ni and Co bearing phases and on the assumption that the solubility of the latter phases effectively controls the aqueous concentrations of stable CO$_3^{2-}$, Co and Ni. While calcite solubility controls the CO$_3^{2-}$ concentration in cementitious systems, the chemical nature of the solubility-controlling phases for Ni and Co is poorly known. Recrystallization of the solubility-limiting solid phases is believed to be responsible for isotopic exchange. The portion of CaCO$_3$ available for isotopic exchange with $^{14}$CO$_3^{2-}$ was estimated to be 0.5 wt.-% in the case of finely divided calcite in the cement matrix (particle size ~ 10 µm) (Wang et al. 2009). The portion of the phases available for isotopic exchange with $^{59,60}$Ni and $^{60}$Co is expected to range in value between 2 – 5 wt.-% (Wieland et al. 2006). It should be noted that the proportions accessible for isotopic exchange were determined in short-term experiments (equilibration time < 140 days). The portion accessible to isotopic exchange may increase over
geological time scales due to slow, but continuous exchange of radioisotopes with the corresponding stable isotopes. In particular, solid-state diffusion may become an important process in the long term while it can be ignored in short-term experiments.

Operational sorption values are estimated assuming isotopic exchange and considering the inventories and aqueous concentrations of Ni, Co and CO$_3^{2-}$ (see Appendix A).

### 4.1.2 Potassium

The binding potential of sodium and potassium alkalis by cementitious materials has been investigated by Hong & Glasser 1999, Hong & Glasser 2002, Tits et al. 2003b, and Yang et al. (2009). Calcium silicate hydrates were found to accommodate significant amounts of Na$^+$ and K$^+$ (Hong & Glasser 1999, Tits et al. 2014). They may substitute for Ca$^{2+}$ in the interlayer of C-S-H phases. Alkali binding by C-S-H phases increases with decreasing C/S ratio of C-S-H phases. Distribution ratios were reported to range in value between ~ $4 \times 10^{-3}$ m$^3$/kg (C/S = 0.85) and ~ $4 \times 10^{-4}$ m$^3$/kg (C/S = 1.8) for both Na$^+$ and K$^+$, indicating comparable sorption properties (Hong & Glasser 1999). The $R_d$ value determined on a C-S-H phase with C/S = 1.8 was found to be consistent with that determined on fresh HCP ($5 \times 10^{-4} - 10^{-3}$ m$^3$/kg, Tits et al. 2003b). Note that C-S-H phases with C/S > 1.6 prevail in fresh cement paste. Furthermore, Hong & Glasser (2002) observed enhanced alkali binding in C-A-S-H phases due to the replacement of bridging Si tetrahedra (Si$^{4+}$) by Al$^{3+}$ and charge compensation by alkali uptake. A (low) nominal value ($R_d = 10^{-4}$ m$^3$/kg) is assigned to K$^+$ uptake in the stages I and II of the cement degradation in accordance with earlier studies (Bradbury & Van Loon 1997). A higher sorption value ($R_d = 10^{-3}$ m$^3$/kg) is assigned to K$^+$ binding in stage III of the cement degradation due to presence of C-S-H phases with a lower C/S ratio (Tab. 6.1).

### 4.1.3 Beryllium

To the best of our knowledge, no data are available for Be uptake by HCP under conditions relevant to a cementitious near field. It was speculated that Be uptake by HCP should be measurable even under alkaline conditions (Wieland & Van Loon 2002). Nevertheless, uptake might be small because the formation of Be(OH)$_3$- and Be(OH)$_4^{2-}$ species at high pH is anticipated which stabilizes the aqueous species and consequently reduces uptake by HCP. Although Be uptake by HCP presumably takes place, a cautious approach is taken by retaining zero sorption as in the previous SDB (Wieland & Van Loon 2002; Tab. 6.1).

### 4.1.4 Chloride

The uptake process of Cl$^-$ in HCP is still poorly understood in spite of new sorption measurements that have been published in the last years (Nielsen et al. 2005, Pointeau et al. 2008) and novel information on the thermodynamics of Cl$^-$ bearing minerals in cement paste (Balonis et al. 2010). The former studies show that the concentration of stable Cl$^-$ has an influence on the extent of $^{36}$Cl uptake by HCP. The relationship between the inventory of stable Cl$^-$ in the cementitious system and $^{36}$Cl uptake has been discussed in detail elsewhere on the basis of a comprehensive compilation of the available literature data (Wang et al. 2009). The $R_d$ value of $^{36}$Cl was found to decrease with increasing concentration of stable Cl$^-$ in solution. The latter trend was recently supported by in-house sorption measurements with $^{36}$Cl on HTS cement (see further details in Section 4.4). Wang et al. (2009) analysed the experimental data reported by Pointeau et al. (2008) with the aim of assessing the influence of cement degradation on the Cl$^-$ content in HCP. The authors found that, due to leaching, the concentration of stable Cl$^-$ in HCP
decreases during cement degradation from stage I to stage II which gives rise to an increase in the uptake of $^{36}$Cl tracer by HCP at pH = 12.5 compared to fresh cement paste (pH > 13) (Pointeau et al. 2008). In stage III of the cement degradation, however, $^{36}$Cl uptake by HCP was found to be reduced compared to that in stage II (pH = 12.5). Thus, the partitioning of stable Cl between HCP and solution in the different stages of the cement degradation seems to be a key factor influencing the extent of $^{36}$Cl uptake by HCP. This finding suggests that $^{36}$Cl binding occurs via an isotopic exchange process while the concentration of stable Cl is controlled by the formation of a solid solution (see below).

The Cl concentration in the near-field pore water is determined by the Cl inventory of HCP and the partitioning of Cl associated with the cement matrix between the solid and liquid phase. The latter assumption is justified if Cl inventories associated with the different waste forms are considered to be negligible and further that ingress of saline groundwater can be excluded (see Section 4.4). It is to be noted that the concentration of stable Cl in solution, and consequently $^{36}$Cl uptake, could also depend on the S/L ratio of the cementitious system. Detailed investigations, however, are presently lacking.

Chloride was found to readily displace OH$^-$, SO$_4^{2-}$ and CO$_3^{2-}$ anions in AFm phases (Glasser & Kindness 1999, Birnin-Yauri & Glasser 1998, Balonis et al. 2010). In CO$_3^{2-}$ containing cements, such as the HTS cement used for the solidification of radioactive waste in Switzerland, chloride binding by AFm phases predominantly occurs due to the formation of a solid solution between calcium monocarboaluminate and Friedel's salt (Nielsen et al. 2005, Balonis et al. 2010). A miscibility gap was observed at low Cl concentration (Balonis et al. 2010). Structural studies further revealed the formation of two polymorph structures of the solid solution series at ambient temperature: a rhombohedral structure over the entire domain of the solid solution and a metastable monoclinic structure at elevated Cl content (Mesbah et al. 2011).

Chemisorption was considered to control Cl retention by C-S-H phases (Beaudoin et al. 1990, Viallis et al. 1999, Hill et al. 2006, Sugiyama 2008). At C/S ratios $\geq$ 1.2 the C-S-H surface is positively charged (Viallis-Terrisse et al. 2001, Jönsson et al. 2004, Pointeau et al. 2006b). This suggests adsorption of Cl onto C-S-H phases with C/S ratio $\geq$ 1.2, such as in fresh cement paste in stage I of the cement degradation and in paste degraded to stage II of the cement degradation. In contrast, Cl uptake by C-S-H phases with C/S ratio $< 1.2$, such as in stage III of the cement degradation, is limited due to the negatively charged sites on the C-S-H surface. In-house sorption studies with $^{36}$Cl on C-S-H phases confirmed Cl uptake by a C-S-H phase with C/S = 1.65 while no uptake at all was observed by a C-S-H phase with C/S = 0.75 (Tab. 4.1). Although the proportion of Cl bound per unit mass of solid material was found to be lower for C-S-H phases than for Friedel's salt (Tab. 4.1), the binding potential of C-S-H phases with a high C/S ratio cannot be ignored in cement pastes because it is the most abundant constituent (~ 50 wt-%) of hydrated cement. In contrast, uptake of Cl by C-S-H phases with low C/S ratio is expected to be negligibly small.

Distribution ratios with $^{36}$Cl on HTS cement were obtained from batch and diffusion experiments on fresh cement paste (stage I of the cement degradation) (Jakob et al. 1999). In the latter study $R_d$ values were found to range in value between 0.02 and 0.05 m$^3$/kg, which corresponds to the value recommended for Cl uptake by HCP in stage I of the cement degradation (Bradbury & Sarott 1994). Note, however, that in the latter studies the $R_d$ values were determined in batch systems at relatively low S/L ratios (batch sorption) using cement pastes with a high w/c of 1.3 (corresponding to a low S/L ratio compared to a paste prepared at w/c = 0.4). The sorption value recommended in Bradbury & Van Loon (1997) ($R_d = 5 \times 10^{-3}$ m$^3$/kg) for both stages of the cement degradation was based on a cautious appraisal regarding the $^{36}$Cl uptake by HCP. This value corresponds to the lower bound of sorption data reported in the
The above value ($R_d = 5 \times 10^{-3} \text{ m}^3/\text{kg}$) is retained for stage I of the cement degradation. Nevertheless, the value is enhanced by an order of a magnitude due to new measurements available for a degraded cementitious system (Pointeau et al. 2008) ($R_d = 5 \times 10^{-2} \text{ m}^3/\text{kg}$; Tab. 6.1).

Tab. 4.1: In-house measured $R_d$ values for $^{36}\text{Cl}$, $^{125}\text{I}$ and $^{75}\text{Se(IV)}$ on cement minerals.

<table>
<thead>
<tr>
<th>Cement phase</th>
<th>$R_d$ [	ext{m}^3/\text{kg}] *</th>
<th>$^{36}\text{Cl}$</th>
<th>$^{125}\text{I}$</th>
<th>$^{75}\text{Se(IV)}$</th>
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<tbody>
<tr>
<td>C-S-H C/S = 0.75</td>
<td>0</td>
<td>0</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>C-S-H C/S = 1.07</td>
<td>0</td>
<td>0.005</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>C-S-H C/S = 1.65</td>
<td>0.003</td>
<td>0.008</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>AFm-Cl$_2$</td>
<td>0.23</td>
<td>0</td>
<td>5.75</td>
<td></td>
</tr>
<tr>
<td>AFm-CO$_3$</td>
<td>0</td>
<td>0</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>AFm-SO$_4$</td>
<td>0.003</td>
<td>0.026</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>AFt-SO$_4$</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

* All sorption values are related to the dry weight of the corresponding cement phase (C-S-H = calcium silicate hydrates; AFm-Cl$_2$: Friedel’s salt; AFm-CO$_3$: calcium monocarboaluminate; AFm-SO$_4$: calcium monosulphoaluminate; AFt-SO$_4$: ettringite).

The uptake of $^{36}\text{Cl}$ by HCP is expected to be much lower in stage III of the cement degradation than in stages I and II for two reasons: Firstly, calcium monocarboaluminate hydrates is depleted from the cement matrix in stage III (Tab. 2.6), which prevents $\text{Cl}^-$ binding in HCP by the formation of a solid solution between calcium monocarboaluminate hydrate and Friedel's salt (Balonis et al. 2010). Secondly, the C/S ratio of C-S-H phases is significantly lower in stage III compared to those of C-S-H phases in stages I and II of the cement degradation. Therefore, $\text{Cl}^-$ binding by C-S-H phases can be ignored in stage III of the cement degradation. As no experimental data are available for this stage we err on the conservative side by assigning zero sorption ($R_d = 0$; Tab. 6.1).

4.1.5 Selenium

$\text{Se(VI)O}_4^{2-}$ is the main selenium species under the oxidizing conditions of a cementitious near field, that is before closure of a cement-based repository, while $\text{Se(IV)O}_3^{2-}$ is the dominant species in a cementitious near field under moderately reducing conditions, that is after closure of the repository. In the last years several studies on the interaction of $\text{Se(IV,VI)}$ with HCP and cement phases have been published (Ochs et al. 2002, Baur & Johnson 2003, Bonhoure et al. 2006, Pointeau et al. 2006a, Ochs & Talerico 2006, Macé et al. 2007, Pointeau et al. 2008). Note that retention of $\text{Se(0)}$ and $\text{Se(-II)}$ in HCP is not discussed in this study as no relevant sorption data are presently available and further, these species were found to be almost insoluble (Seby et al. 2001a).
Strong uptake of Se(VI) was observed by ettringite and HCP under conditions where secondary ettringite formed (Ochs et al. 2002). In contrast, Se(VI) uptake by primary ettringite, which forms in the early stage of cement hydration, was much weaker (Baur & Johnson 2003). In the latter study calcium monosulphoaluminate was observed to strongly bind Se(VI). The above studies suggest that ettringite and/or calcium monosulphoaluminate may be responsible for SeO_4^{2-} binding to HCP.

Ochs et al. (2002) developed a simplified solid solution model on Se(VI)-ettringite interaction, which resulted in an empirical relationship between Se(VI) uptake by HCP and the SO_4^{2-} concentration in solution. Sorption values for SeO_4^{2-} were reported to typically range between ~10^{-3} m^3/kg and ~2 \times 10^{-2} m^3/kg for fresh and aged HCP (Bonhoure et al. 2006, Ochs et al. 2010). The sorption value recommended in the earlier SDB for SeO_4^{2-} binding by HCP was selected by taking into account the large spread in reported sorption data (Wieland & Van Loon 2002). This value is retained, i.e. R_d = 10^{-3} m^3/kg for stages I and II of the cement degradation (Tab. 6.1). In stage III of the cement degradation, however, ettringite or calcium monosulphoaluminate, might be depleted from cement paste, implying very weak retention of SeO_4^{2-} by strongly degraded HCP. As a consequence, zero sorption (R_d = 0) is assigned to stage III of the cement degradation (Tab. 6.1).

Uptake of SeO_3^{2-} by HCP was found to be less specific with respect to the mineral phase involved. Moderate uptake was observed on AFm and C-S-H phases while uptake by ettringite was weak (Baur & Johnson 2003). In-house sorption measurements with SeO_3^{2-} on ettringite, the most important AFm phases (AFm-CO_3, AFm-SO_4, AFm-Cl) and C-S-H phases with C/S ratio = 0.75, 1.07 and 1.65 further support the findings from the earlier study (Tab. 4.1). Bonhoure et al. (2006) investigated Se(IV) uptake by non-degraded cement paste (pH = 13.3) while Pointeau et al. (2006a) studied the influence of organics (EDTA, isosaccharinic and gluconic acids) on Se(IV) uptake by HCP. The reported R_d values were found to range between 0.08 m^3/kg and 0.12 m^3/kg under conditions corresponding to stage I of the cement degradation. Uptake was found to be significantly higher on degraded HCP (R_d ~ 0.2 m^3/kg to ~1 m^3/kg; Pointeau et al. 2006a). The latter material had a composition similar to that of HCP altered either to stage II or III of the cement degradation. Competition between SeO_3^{2-} and SO_4^{2-} allowed the influence of cement degradation in these experiments to be interpreted, indicating that uptake of SeO_3^{2-} by HCP involves either ettringite or calcium monosulphoaluminate as sorbent. Increasing uptake with progressing cement degradation is conceivable as the SO_4^{2-} concentration is expected to be about an order of a magnitude lower in stage II than in stage I of the cement degradation. The organics added in these experiments had an influence on Se(IV) uptake solely at concentrations in the millimolar range (Pointeau et al. 2006a). It should be noted that the concentration of organics employed in the latter study was much higher than the average concentration relevant to a repository system.

In a subsequent study, Pointeau et al. (2008) investigated Se(IV) uptake by degraded HCP in the pH range 11.5 – 13.3. The authors corroborated the earlier findings suggesting strong Se(IV) uptake in stage II of the cement degradation (R_d ~ 1 m^3/kg to ~3 m^3/kg) compared to stage I. Macé et al. (2007) determined sorption values ranging between ~1 m^3/kg and ~5 m^3/kg on similar HCP systems which is in excellent agreement with the values reported by Pointeau et al. (2008). Thus, on the basis of the consistent set of sorption data available for SeO_3^{2-} uptake by degraded HCP it is recommended to increase the sorption value for Se(IV) from 0.03 m^3/kg to 0.3 m^3/kg for stage II of the cement degradation (Tab. 6.1). In contrast, the sorption value is retained for stage I of the cement degradation as recommended in the earlier SDB (Wieland & Van Loon 2002). It is anticipated that SeO_3^{2-} retention in HCP occurs predominantly due to the replacement of SO_4^{2-} by SeO_3^{2-} in ettringite or calcium monosulphoaluminate hydrate, respectively, in the first two stages of the cement degradation. Nevertheless, uptake of SeO_3^{2-} by
C-S-H phases cannot be ignored (Tab. 4.1), particularly for the last stage of the cement degradation. In a strongly degraded cement paste, AFm phases and possibly ettringite will be absent (Tab. 2.6) while C-S-H phases with C/S ratio \( \sim 0.7 \) are expected to persist. Therefore, a nominal sorption value \( = 10^{-2} \text{m}^3/\text{kg} \) is assigned to \( \text{SeO}_3^{2-} \) uptake by degraded HCP in stage III of the cement degradation due to presence of a C-S-H phase with low C/S ratio. Hence, reduced retention due to absence of AFm and possibly ettringite is considered in stage III of the cement degradation.

### 4.1.6 Strontium

Uptake of Sr by cementitious materials has been studied in detail in the past decades (Wieland et al. 2008 and references therein). In all these studies uptake of Sr was found to be lower on degraded cement paste \( (R_d \sim 10^{-3} - 10^{-2} \text{m}^3/\text{kg}) \) compared to an unaltered paste \( (R_d \sim 10^{-1} \text{m}^3/\text{kg}) \), suggesting that the aqueous Ca concentration could have an influence on Sr binding to cementitious materials. New information on the uptake of Sr(II) by C-S-H phases and HCP is available from in-house sorption measurements (Tits et al. 2006a, Wieland et al. 2008). In the latter study, it is shown that the uptake of \( ^{85}\text{Sr} \) by HCP can be interpreted in terms of an isotopic exchange process with stable Sr bound in the cement matrix (Tab. 2.3). Sr uptake was found to be linear and reversible, indicating a sorption-type uptake mechanism. Furthermore, it was suggested that C-S-H is the uptake-controlling cement phase for Sr(II) in HCP (Wieland et al. 2008).

Tits et al. (2006a) showed that Sr(II) uptake by C-S-H phases can be modelled in terms of an ion exchange mechanism. The model was based on \( \text{Sr}^{2+}-\text{Ca}^{2+} \) and \( \text{Sr}^{2+}-\text{Na}^+/\text{K}^+ \) replacement on the surface of C-S-H phases as the structural information gained from extended X-ray absorption fine structure (EXAFS) spectroscopy did not suggest \( \text{Sr}^{2+} \) binding in the interlayer of C-S-H phases (Wieland et al. 2008). Competition with alkalis was found to reduce Sr uptake in stage I compared to stage II while decreasing Ca concentration in solution enhanced Sr uptake in stage I compared to stage II of the cement degradation. Sr(II) uptake by C-S-H phases and HCP was predicted to be higher in stages I and III of the cement degradation due to the low aqueous Ca concentrations \((|\text{Ca}|_t \sim 2 \text{mM})\) in these degradation stages compared to stage II where the Ca concentration is about an order of a magnitude higher \((|\text{Ca}|_t \sim 20 \text{mM})\). An increase in the Ca concentration by an order of a magnitude gives rise to a proportional decrease in the \( R_d \) value for Sr(II) in stage II. Therefore, the sorption value for Sr(II) in stage I of the cement degradation is retained as given in Wieland & Van Loon (2002) \( (R_d = 0.1 \text{m}^3/\text{kg}) \), and the same sorption value is assigned to stages I and III. The \( R_d \) value for stage II, however, is revised upwards from \( 10^{-3} \text{m}^3/\text{kg} \) (as given in Wieland & Van Loon 2002) to \( 10^{-2} \text{m}^3/\text{kg} \), thus taking into account the one order of a magnitude difference in the aqueous Ca concentration between stages I and II of the cement degradation (Tab. 6.1). The same sorption values are assigned to oxidizing and reducing conditions as Sr(II) is not a redox-sensitive element.

### 4.1.7 Radium

Bayliss et al. (1989), Holland & Lee (1992), Bayliss et al. (2000) and Tits et al. (2006b) report sorption measurements with Ra(II) on cementitious materials. Ra uptake by HCP and C-S-H phases was found to be high with sorption values ranging from \( \sim 5 \times 10^{-2} \text{m}^3/\text{kg} \) at pH = 12.5 to \( \sim 2 \text{m}^3/\text{kg} \) at pH = 11.5 (Bayliss et al. 1989, Holland & Lee 1992, Bayliss et al. 2000). Tits et al. (2006b) investigated the uptake of Ra(II) by C-S-H phases as well as fresh and degraded HCP. Sorption values on fresh and aged HCP were determined to be \( < 0.1 \text{m}^3/\text{kg} \) and \( < 0.4 \text{m}^3/\text{kg} \), respectively, which is consistent with sorption data reported by Holland & Lee (1992) for Ra uptake by OPC.
Ra uptake was found to increase with decreasing C/S ratio of the C-S-H phases (Tits et al. 2006b). Comparison with Sr uptake by C-S-H phases further revealed that an adapted Sr$^{2+}$ – Ca$^{2+}$ ion exchange model developed earlier by Tits et al. (2006a) allows the Ra uptake by C-S-H phases to be predicted for a wide range of solution compositions (Tits et al. 2006b). Dependence on the aqueous Ca concentration, previously found for Sr binding to C-S-H phases, was also observed in the case of Ra. The latter finding implies that Ra uptake is higher in stages I and III compared to stage II of the cement degradation. In general, sorption values for Ra were found to be about a factor of 5 greater than those determined for Sr, which is reflected in the difference between the selectivity coefficients of the Ra$^{2+}$ – Ca$^{2+}$ and Sr$^{2+}$ – Ca$^{2+}$ exchange processes (Tits et al. 2006b).

In particular, the C-S-H-based sorption model developed for Sr$^{2+}$ was capable of correctly predicting Ra uptake by HCP. Uptake of Ra by HCP could be interpreted in terms of Ra binding to C-S-H phases (Tits et al. 2006b). The trends previously observed for Sr are also valid for Ra: Competition with alkalis leads to weaker uptake in stage I compared to stage II of the cement degradation while decreasing Ca concentrations gives rise to the opposite effect, i.e. an increasing Ra uptake in stage I compared to stage II of the cement degradation. The latter finding implies that Ra uptake is enhanced in stages I and III compared to stage II of the cement degradation.

The new information available on the uptake of Ra by C-S-H phases and HCP (Tits et al. 2006a) enables us to undertake a reappraisal of the sorption values recommended in the earlier SDBs (Wieland & Van Loon 2002). The sorption value for Ra in stage I is revised upwards compared to that recommended earlier ($R_d = 0.5$ m$^3$/kg instead of 0.1 m$^3$/kg as in Wieland & Van Loon (2002) (Tab. 6.1). Ra uptake by HCP is expected to decrease during the course of cement degradation from stage I to stage II due to an increase in the Ca concentration. This effect is reflected in the lower sorption value assigned to stage II. Furthermore, the same values are assigned to stages I and III of the cement degradation because the aqueous Ca concentrations are comparable.

4.1.8 Zirconium

New data on Zr uptake by cementitious materials have been reported by Pointeau et al. (2004a) and Baston et al. (2012). Pointeau et al. (2004a) carried out sorption tests with Zr(IV) on degraded HCP and C-S-H phases in the pH range 10 – 12.5 while Baston et al. (2012) studied Zr(IV) uptake by untreated and aged NRVB. Zr uptake was found to be high ($R_d \sim 10 - 1000$ m$^3$/kg) in both studies. Pointeau et al. (2004a) observed increasing uptake with progressive cement degradation (or decreasing pH). The latter observation was explained by changes in Zr(IV) speciation in solution in the alkaline pH range. The concentration of the Zr(OH)$_5$ species in solution decreases with decreasing pH, which gives rise to an increase in the uptake of Zr(IV) by HCP. The above study, however, did not give any conclusive information on the uptake mechanism of Zr(IV) in HCP. Nevertheless, with a view to the binding mechanisms deduced for the tetravalent actinides (see Section 4.1.19) it is conceivable that C-S-H phases are the uptake-controlling phase in HCP.

The sorption value recommended earlier in Wieland & Van Loon (2002) for Zr uptake in stage I of the cement degradation is retained ($R_d = 10$ m$^3$/kg) on the basis of the new experimental data that have become available. In accordance with the study by Pointeau et al. (2004a) it is further considered that Zr(IV) uptake by HCP is a factor of 10 higher in stage II due to a reduction in the concentration of the Zr(OH)$_5$ species at decreasing pH. Furthermore, the $R_d$ values were found to be comparable in stages II and III of the cement degradation (Pointeau et al. 2004a) which is in accordance with the above consideration on the influence of the concentration of
hydrolysis products on radionuclide uptake. A cautious approach is taken in this study by ignoring the expected trend to higher uptake at decreasing pH. As a consequence, the same value is assigned to all stages of the cement degradation ($R_d = 10 \, \text{m}^3/\text{kg}$).

### 4.1.9 Niobium

Current data on redox potential suggest dominance of the $+V$ oxidation state in aqueous media with $\text{Nb}(\text{OH})_6^{\text{V}^-}$ (Baes & Mesmer 1976) and possibly $\text{Nb}(\text{OH})_7^{2-}$ (Talerico et al. 2004) as the prevailing hydrolysis species. The latter species are limited in concentration possibly due to the low solubility of Ca-niobate in HCP or $\text{Nb}_2\text{O}_5$ (Talerico et al. 2004, Baes & Mesmer 1976). Pointeau et al. (2004a) investigated $\text{Nb}(V)$ uptake by degraded cement as a function of time. The authors used very low $\text{Nb}$ concentrations in their experiments to avoid formation of $\text{Nb}(V)$ precipitates though the initial $\text{Nb}(V)$ concentration was above the expected solubility limit of $\sim 5 \times 10^{-9} \text{M} - 5 \times 10^{-8} \text{M}$ (Ochs et al. 2010). Pointeau and co-workers observed a high uptake of $\text{Nb}(V)$ by HCP and C-S-H phases in the pH range 10 – 12.5 with $R_d$ ranging in value between 40 m$^3$/kg and 240 m$^3$/kg. The observed, strong uptake is indicative of the cationic nature of the $\text{Nb}(V)$ species. Note that the high uptake by HCP can tentatively be rationalized in terms of the ionic potential of $\text{Nb}(V)$, that is the charge-to-size ratio ($z/d \sim 2.3$ for $\text{Nb}(V)$), and the general trend developed between the $z/d$ ratio and $R_d$ value of metal cations on HCP (Wieland & Van Loon 2002). At the present time, no information is available on the uptake mechanism.

The sorption values determined by Pointeau et al. (2004a) are significantly greater than those recommended in Bradbury & Van Loon (1997) and retained by Wieland & Van Loon (2002) ($R_d = 1 \, \text{m}^3/\text{kg}$) for $\text{Nb}$ uptake by HCP. The latter value was selected on the basis of a cautious appraisal of the available literature data. The new data by Pointeau et al. (2004a) are further consistent with those reported earlier by Pilkington & Stone (1990). Note, however, that information on the uptake mechanism is currently lacking and further, $\text{Nb}(V)$ speciation under alkaline conditions is poorly known. The study by Pointeau et al. (2004a) suggests no major changes in the species distribution in the alkaline pH range as $\text{Nb}(V)$ uptake did not depend on pH. A detailed assessment of the pre-dominance of the $\text{Nb}$ redox states under the oxidizing and reducing conditions of a cementitious near field failed due to lack of reliable thermodynamic data. A cautious approach is taken as the $\text{Nb}$ speciation under the experimental conditions reported in Pointeau et al. (2004a) could not be assessed. Therefore, the sorption value recommended in Bradbury & Van Loon (1997) is retained ($R_d = 1 \, \text{m}^3/\text{kg}$; Tab. 6.1) although ample evidence exists that $\text{Nb}(V)$ uptake by HCP could be much higher ($R_d = 50 \, \text{m}^3/\text{kg}$). Furthermore, the same sorption value is assigned to all stages of the cement degradation.

### 4.1.10 Molybdenum

$\text{MoO}_4^{2-}$ is the only aqueous species relevant to cementitious systems under both oxidizing and reducing conditions (Tab. 2.5, Baes & Mesmer 1976, Cornelis et al. 2008). Sorption measurements have been carried out in the framework of the Japanese waste management programme (Ochs et al. 2010 and reference therein) while no further information on $\text{Mo}(VI)$ uptake by HCP is available in the open literature. $\text{SeO}_4^{2-}$ is considered to be a good chemical analogue for $\text{MoO}_4^{2-}$ because the two anions are isostructural and the central atoms carry the same charge (Ochs et al. 2010). Note, however, that the ionic radii and the electronegativity of the two oxyanions are different (Mo(VI): 0.62 Å/1.8; Se(VI): 0.42 Å/2.4). These differences could have an effect on their retention in cementitious materials. For example, it was shown that $\text{SeO}_4^{2-}$ is predominately taken up into the structure of ettringite in HCP (see Section 4.1.5). This would imply that $\text{MoO}_4^{2-}$ is preferentially taken up by ettringite in HCP. Nevertheless, it was observed that $\text{MoO}_4^{2-}$ uptake by ettringite is negligibly small (see Cornelis et al. 2008 and references...
therein). This finding is consistent with the idea that the extent of solid solution formation with ettringite is inversely proportional to the difference in size and electronegativity of the involved oxyanions in comparison to \( \text{SO}_4^{2-} \) (Zhang & Reardon 2003). Therefore, a cautious approach is taken by assigning \( R_d = 0 \) to all stages of the cement degradation due to lack of a robust set of sorption data for Mo(VI) on HCP and in particular due to the presently very limited knowledge of the uptake mechanism (Tab. 6.1).

4.1.11 Technetium

Sorption studies with Tc on cementitious materials were reported by Bayliss et al. (1992), Bayliss et al. (1996b), Baker et al. (2004), Cowper et al. (2004), and Pointeau et al. (2004a). Baker et al. (2004) and Cowper et al. (2004) studied the uptake of Tc(VII) by encapsulation grouts and Nirex reference fault backfill (NRVB) under oxidizing conditions. Uptake of Tc(VII) was found to be very weak (\( R_d \approx 1 - 2 \times 10^{-3} \text{ m}^3/\text{kg} \)) under the latter conditions. However, addition of potentially reducing components, such as blast furnace slag, significantly increased Tc uptake by these materials, thus indicating partial reduction of Tc(VII) to Tc(IV).

Bayliss et al. (1992) and Pointeau et al. (2004a) studied the uptake of Tc(IV) by fresh and degraded cement. The authors determined \( R_d \) values ranging between ~1 and 10 m\(^3\)/kg depending on the degree of cement degradation. Note that these values are comparable to those determined with Tc(IV) on C-S-H phases (2±1 m\(^3\)/kg, Pointeau et al. 2004a). In the latter case no influence of the C/S ratio on Tc(IV) uptake was observed.

The uptake mechanism of Tc(IV/VII) by HCP is poorly understood. AFm or AFt phases might be responsible for Tc(VII) retention in the cement matrix as for other oxyanions (e.g. Se(VI)). In contrast, Tc(IV) is expected to sorb strongly onto all cement phases. One may speculate that, as in case of the tetravalent actinides, Tc(IV) could be taken up into the interlayer of C-S-H phases.

The new data support appraisals made earlier by Wieland & Van Loon (2002) where a sorption value of 10\(^{-3}\) m\(^3\)/kg was assigned to Tc(VII) uptake by HCP in stages I and II of the cement degradation. No sorption (\( R_d = 0 \)), however, is expected in stage III as AFm phases and eventually ettringite could be depleted from the cement matrix.

Uptake is considered to be higher under reducing conditions in both stages of the cement degradation due to presence of Tc(IV) (\( R_d = 1 \text{ m}^3/\text{kg} \)) (Tab. 6.1). Therefore, the sorption values for Tc(IV) are retained as given in Wieland & Van Loon (2002) which is further in accordance with the data reported by Pointeau et al. (2004a). Our current knowledge of the speciation and the set of experimental data that are presently available do not allow stage-specific sorption values to be assigned. Nevertheless, high uptake of Tc(IV) is expected in all stages of the cement degradation as C-S-H phases might be the dominant sorbing cement mineral. Therefore, in the case of Tc(IV), the same sorption value is assigned to all stages of the cement degradation.

4.1.12 Silver

No sorption data are available for Ag. The prevailing oxidation state is expected to be Ag(I) under alkaline conditions. The distribution ratio is expected to be different from zero in all stages of the cement degradation. In accordance with the appraisals made earlier (Bradbury & Van Loon 1997, Wieland & Van Loon 2002), however, the distribution ratio is set to zero due to the expected strong competitive effect of Na\(^+\) and K\(^+\) in stage I of the cement degradation and the strong tendency of Ag to form chloro complexes at increasing Cl\(^-\) concentration which are expected for stages II and III of the cement degradation (Tab. 2.6).
4.1.13 Tin

Sn is expected to exist predominantly in the +IV oxidation state under the conditions prevailing in a cement-based repository due to the stability of the hydrolysis species (Seby et al. 2001b, Berner 2014). Sn readily hydrolyses in the pH range > 8 to form Sn(OH)$_4$$^-$ and Sn(OH)$_6^{2-}$ complexes (Amaya et al. 1997). Sorption studies on cementitious materials were reported by Bayliss et al. (1989), Baker et al. (1994), Heath et al. (1996), Bonhoure et al. (2003), Ochs & Talerico (2006) and Baston et al. (2012). Wieland & Van Loon (2002) reported in-house sorption data for Sn(IV) on HCP at pH = 13.3. The sorption experiments were carried out at Sn concentrations well below the solubility limit with regard to sparingly soluble Ca-stannate (CaSn(OH)$_6$(s)). All above studies observed strong interaction of Sn(IV) with cementitious materials in stages I and II of the cement degradation with $R_d$ ranging in value from 1 to 100 m$^3$/kg (Ochs et al. 2010). A structure model for Sn immobilization in HCP was proposed based on EXAFS measurements suggesting that Sn may be taken up by ettringite (Bonhoure et al. 2003). Nevertheless, conclusive evidence for the proposed model is lacking, particularly in the light of a recent study, which shows that C-S-H phases are the uptake-controlling cement phase for tetravalent actinides in the cement matrix (Gaona et al. 2011) which could apply to Sn as well.

The $R_d$ value was set to 10 m$^3$/kg for stages I and II of the cement degradation (Wieland & Van Loon 2002) which is close to the lower limit of reported sorption values. No sorption data are available for stage III. However, Sn(IV) uptake by HCP is expected to increase with decreasing pH under alkaline conditions due to decreasing concentrations of hydrolysed species. Thus, decreasing concentrations of Sn(OH)$_4$$^-$ and Sn(OH)$_6^{2-}$ hydrolysis species with decreasing pH gives rise to an increase in the uptake of Sn(IV) by HCP which was previously observed in the case of Zr(IV) uptake by HCP (see Section 4.1.8, Ochs et al. 2010). Nevertheless, we err on the conservative side and choose the same $R_d$ value across the three stages of the cement degradation (Tab. 6.1).

4.1.14 Iodine

Iodide (I$^-$) and iodate (IO$_3^{-}$) are the reduced and oxidized forms of inorganic iodine within the stability field of water (Liu & von Gunten 1988, Ochs et al. 2010). While IO$_3^{-}$ should be the dominant chemical form of iodine in oxidized cementitious systems (Ochs et al. 2010) spectroscopic investigations of I$^-$ uptake by HCP (prepared from HTS cement) did not indicate oxidation of I$^-$ to IO$_3^{-}$ (Bonhoure et al. 2002). The latter finding can either be attributed to kinetic hindrance of I$^-$ oxidation by molecular oxygen in aqueous media (Atkins & Glasser 1990, Atkins & Glasser 1992) or the presence of small amounts of supplementary materials in cement, such as slag, thus maintaining reducing conditions in the cementitious systems. In this study I$^-$ is considered to be the dominant chemical form of iodine subject to immobilization process in HCP.

Numerous studies on the interaction of HCP and cement minerals have been reported over the last 30 years. Sorption data were compiled in Liu & von Gunten (1988) and further discussed by Bradbury & Sarott (1994), Bradbury & Van Loon (1997), and Wieland & Van Loon (2002). Wang et al. (2009) provide a comprehensive compilation of sorption data in cementitious systems. More recent sorption studies with I$^-$ on cementitious materials include those reported by Toyohara et al. (2002) and Pointeau et al. (2008). The former authors investigated the uptake of I$^-$ by alumina cement mixed with portlandite and calcium sulphate. Mixing of the solid phases caused in situ precipitation of calcium monosulphoaluminate and tetracalcium aluminate hydrates. Both compounds typically form during hydration of clinker minerals. Toyohara et al. (2002) observed significant I$^-$ uptake by these mixes ($R_d$ ~ 0.25 m$^3$/kg). Furthermore, the uptake
process was found to be reversible. Pointeau et al. (2008) investigated $^{125}I$ uptake by degraded HCP and observed that uptake increased in HCP degraded to stage II of the cement degradation. These results were further consistent with observations made on $^{36}Cl$ uptake by degraded HCP by the same authors. Pointeau et al. (2008) determined the sorption value of $^{125}I$ on degraded HCP to be about a factor of 5 – 10 greater than that of $^{36}Cl$. Although numerous sorption measurements exist, the chemical processes controlling $\Gamma^-$ interaction with HCP are still poorly understood.

Adsorption via surface processes and/or incorporation into the structures of selected cement minerals is believed to account for the observed $\Gamma^-$ uptake by HCP (Evans 2008). The concentration of competing anions, such as OH$^-$, CO$_3^{2-}$, Cl$^-$ and SO$_4^{2-}$, could exert a strong effect on $\Gamma^-$ binding by HCP in the case of structural uptake while in the case of an adsorption process the surface charge of the uptake-controlling cement phases could further play a decisive role in determining the extent of $\Gamma^-$ uptake in addition to the presence of competing anions. Ochs et al. (2010) assessed the sorption potential of cement minerals and reported a ranking in decreasing order from AFm > C-S-H with high C/S ratio ~ AFt > C-S-H with low C/S ratio. Recent in-house sorption studies with $^{125}I$ on selected cement minerals largely support the proposed sequence (Tab. 4.1). Monosulphoaluminate (AFm-SO$_4$) was found to exhibit the largest sorption potential while $\Gamma^-$ binding to C-S-H with high C/S ratios (C/S > 1) was much weaker. Interestingly, $\Gamma^-$ uptake was not detectable on AFt and C-S-H phases with a low C/S ratio (C/S = 0.7). In HCP, however, the amount of $\Gamma^-$ bound onto C-S-H phases with high C/S ratios may equal that of $\Gamma^-$ taken up by AFm-SO$_4$ as the higher affinity of AFm-SO$_4$ for $\Gamma^-$ (AFm-SO$_4$: Rd = 0.026 m$^3$/kg; C-S-H: Rd = 0.008 m$^3$/kg; Tab. 4.1) might be compensated by the large portion of C-S-H present in the cement matrix (C-S-H: ~ 50 wt.-%, AFm-SO$_4$: ~10 wt.-%, Tab. 2.2).

Recent in-house studies on $\Gamma^-$ uptake by AFm phases confirmed the formation of AFm-I$_2$ (3CaO·Al$_2$O$_3$·CaI$_2$·12H$_2$O) at high iodide concentrations (Aimoz et al. 2012a), thus supporting the observations made earlier by Brown and Grutzeck (1985a), Brown & Grutzeck (1985b) and Toyohara et al. (2002). In addition, however, it was observed that $\Gamma^-$ strongly binds onto AFm-SO$_4$ as the latter phase is capable of taking up the anion into the interlayer in contrast to AFt and other AFm-type minerals, such as monocarbonate (AFm-CO$_3$) and Friedel's salt (AFm-Cl$_2$). In thermodynamic terms $\Gamma^-$ uptake by AFm-SO$_4$ could be modelled as solid solution formation between the AFm-SO$_4$/AFm-I$_2$ end members (Aimoz et al. 2012b). The study by Aimoz et al. (2012a) further shows that CO$_3^{2-}$ and Cl$^-$ are competing anions which may significantly reduce $\Gamma^-$ uptake by AFm phases. High concentrations of the competing anions in cementitious systems promote conversion of AFm-SO$_4$ to AFm-CO$_3$ or AFm-Cl$_2$, which may strongly reduce the $\Gamma^-$ sorption capacity of HCP. Therefore, the presence or absence of AFm-SO$_4$ in the cement paste has a major impact on its capability to retard $\Gamma^-$. Note that changes in the mineral composition of the cement paste may further be key to understanding differences in sorption values obtained from diffusion and sorption experiments. As noticed in Wieland & Van Loon (2002) diffusion-derived $R_d$ values for $\Gamma^-$ are about an order of a magnitude lower than batch sorption data (see Wieland & Van Loon 2002 and references therein). It is conceivable that the pore water composition may depend on the S/L ratio of the cementitious system, which in turn has an influence on the mineral composition, in particular the type of AFm phases formed. Note, however, that detailed predictions of the influence of competing anions on $\Gamma^-$ retention by HCP in dilute and compact systems are currently lacking.

The sorption values for $\Gamma^-$ in the first two stages of the cement degradation are accepted as given in the previous SDB. In Wieland & Van Loon (2002) a cautious approach was taken by assigning $R_d = 10^{-3}$ m$^3$/kg across the first two stages of the cement degradation (Tab. 6.1). A possible increase in $\Gamma^-$ uptake from stage I to stage II, which was indicated in the experiments by Pointeau et al. (2008), is currently not taken into account because the underlying uptake
mechanism leading to a noticeable increase is presently unclear. The $R_d$ value is set to zero in stage III due to absence of AFm-SO$_4$ and the low C/S ratio found for C-S-H phases in this stage of the cement degradation (Tab. 6.1). Furthermore, the same values were selected for reducing and oxidizing conditions. Using iodide sorption values under all possible near field conditions is a cautious approach in view of the higher sorption values reported for IO$_3^-$ (Atkins & Glasser 1992). Furthermore, it is to be noted that the recommended values only apply at low chloride concentrations (see Section 4.4).

4.1.15 Caesium

Bradbury & Sarott (1994) and Wieland & Van Loon (2002) presented reviews of the earlier sorption studies with Cs on HCP. Caesium uptake by HCP is expected to be weak in the three stages of the cement degradation (Bradbury & Sarott 1994). In stage I, competition between Cs$^+$ and Na$^+$/K$^+$ appear to strongly reduce uptake by HCP with $R_d$ values ranging from $\sim 2 \times 10^{-3}$ m$^3$/kg to $\sim 4 \times 10^{-3}$ m$^3$/kg (Wieland & Van Loon 2002 and references therein). This range is further consistent with that reported for $R_d$ values deduced from diffusion studies ($R_d \sim 8 \times 10^{-4}$ m$^3$/kg – $\sim 3 \times 10^{-3}$ m$^3$/kg) (Wieland & Van Loon 2002 and references therein). Competition with Na$^+$ and K$^+$ ions is considered to be the main reason for the large scatter in the sorption values reported for Cs on HCP in stage I of the cement degradation. The competitive effect of Na and K is expected to be reduced in stage II due to rapid alkali release during the course of stage I of the cement degradation. Depletion of alkalis from the cement matrix causes a pH decrease from $> 13$ to $\sim 12.5$ and further gives rise to an increase in the $R_d$ value reported for Cs under these conditions (Wieland & Van Loon 2002). For example, Holland & Lee (1992) determined the $R_d$ value for Cs uptake on sulphate-resistant Portland cement to be 0.017 m$^3$/kg under the conditions relevant to stage II of the cement degradation. The latter value is significantly greater than the range of values determined for stage I of the cement degradation.

New information on the uptake mechanism of Cs in HCP is available from Pointeau et al. (2001) and Ochs et al. (2006). These studies support the idea that C-S-H phases are the uptake-controlling cement phase for Cs in HCP and that ion exchange is the prevailing uptake mechanism on C-S-H phases (Aggarwal et al. 2000). Ochs et al. (2006) developed a simplified model, which allows the $R_d$ values of Cs in HCP to be predicted as a function of pH and the concentration of competing cations, in particular Na, K and Ca. The influence of pH was taken into account based on the varying C/S ratios of C-S-H phases. Cs uptake was found to increase with decreasing pH, and therefore decreasing C/S ratio of C-S-H phases. This implies that C-S-H phases with a high C/S ratio, such as in stages I and II of the cement degradation, have a lower affinity for Cs than the C-S-H phases with a low C/S ratio as in stage III. The concentration of sorption sites associated with C-S-H phases was identified as the other important parameter, which determines Cs uptake. In the simplified model developed by Ochs et al. (2006) the concentration of sorption sites varies with pH or the C/S ratio of C-S-H phases. The model proposed in Ochs et al. (2006) allows Cs uptake by HCP to be predicted for a wide range of solution and cement compositions.

The studies by Pointeau et al. (2001) and Ochs et al. (2006) significantly improve our current understanding of Cs uptake by HCP. The novel insights support the appraisals made in the previous SDBs (Bradbury & Sarott 1994, Wieland & Van Loon 2002). The observed trend in Cs uptake by C-S-H phases was already taken into account in the recommended sorption values for the different stages of the cement degradation as given in Wieland & Van Loon (2002). Thus, the sorption values are retained for stages I and II of the cement degradation. Cs uptake in a cement paste degraded to stage III of the cement degradation is expected to be higher than in stages I and II. In this study, however, a cautious approach is taken by assigning the same $R_d$ values to stages II and III of the cement degradation (Tab. 6.1).
4.1.16  Lead  
Sorption measurements with Pb on cement paste were reported by Bayliss et al. (1988) and more recently by Ochs et al. (2003). The latter authors investigated the uptake of Pb by various cementitious materials, i.e. hydrated fresh and degraded OPC, high-alumina cements, different C-S-H phases, including tobermorite, and important cement minerals, such as portlandite, ettringite, hydrotalcite and hydrogarnet. Sorption values on fresh and aged HCP were reported to range in value between ~ 1 m$^3$/kg and ~ 100 m$^3$/kg. The authors concluded that C-S-H phases are the uptake-controlling cement phase for Pb in HCP. Furthermore, systematic trends in Pb uptake by HCP were observed: 1) Uptake was found to decrease with increasing pH in the pH range 10 – 13, 2) Uptake increases with increasing Fe content of HCP, and lastly, 3) Uptake was found to depend on the Pb concentration in solution. The authors developed an empirical relationship between Pb uptake by HCP and the afore-mentioned parameters.

Rose et al. (2000), Benard et al. (2003, 2009) carried out EXAFS studies on Pb loaded C-S-H phases, and unaltered and altered HCP. Rose and co-workers showed that Pb is directly bonded to the chain of silica tetrahedra of C-S-H phases, thus implying inner-sphere coordination of Pb on the C-S-H surface. Benard et al. (2003, 2009) further concluded that C-S-H phases are the cement phases controlling Pb uptake in unaltered and altered HCP. The presence of Fe in the coordination sphere of Pb could not be excluded in altered cement paste indicating that, in addition to C-S-H phases, a Fe-bearing cement mineral, such as Fe-substituted hydrogarnet or non-reacted ferrite, could contribute to Pb retention in altered HCP. While the latter consideration cannot be ignored, it is evident that the spectroscopic studies do not disapprove the hypothesis that C-S-H phases play a prominent role in Pb retention by HCP and further that adsorption onto the C-S-H surface is the dominant sorption mechanism.

Changes in the hydrolysis speciation with pH was found to exert a strong effect on Pb uptake by HCP (Ochs et al. 2003). Pb(OH)$_2^-$ dominates the speciation in solution at pH > 11 while Pb(OH)$_3^-$ is the main hydrolysis species in the pH range 10 to 11. Therefore, an increase in pH from 12.5 (stage II of the cement degradation) to 13.3 (stage I of the cement degradation) should cause a reduction in radionuclide uptake by a factor of about 6 in accordance with an equivalent increase in the Pb(OH)$_2^-$ concentration. In line with these considerations the sorption value for Pb(II) in stage I of the cement degradation is retained as recommended by Bradbury & Van Loon (1997). However, the sorption value in stage II is revised upwards from $R_d = 0.5$ m$^3$/kg to $R_d = 3$ m$^3$/kg in agreement with changes of the Pb speciation with pH (Tab. 6.1). Bringing forward the same argument, it is expected that the sorption value assigned to stage III of the cement degradation should be about an order of a magnitude higher than that selected for stage II (Ochs et al. 2010). This leads to a best estimate for stage III ($R_d = 30$ m$^3$/kg) which agrees with the sorption value proposed elsewhere (Ochs et al. 2010).

4.1.17  Polonium  
To the best of our knowledge, no relevant sorption data have been reported for Po to date. On the basis of the earlier appraisal (Bradbury & Van Loon 1997) the sorption values of Po is set to zero for all stages of the cement degradation both under oxidizing and reducing conditions (Tab. 6.1). Chemical analogy with Th(IV) rather than other group VI elements (e.g. Se, Tc) was considered for estimating solubility limits (Berner 2014). Nevertheless, due to lack of supporting experimental evidence, chemical analogy is currently not taken into account to estimate $R_d$ values.
4.1.18 Trivalent lanthanides and actinides

Several investigations on the uptake of trivalent lanthanides, i.e. Eu(III) and Nd(III), and trivalent actinides, i.e., Am(III) and Cm(III), by cementitious materials have been published in the last years (Tits et al. 2003a, Stumpf et al. 2004, Pointeau et al. 2004a, Schlegel et al. 2004, Cowper et al. 2006, Mandaliev et al. 2009, Mandaliev et al. 2010a,b, Mandaliev et al. 2011). Trivalent lanthanides are considered as suitable chemical analogues for trivalent actinides. The recently published in-house studies complement sorption measurements reported earlier by Tits et al. (1998) and Wieland et al. (1998). Sorption measurements with lanthanides and actinides on HCP and C-S-H phases carried out before 2002 are discussed by Bradbury & Sarott (1994), Bradbury & Van Loon (1997), and Wieland & Van Loon (2002).

Mandaliev et al. (2009, 2010a,b, 2011) studied the uptake of Nd(III) and Eu(III) by HCP and C-S-H phases using EXAFS spectroscopy. The authors proposed an uptake mechanism involving several steps: Nd is bound to surface sites of C-S-H phases in the initial stage of Nd interaction with the cementitious materials. However, over time, Nd is taken up into the structure of C-S-H phases where it occupies crystallographic positions close to bridging Si tetrahedra in the interlayer and replaces Ca in the Ca sheets. These observations agree with findings on Cm(III) uptake by HCP and C-S-H phases reported earlier by Tits et al. (2003a) and Stumpf et al. (2004). Using time-resolved laser fluorescence spectroscopy (TRLFS) Tits and co-workers showed that the presence of Cm species with long fluorescence emission lifetimes can be interpreted in terms of Cm incorporation into the structure of C-S-H phases. Stumpf and co-workers further observed the same peak maxima in the characteristic emission spectra of the Cm species, i.e., the same shift in the fluorescence emission lines, and similar lifetimes of the long-lived Cm species in the Cm(III)/HCP and Cm(III)/C-S-H systems. The latter finding suggests that Cm occupies similar coordination environments in HCP and C-S-H phases, which further implies that C-S-H phases are the uptake-controlling cement phase for Cm in the complex cement matrix. Eventually, Schlegel et al. (2004) carried out an EXAFS study on Eu(III) doped C-S-H phases, which support the idea that Eu is incorporated into the structure of C-S-H phases in the long term.

The measured sorption values, however, reveal large discrepancies in contrast to the rather consistent mechanistic picture that has emerged in the last years on the interaction of trivalent actinides and lanthanides with cementitious materials. Wieland & Van Loon (2002) recommended an $R_d = 100\ m^3/kg$ for the uptake of trivalent actinides and lanthanides by HCP. The recommendation was based on the appraisal of a large and consistent set of sorption data obtained from in-house sorption measurements. The latter measurements were carried out with Eu(III) or Am(III), respectively, on HCP, C-S-H phases and calcite (Tits et al. 1998, Wieland et al. 2002, Tits et al. 2005). All these measurements reveal a very strong interaction of trivalent actinides and lanthanides with the different solids under hyper alkaline conditions.

Pointeau et al. (2004a) and Cowper et al. (2006) reported new series of sorption measurements with Am on HCP and C-S-H phases. Pointeau et al. (2004a) carried out sorption studies with Am on degraded HCP. The authors observed a strong interaction of Am with HCP, which resulted in sorption values ranging between ~ 20 m$^3$/kg and ~ 100 m$^3$/kg. Taking into account the relatively large uncertainties on the sorption data the study indicates no significant influence of the stage of the cement degradation on radionuclide uptake. The latter finding further implies that pH changes have no significant effect on the uptake of trivalent actinides and lanthanides by HCP. The experiments reported in Pointeau et al. (2004a) were carried in very dilute systems (S/L ratio = 0.5 g/L) while the technique used to separate solid and liquid phase was not reported. It is assumed that centrifugation was used in the latter study as separation technique.
Cowper et al. (2006) determined the uptake of Am by HCP in various media. The authors reported sorption values ranging between ~ 5 m$^3$/kg and ~ 32 m$^3$/kg. In contrast to the study of Pointeau and co-workers these experiments were carried out using suspensions at a relatively high S/L ratio (10 g/L). Cowper et al. (2006) tested several separation techniques, such as centrifugation (bench-top centrifuge for 30 min at 4'500 rpm) and filtration using two different size cut-offs (0.45 µm and 10'000 nominal molecular weight cut-off).

The S/L ratio used in combination with the total activity or concentration of a radiotracer added to the system, as well as the separation technique employed, are considered to have an effect on the sorption data (Tits et al. 2002). The S/L ratio in combination with the total activity (or concentration) of the sorbing tracer used are the main factors that determine the experimental window for which statistically meaningful sorption values can be accurately obtained (Tits et al. 2002). It was noted that sorption measurements with strongly sorbing tracers tend to be made outside the acceptable experimental window in all those cases where high S/L ratios were used along with low initial tracer activities. The actual tracer activity (or concentration) in solution might be close to, or even below the detection limit of the analytical technique under these conditions. Sorption values determined close to or at the detection limit of the analytical technique correspond to maximum sorption values that can be measured under the given conditions rather than "true" (or accurate) sorption values. It is further to be noted that the "true" sorption value is always greater than the measured one outside the experimental window.

The separation technique used in sorption studies determines the efficiency of phase separation, in particular the degree to which colloidal matter is being removed from solution. For example, Cowper et al. (2006) showed that the sorption value for Am on HCP was lower when centrifugation was carried out at a low centrifugal acceleration (e.g. using a bench-top centrifuge for 30 min at 4'500 rpm). This finding can be explained as follows: lowering the centrifugal acceleration increases the colloid inventory in solution, onto which the strongly sorbing radionuclide sorbs, which corresponds to an increase in the aqueous (free plus colloidal) concentration of Am. In general, lower sorption values have been determined after centrifugation at low centrifugal acceleration.

The sorption values reported by Pointeau et al. (2004a) and Cowper et al. (2006) can be assessed with a view to the afore-mentioned experimental aspects, i.e., the experimental window and the technique used for phase separation. Pointeau et al. (2004a) carried out sorption experiments at a low S/L ratio of 0.5 g/L while the initial tracer activity was not reported. Nevertheless, the low S/L ratio used by these authors suggests that, very probably, the sorption measurements were performed within the experimental window, which, in principle, allows reliable sorption measurements with strongly sorbing tracers to be conducted. Pointeau et al. (2004a) used centrifugation for phase separation while details of the protocol were not reported. Therefore, an influence of colloids on the sorption measurements in these experiments cannot be excluded in general. In contrast, Cowper et al. (2006) reported the separation technique while the S/L ratio in these experiments was high (10 g/L) with reference to the acceptable experimental window for strongly sorbing tracers (Tits et al. 2002). Thus, the experimental set-up used in the study of Cowper et al. (2006), in particular the combination of high S/L ratio and low initial Am concentration, most likely resulted in maximally measurable sorption values rather than "true" sorption values. In summary, one cannot exclude that the studies by Pointeau et al. (2004a) and Cowper et al. (2006) show experimental shortcomings that may have an effect on the measured R$_d$ values. In particular, both experimental protocols may have resulted in sorption values that underestimate "true" uptake of Am by HCP. As a consequence of the above assessment it is believed that the sorption value recommended earlier in Wieland & Van Loon (2002) (R$_d$ = 100 m$^3$/kg) adequately represents uptake of trivalent actinides and lanthanides by HCP.
Np(III) and Pu(III) are considered to exist under strongly reducing conditions. Sorption measurements with both redox species in cementitious systems are lacking. It is assumed that the sorption behaviour of Np(III) and Pu(III) is analogous to that of the other trivalent actinides.

Stumpf et al. (2004) and Mandaliev et al. (2009) showed that C-S-H phases are the uptake-controlling cement phase for trivalent actinides and lanthanides in HCP. Therefore, the same sorption value is assigned to all stages of the cement degradation because C-S-H phase will persist in degrading cement paste over time (Tab. 6.1).

4.1.19 Th(IV) and tetravalent actinides

Bradbury & Sarott (1994) and Wieland & Van Loon (2002) reviewed the earlier sorption measurements with Th(IV) and the tetravalent actinides (Np(IV), Pu(IV), U(IV)) on cementitious materials. A detailed review of more recent experimental data is given in Wang et al. (2009).

Cowper et al. (2006) and Tits et al. (2014) report new series of sorption measurements with Th(IV) on cementitious materials. The former authors investigated Th(IV) uptake by HCP while the latter authors report sorption studies with Th(IV) on C-S-H phases. Th(IV) was found to sorb very strongly on both cementitious materials under alkaline conditions. Thus, the experimental constraints previously outlined for measurements with the strongly sorbing trivalent actinides and lanthanides also apply to Th(IV). Cowper et al. (2006) used a S/L ratio of 10 g/L, as in the sorption studies with Am, and a relatively low initial Th(IV) concentration. This may limit the accuracy of the measured sorption values. The authors determined R_d values ranging from ~ 6 m^3/kg to ~ 430 m^3/kg. In contrast, Tits et al. (2014) used a lower S/L ratio (< 2 g/L) and a relatively high initial tracer concentration in the Th(IV) sorption studies. This resulted in sorption values ranging between ~ 100 m^3/kg and ~ 1'000 m^3/kg. Note that the high sorption value reported earlier for Th(IV) by Wieland et al. (1998) is not considered in the current assessment due to the very low S/L ratio used in the experiments.

Pointeau et al. (2004a) report a strong uptake of Pu(IV) by HCP. The sorption value for Pu(IV) on HCP degraded to the pH range 10 – 12 was found to vary between ~ 10 m^3/kg and ~ 1'000 m^3/kg. While the S/L ratio of the suspensions used by Pointeau and co-workers was low (0.5 g/L), details of the protocol used for phase separation were not reported. Note that the large scatter in the data could be due to insufficient removal of colloidal matter from solution (see Section 4.1.18).

In-house sorption studies provide novel information on Np(IV) uptake by HCP and C-S-H phases (Gaona et al. 2011, Tits et al. 2011a). Gaona et al. (2011) carried out EXAFS measurements on Np(IV) loaded C-S-H and HCP samples which had been prepared under controlled, reducing conditions. In this study, special precautions had been taken to prevent any oxygen ingress into the samples. The EXAFS measurements on the Np(IV)-doped C-S-H samples revealed that the local structure of Np(IV) changes as a function of the C/S mol ratio of the C-S-H phases. The large number of neighbouring Ca and Si atoms (C/S ratio 1.65: ~ 13 Ca and ~ 3 Si; C/S 0.75: ~ 8 Ca and ~ 5 Si) indicate that Np(IV) is taken up into the interlayer of C-S-H phases in the long term although initial adsorption onto the surface of C-S-H phases cannot be excluded. EXAFS investigations on the Np(IV) loaded HCP samples further showed a similar molecular environment of Np(IV) in the C-S-H phase with C/S ratio 1.65 and HCP. This finding indicates that C-S-H phases are the main sorbing phase for Np(IV) in HCP. Note that C-S-H phases with C/S ratio > 1.5 prevail in fresh cement paste (Taylor 1997). C-S-H phase with C/S ratio > 1.5 are further expected to dominate in cement paste altered to stage II of the cement degradation while C-S-H phases with lower C/S ratios (lower bound C/S ~ 0.75) are expected to
persist in stage III of the cement degradation. The above findings indicate that C-S-H phases are responsible for Np(IV) uptake by HCP in all stages of the cement degradation and that incorporation into the interlayer of the C-S-H structure is the dominant uptake mechanism.

Sorption measurements with Np(IV) on C-S-H phases (Tits et al. 2011a) and HCP (Gaona et al. 2011, in-house unpublished data) reveal very strong uptake of Np(IV) by these materials. Note that Baston et al. (2012) also observed very strong sorption of Np(IV) on untreated and aged NRVB. The authors concluded that C-S-H phases are responsible for most of the radionuclide uptake by NRVB.

Figure 4.1a shows the $R_d$ value determined on C-S-H phases with varying C/S ratio. Note that these experiments were carried out in alkali-free solutions for which the pH ranged between ~10.5 and ~12.5 depending on the composition of the equilibrium solution at the given C/S ratio of the C-S-H phases (Tits et al. 2014). In Fig. 4.1b $R_d$ values on C-S-H phases with varying C/S ratios which were determined in alkali-containing cement pore water typically observed in stage I of the cement degradation are displayed. Interestingly, the sorption values for Np(IV) and Th(IV) agree within the limits of uncertainty, thus supporting the idea that Th(IV) is an appropriate chemical analogue for the tetravalent actinides with respect to their uptake by cementitious materials.

Sorption measurement with U(IV) on cementitious materials are scarce (Bayliss et al. 1996) and in particular, no new sorption measurements have been reported in the last years. Appraisals of the earlier data are given in Bradbury & Van Loon (1997) and Wieland & Van Loon (2002).

The new sorption data available for Th(IV) and Np(IV) indicate that Th(IV), and in analogy all tetravalent actinides, strongly sorbs onto HCP. The low sorption values reported by Cowper et al. (2006) and Pointeau et al. (2004a), in comparison to those reported by Tits et al. (2014), can be rationalized on the basis of the different experimental protocols that have been applied (e.g. procedures used for solid-liquid phase separation and appearance of colloids as disturbance in solid-liquid phase separation). Therefore, it is believed that the sorption value recommended earlier by Wieland & Van Loon (2002) for Th(IV) ($R_d = 100 \text{ m}^3/\text{kg}$), and on the basis of chemical analogy for all tetravalent actinides, can be retained even in the light of the new information available. Furthermore, the same sorption value is assigned to Th(IV) and all tetravalent actinides (Np(IV), Pa(IV), Pu(IV), U(IV)) for stages I – III of the cement degradation ($R_d = 100 \text{ m}^3/\text{kg}$; Tab. 6.1).
4.1.20 Penta- and hexavalent actinides

Rather consistent sets of sorption data have been reported for U(VI) uptake by cementitious materials while sorption data are scarce for the other penta- and hexavalent actinides (i.e. Pu(V), Pa(V), Np(V), Np(VI)). Bradbury & Sarott (1994), Bradbury & Van Loon (1997), Wieland & Van Loon (2002) and Wang et al. (2009) published comprehensive reviews of the available sorption data.

In the last years new information on U(VI) uptake by cementitious materials has been made available from numerous studies. Sorption measurements are reported in Sutton et al. (2003), Pointeau et al. (2004b), Tits et al. (2008), Baston et al. (2012) and Tits et al. (2014) while Harfouche et al. (2006), Wieland et al. (2010), Tits et al. (2011a) and Macé et al. (2013) carried out spectroscopic investigations on U(VI) uptake by cementitious materials. Sutton et al. (2003) studied U(VI) uptake by pre-equilibrated and leached grouted mixes of OPC and pulverised fuel ash. The authors determined Rd values ranging from ~ 1.5 m$^3$/kg to ~ 3.6 m$^3$/kg and linear sorption. Baston et al. (2012) determined U(VI) uptake on untreated and aged NRVB while Pointeau et al. (2004b) studied U(VI) uptake by HCP as a function of cement degradation in the pH range 10 – 12.5 and by C-S-H phases. Sorption values were reported to range from ~ 10 m$^3$/kg to ~ 200 m$^3$/kg on degraded HCP. Pointeau et al. (2004b) and Baston et al. (2012) observed an increase in U(VI) uptake with decreasing pH or increasing degree of cement degradation, respectively, which can be interpreted in terms of pH dependent formation of U(IV) hydrolysis products (Gaona et al. 2012a).

Tits et al. (2008, 2014) investigated U(VI) uptake by C-S-H phases with different C/S ratios. Sorption and co-precipitation experiments were carried out with the aim of distinguishing U(VI) sorbed species from U(VI) species incorporated in the C-S-H structure. The authors showed that the Ca concentration has an effect on U(VI) uptake by C-S-H phases and further observed that Rd's determined from sorption and co-precipitation experiments are similar in value. This indicates that no additional sorption sites for U(VI) binding were generated during co-precipitation. The latter finding further implies that either U(VI) is not taken up into the structure of
C-S-H phases or, in addition to surface sites, the same structural sites were made available for U(VI) binding in the course of both sorption and co-precipitation processes. The latter conclusion is supported by spectroscopic studies, suggesting U(VI) incorporation into the C-S-H structure with a coordination environment of U(VI) comparable to that in uranyl silicates (Harfouche et al. 2006, Tits et al. 2011b, Macé et al. 2013).

Novel information on Np(V) and Np(VI) uptake by HCP and C-S-H phases is available from in-house spectroscopic and sorption studies (Fig. 4.1, Gaona et al. 2013). In the earlier SDB it was assumed that Np(V) sorbs relatively weakly onto HCP and C-S-H phases as the effective charge of the metal cation in the NpO$_2^+$ species is $+2.3 \pm 0.1$ (Wieland & Van Loon 2002). In contrast to the expectations, however, recent experimental data indicate strong uptake of Np(V) by HCP and C-S-H phases and Rd's comparable in value to those determined for Np(IV) (Fig. 4.1). Furthermore, the presence of aqueous Np(VI) anionic species (NpO$_2$(OH)$_3^-$ and NpO$_2$(OH)$_4^{2-}$) was observed under oxidizing conditions in analogy to U(VI) (Gaona et al. 2012b). The latter finding implies that the stability field of Np(V) is narrower than predicted on the basis of the presently available thermodynamic data. The sorption behaviour of Np(VI) was found to be similar to that of U(VI) with a pronounced dependence on pH (Tits, pers. comm.). Formation of negatively charged hydroxo species dominates the aqueous speciation of Np(VI) and U(VI) above pH 11, which results in decreasing Np(VI) and U(VI) uptake by HCP and C-S-H phases (Tits, pers. comm.).

The EXAFS study by Gaona et al. (2013) reveals that the coordination environment of Np(V,VI) in fresh HCP (pH = 13.3) corresponds to that of Np(V,VI) taken up by a C-S-H phase with a C/S ratio = 1.65. Note again that C-S-H phases have a C/S ratio > 1.5 in fresh cement paste (Taylor 1997) and therefore, the notion of Np(V,VI) binding to C-S-H phases is consistent with the mineralogy reported for HCP. The above finding further implies that C-S-H phases are the uptake-controlling phase for Np(V,VI) in HCP. In the EXAFS study strong interference from the neptunyl moiety significantly limited determination of the neighbouring atoms from the more distant shells (Gaona et al. 2013). The short Np-O$_{eq}$ distances observed in combination with the presence of a neighbouring Si atom, however, suggests that an incorporation mechanism controls Np(V,VI) uptake by C-S-H phases.

The new set of sorption data allow a re-appraisal of Np(V,VI) and U(VI) uptake by HCP to be undertaken. The sorption value for U(VI) in stage I ($R_d = 2$ m$^3$/kg) is retained as given earlier (Bradbury & Van Loon 1997, Wieland & Van Loon 2002). The well supported Rd value for U(VI) in stage I of the cement degradation ($R_d = 2$ m$^3$/kg) is further assigned to Np(V,VI) and other pentavalent actinides (Pa(V), Pu(V)) for which no data are available. The recently published sorption studies indicate significantly stronger interaction of Np(V,VI) and U(VI) with HCP in stage II of the cement degradation compared to stage I. Furthermore, uptake was found to further increase in stage III of the cement degradation due to decreasing concentration of the negatively charged hydrolysis species. Acknowledging the comprehensive set of sorption data reported by Pointeau et al. (2004b) it is justified to assign a higher sorption value to U(VI) in stage II of the cement degradation ($R_d = 20$ m$^3$/kg) (Tab. 6.1). The same sorption value is assigned to Np(V) and Np(VI), thus ignoring the higher uptake observed for Np(V) by C-S-H phases. The latter sorption value is further assigned to Pa(V) and Pu(V) due to the limited data set reported for these radionuclides (Wang et al. 2009). A cautious approach is taken by assigning the same sorption values to stages II and III of the cement degradation, thus ignoring the experimentally observed increase in uptake by HCP with decreasing pH.
4.1.21 Small organic compounds

$^{14}$C, possibly in the form of small organic compounds resulting from steel corrosion under reducing conditions, is a potentially major contributor to the long-term activity release rate (mSv per year) from the cementitious near field into the far field. These compounds may be either inorganic, i.e. $^{14}$CO$_3^{2-}$ under hyper alkaline conditions, or organic, i.e. $^{14}$C containing oxygenated hydrocarbons, such as alcohols, aldehydes, carboxylic acids, or non-oxygenated, volatile hydrocarbons, such as methane, ethane, ethene etc. (Deng et al. 1997, Sasoh 2008a,b). Interaction of the latter compounds with HCP is expected to be negligible while oxidized hydrocarbons will be present as dissolved species and therefore, interaction with the surface of cement minerals is possible. Preliminary in-house sorption measurements with $^{14}$C labelled formic and acetic acids as well as sorption studies published earlier by Sasoh 2008a showed that the uptake of oxidized hydrocarbons by HCP is very low ($\text{R}_d \leq 10^{-3}$ m$^3$/kg). This finding implies that sorption measurements with these compounds on HCP have to be conducted using an experimental system with a high S/L ratio.

As a consequence of the above, the uptake of selected, small organic molecules (methanol, ethanol, formaldehyde, acetaldehyde, formic acid, acetic acid) was investigated on intact hydrated cement. The samples were prepared by mixing un-hydrated cement (CEM I 52.5 N HTS, Lafarge, France) with methanol, ethanol, formaldehyde, acetaldehyde, formic acid or acetic acid containing solutions (w/c = 0.5). Note that aldehydes could disproportionate to carboxylic acid and alcohols under alkaline conditions and therefore, a higher uncertainty is associated with the $\text{R}_d$ values given for the aldehydes compared to those for the carboxylic acids and alcohols. The samples were hydrated for 28 and 360 days. The cement pore water was squeezed from the aged samples using the steel die method at pressures up to 530 N mm$^{-2}$. Total organic carbon (TOC) was determined in the filtered pore solutions using a Shimadzu TOC-V analyser with UV-promoted persulphate wet oxidation and non-dispersive infrared detection of the generated CO$_2$. Linearity of TOC analysis was verified in the concentration range from 0 - 10 ppm C, which was used as the dynamic range for the TOC measurements. The $\text{R}_d$ values were estimated on the basis of mass balance calculations. The amount of compound sorbed was estimated as the difference between the initial concentration added and the concentration determined in the extracted solutions of the samples aged for 28 and 360 days. The S/L ratio of the HCP samples was estimated to be 7.3 kg/L after 28 days hydration time and 9.0 kg/L after 360 days hydration time by considering the reduction of free water during cement hydration. Complementary to the hydration experiments short-term experiments were carried out by contacting unhydrated cement with solutions containing the above compounds (w/c = 0.5) for 1 hour. TOC analysis was carried out on the filtered solutions and the $\text{R}_d$ values were determined on the basis of mass balance calculations.

Uptake of the above small organic molecules by hydrating cement was found to be very weak (Fig. 4.2). Nevertheless, the approach applied in this study allows the low sorption values to be quantified accurately. $\text{R}_d$ values were found to typically range from $10^{-5}$ to $10^{-3}$ m$^3$/kg for all compounds. The sorption values from the short-term sorption experiments and those determined for the hydrated samples agree within the limit of uncertainty (Fig. 4.2), indicating only weak time dependence. Note that the low $\text{R}_d$ value determined for ethanol after 360 days reaction is most likely an outlier caused by an experimental artefact. The retention sequence can tentatively be given as: formic acid > acetic acid > acetaldehyde > formaldehyde > methanol > ethanol, thus suggesting decreasing uptake with decreasing oxidation state of the hydrocarbons. Uptake of the organic molecules into the structure of the cement phases formed during cement hydration seems to be insignificant because the extent of interaction of the compounds with HCP is largely independent of the hydration time. It is to be noted that very weak adsorption onto HCP was observed even for the smallest and the least oxidized species, such as methanol.
Using the complete set of sorption data the average $R_d$ value was determined to be $\sim 10^{-4} \text{ m}^3/\text{kg}$. A cautious approach is taken by recommending $R_d = 10^{-5} \text{ m}^3/\text{kg}$ as best estimate for use in PA (lower limit: $R_d = 0$; upper limit: $R_d = 10^{-3} \text{ m}^3/\text{kg}$) (Tab. 6.1).

![Graph](image)

**Fig. 4.2:** Uptake of small organic molecules by HCP as a function of equilibration time.

The shaded area indicates the range of measured sorption values for all simple, oxidized organic compounds used in this study.

### 4.2 Uncertainties on sorption values

In this study, experimental uncertainties of the sorption values are treated separately from the large uncertainty range emerging if all the sorption values reported in the literature are considered. The former limit of uncertainty is treated as given in CEM-02 (Wieland & Van Loon 2002) while the latter uncertainty is based on appraisals made in the framework of an elicitation process reported by Wang et al. (2009).

#### 4.2.1 Experimental uncertainties

Experimental uncertainties in the sorption values arise from sample manipulations, e.g. the preparation of the solid material and the suspensions, the separation of solid and liquid phase, and radiochemical analysis. Batch-type sorption studies are usually performed using crushed cement materials. In general, crushing and grinding increases the surface area of materials that gives rise to an increase in the sorption capacity. In the case of cement paste, however, crushing and grinding seems to have no significant effect on the surface area as indicated by Rowan et al. (1988). The authors determined water vapour adsorption on crushed materials for different average particle sizes ($50 – 125 \mu m$, $125 – 250 \mu m$, $0.5 – 1.0 \text{ mm}$) using the BET method. The specific surface areas were found to range between 73 m$^2$/g and 91 m$^2$/g irrespective of the markedly different size ranges of the fragmented samples. This indicates that the surface area is dominated by the contribution from the gel pore structure of HCP which, obviously, is largely unaffected by crushing and grinding. Therefore, one may infer that the procedure applied to crush and grind HCP material and therefore, differences in particle size fractions used in sorption studies, is not a major contributor to experimental uncertainty.
A major uncertainty arises from the preparation of cement suspensions and the separation of the solid and liquid phase after equilibration. Cement suspensions are usually prepared by mixing crushed cement paste with an equilibrium solution (for unaltered samples) or Milli-Q water (for degraded samples). It was observed that in sorption studies with strongly sorbing radionuclides the solid content of the suspensions had to be reduced to $10^{-3}$ kg/L or less in order to achieve accurate measurements of the radionuclide activities in solution (Wieland et al. 1998, Tits et al. 2002). It is conceivable that the preparation of suspensions with S/L ratios of $10^{-4}$ kg/L or less involves large uncertainties in the effective cement content and the homogeneity of the cement material. Preliminary tests revealed variations in the solid contents by up to a factor of 4 at low S/L ratios. This partially explains the large uncertainty in $R_d$ values obtained from in-house sorption measurements with the strongly sorbing radionuclides, which were carried at S/L ratios typically ranging between 0.01 and 0.1 g/L. Furthermore, solid-liquid phase separation by centrifugation may be the cause of colloid-induced artefacts (see Section 4.1.18). Hence, it is expected that uncertainties associated with activity measurements (radio assay) are negligible in view of the large uncertainties associated with sample preparation and solid-liquid phase separation.

In line with the earlier SDB (Wieland & Van Loon 2002) an uncertainty factor, $f_E$, is used to estimate the upper and lower limits of sorption values according to:

\[
R_{d,\text{max}} = R_d \times f_E \quad [\text{m}^3/\text{kg}] \quad (4a) \\
R_{d,\text{min}} = R_d / f_E \quad [\text{m}^3/\text{kg}] \quad (4b)
\]

The expected experimental uncertainties associated with the selected $R_d$ values are listed in Tab. 6.1. The uncertainty range of sorption values is assumed to be about one order of magnitude in case of the strongly sorbing radionuclides ($R_d \geq 10$ m$^3$/kg). This corresponds to $f_E = 3$. Similar experimental uncertainty factors ($f_E = 3$) were applied in the sorption data bases for argillaceous rocks (Baeyens et al. 2014). The uncertainty accounts for variations in the solid contents, the homogeneity of the material at very low S/L ratio and possible effects of colloidal disturbance. Sorption measurements with weakly sorbing radionuclides ($R_d$ ranging from $10^{-3}$ m$^3$/kg to $10$ m$^3$/kg), however, are usually determined at higher S/L ratio, which should reduce uncertainties associated with sample preparation, solid-liquid phase separation and colloidal disturbance. In this case, experimentally determined $R_d$ values are expected to vary only within a factor of 2 which corresponds to an uncertainty factor $f_E = 1.4$.

### 4.2.2 Uncertainties associated with the use of sorption values obtained from dispersed cementitious systems for predictions in intact systems

Wieland & Van Loon (2002) discussed limits of uncertainties associated with the use of sorption values determined on dispersed systems (batch-type experiments) for predictions in intact (compact) systems. These uncertainties are believed to be attributable to differences in the water composition and in the accessibility of the solid surfaces in dispersed and intact systems. The composition of the pore water in intact cementitious systems is controlled by the solubility of cement phases which can be predicted for fresh cement paste and paste degraded by ground-water ingress from the surrounding host rock in a cement-based repository. Furthermore, the inventory of cement phases is large due to the high S/L ratio in the cementitious near field, which prevents cement phases from being completely depleted from the cement matrix in stages I and II of the cement degradation. Contrary to dense cementitious systems, however, there is the risk of complete dissolution of selected cement phases in the course of establishing equilibrium conditions in dispersed laboratory system (i.e. at low S/L ratio). Proper design of the batch-type experiments allows sorption values to be determined in dispersed systems under...
pore water conditions, which are relevant to those of intact systems. This requires, however, that sorption measurements are carried out on HCP samples where the crushed HCP material is immersed in solutions with a chemical composition in equilibrium with the HCP. Sorption values determined in batch-type sorption experiments on dilute systems and diffusion experiments in intact systems under comparable pore water conditions were found to deviate by less than a factor 4 (Tits et al. 2003b).

Hence, uncertainties associated with possible, small changes in the pore water composition are expected to have a small effect on sorption values in cementitious systems on condition that sorption measurements are carried out under equilibrium conditions. In principle, differences in the surface areas between crushed HCP materials used for batch-type sorption studies and intact HCP are expected to be more important. However, as discussed in Section 4.2.1, differences in the specific surface areas of intact and crushed HCP materials seem to be negligible. On the basis of the above assessment, it is concluded that no major uncertainties are associated with the use of batch sorption values for intact systems if adsorption is the dominant uptake mechanism of the radionuclide of interest. Uncertainties may be larger, however, if mechanism other than adsorption are responsible for radionuclide binding, e.g. solid solution formation.

4.2.3 Uncertainties on published sorption values

A great number of sorption data on the interaction of most safety-relevant radionuclides with cementitious materials are available from literature. Systematic compilations of the relevant sorption measurements carried out in the past are given in Wang et al. (2009) and Ochs et al. (2010). These studies reveal that the uncertainty range of $R_d$ values roughly increases with increasing number of measurements that are available. In particular for some specific radioelements, such as nickel, iodine and the tri- and tetravalent actinides (i.e. strongly sorbing radionuclides), uncertainty ranges covering up to four orders of magnitude emerge for measurements carried out under comparable experimental conditions. In some cases the large scatter in data can tentatively be attributed to technical aspects, such as reproducibility of the solid-liquid phase separation in those systems with strongly sorbing radionuclides, while in other cases the underlying reason for the large uncertainty range of sorption data remains uncertain. For example, the reason for the large spread in the sorption values of nickel and iodine is still unknown and might be due to chemical conditions that were controlled in the experiments and which had a strong effect on the operationally defined distribution ratio. In the present study, the large scatter in measured sorption values is acknowledged by assigning lower and upper limits to the best estimates listed in Tab. 6.1. The lower and upper bounds are estimated on the basis of the comprehensive compilation of sorption values given in Wang et al. (2009) and Ochs et al. (2010). In these studies, best estimates for sorption values along with the corresponding lower and upper limits were selected in the framework of a well-documented elicitation process. The lower and upper bounds listed in Tab. 6.2 are accepted as given in Wang et al. (2009) and Ochs et al. (2010), except where indicated.

4.3 Sorption reduction by cementitious colloids

4.3.1 Relevance of cementitious colloids

Colloids dispersed in the pore water of the saturated near fields of the ILW and L/ILW repositories could enhance the transport of radionuclides into the far field. Colloid-facilitated radionuclide migration in the near field could occur in a way similar to colloid-facilitated transport of contaminants in subsurface aquifers (e.g. Ramsay 1988, McCarthy & Zachara 1989, McCarthy & Degueldre 1993, Swanton 1995, Ryan & Elimelech 1996, Kretzschmar et al. 1999). The
following criteria must be met to enable colloid-facilitated radionuclide migration: 1) Generation by, and release of colloids from near-field materials giving rise to significant colloid concentrations in the pore water, 2) physico-chemical stability of the colloidal matter in the near field, i.e., absence of aggregation and filtration processes and absence of chemical gradients causing the dissolution of colloids, 3) mobility of colloids in the near field, 4) irreversible uptake of radionuclides by near-field colloids.

Laboratory-scale experiments and field studies showed that colloids are present in cement-type pore waters, thus suggesting that colloids will be present in the saturated cementitious near fields of ILW and L/ILW repositories (Wieland 2001, Wieland & Spieler 2001, Fujita et al. 2003). The colloids detected in cementitious environments have a composition similar to that of C-S-H phases which are the main component of HCP (Ramsay et al. 1988, Fujita et al. 2003). Note that HCP is a major component in the near fields of ILW and L/ILW repositories (~ 20 wt.-%). The colloid concentration in cement-type pore waters was reported to be very low, i.e. well below 1 mg/L (experimentally: 0.01 – 0.2 mg/L) (Wieland 2001). The low colloid inventory is the consequence of high ionic strength and the relatively high Ca concentration in cement-type pore waters. These chemical parameters facilitate colloid-colloid interactions (aggregation-sedimentation process) or attachment of colloids to the surface of the backfill material. The latter processes control the concentration of colloids dispersed in the pore water of the cementitious near fields. The influence of ionic strength and Ca concentrations on colloidal stability has been demonstrated in numerous studies (e.g. see review in Wieland 2001 and Filella 2007).

The low colloid concentration observed under the hyper alkaline conditions of a cement-type pore water is an important factor limiting radionuclide mobility in the cementitious near field. High ionic strength and Ca concentrations in the millimolar range are capable of establishing favourable conditions for colloid destabilisation or colloid attachment to the surface of backfill material, respectively. A low inventory of dispersed colloids, however, requires low or stagnant water flow in the near field of a repository in order to minimize colloid generation by re-dispersion. Under the latter conditions, the shear forces generated are expected to be too low to allow disaggregation and colloid detachment from the surface of the backfill material.

### 4.3.2 Colloid concentrations and physico-chemical stability

Wieland & Spieler (2001) determined the colloid concentration in the backfill mortar foreseen for use in the planned Swiss ILW and L/ILW repositories. Colloid concentrations were determined using a carefully calibrated, in-house developed particle counting system with three sensors arranged in series. The colloid detection system operated on the principle of laser light scattering. The colloid concentration was determined to be typically lower than < 0.1 mg/L in the cement-type pore water of the backfill material (pH > 12). Fujita et al. 2003 determined the colloid concentration in leachates collected from different cement formulations. The concentration was found to range in value between $10^{11}$ and $10^{12}$ particles/L. The mean particle size (diameter) was estimated to be < 100 nm from scanning electron microscopy (SEM). Using SEM the authors further observed that the colloidal matter predominately consisted of C-S-H-type particles. The colloid concentration was estimated to range in value between ~0.1 and ~1.1 mg/L on the assumption that the large portion of colloidal matter was C-S-H with an approximate composition CaO-SiO$_2$-H$_2$O (MW: 134.18; density: 2 g/cm$^3$) and a mean particle size of 100 nm. Thus, the results reported by Wieland & Spieler (2001) and Fujita et al. (2003) are in excellent agreement, suggesting that the high ionic strength and the high Ca concentration of cement-type pore water are unfavourable to generating large colloid inventories in solution (Wieland 2001).
Measurements of colloid concentrations were conducted in groundwater sampled at the Maqarin site in the framework of the natural analogue project (Wetton et al. 1998). The pH of the groundwater at the Maqarin site was determined to be 12.74, and high concentrations of calcium (16.8 mM), sodium (0.51 mM), chloride (1.48 mM) and sulphate (3.18 mM) were detected. The colloid concentration was found to range in value between 0.03 mg/L and 0.19 mg/L, depending on the sampling site and the method used for calculating the colloidal mass (Wetton et al. 1998). Thus, the colloid concentration from field measurements agrees very well with values determined under laboratory conditions (Wieland & Spieler 2001, Wieland 2001, Fujita et al. 2003), thus further supporting the idea that the low colloid concentration observed can be explained by the chemical conditions prevailing in cement-type pore waters.

It has been acknowledged that destabilisation of colloids under conditions of high ionic strength and/or Ca concentration in the millimolar range occurs (see reviews in Wieland 2001 and Filella 2007). Colloidal suspensions become destabilised when the net surface charge of particles is close to zero. Under these conditions, colloid-colloid interaction and colloid attachment to surfaces are facilitated. Colloid-colloid interaction generates aggregates that are sufficiently large to settle out of solution. Hence, the zero point of charge (ZPC) of particles, i.e., the pH at which the net total particle charge is zero, is an important surface parameter used to assess the destabilisation of colloidal suspensions. The surface charge of C-S-H-type particles was studied by Viallis-Terrisse et al. (2001), Pointeau et al. (2006b), and Labbez et al. (2007). A review of earlier studies on the surface charge of cementitious materials is given elsewhere (Wieland 2001). These earlier studies showed that Ca$^{2+}$ is the main potential-determining ion on the C-S-H surface in cementitious environments. The ZPC of C-S-H phases (molar C/S ratio = 0.66 and 1.5) is reached at the Ca concentration of ~2 mM (Viallis-Terrisse et al. 2001). The variation in zeta potential which is a measure of the surface charge was determined in the pH range between 11 and 13 (Viallis-Terrisse et al. 2001, Labbez et al. 2007). At the maximum Ca concentration, i.e. \([\text{Ca}] \sim 20 \text{ mM}\), the zeta potential of C-S-H phases was determined to be about +20 mV while a negative potential of about -20 mV was reported for the lowest Ca concentration, i.e. \([\text{Ca}] \sim 0.1 \text{ mM}\). Hence, the surface charge is positive at a Ca concentration above \(\sim 2 \text{ mM}\) while the charge is negative below \(\sim 2 \text{ mM}\). Note that the Ca concentration in pore water solutions in equilibrium with fresh, intact HCP ranges between \(\sim 1\) and \(\sim 2 \text{ mM}\) (pH > 13) while it was found to be dependent on pH in degraded systems, i.e. \(\sim 0.1 \text{ mM}\) at pH 11.5 and \(\sim 20 \text{ mM}\) at pH 12.5 (Pointeau et al. 2006b).

The presence of alkalis, e.g. Na, was found to reduce the zeta potential of C-S-H phases compared to an alkali-free system (Viallis-Terrisse et al. 2001). The concentration of alkalies (Na, K) in cement pore water amounts to \(\sim 0.3 \text{ M}\) (pH 13.3) in fresh HCP. In the first phase of the cement degradation alkalis are depleted and the pH of the pore water steadily drops from pH > 13 to pH 12.5. The surface charge of C-S-H particles was found to be very low in fresh HCP (Pointeau et al. 2006b). The latter authors also determined the zeta potential in degrading cementitious systems and observed that the zeta potential was at maximum (+ 20 mV) at pH = 12.5, corresponding to the pH established by portlandite solubility, while it was significantly lower in the pH ranges above and below pH 12.5. Thus, it appears that, in general, the surface potential or charge of cement particles is low (either slightly negative or positive) or zero over the entire pH range of cementitious systems (pH \(\sim 10.5 – 13.5\)). This finding implies that the concentration of dispersed colloid inventory should reach its maximum at pH \(\sim 12.5\) in cement-type pore water. Note that Wieland & Spieler (2001) and Fujita et al. (2003) determined colloid concentrations under exactly these conditions for cementitious systems. The lower surface charge observed above and below pH 12.5 facilitates colloid-colloid and colloid-surface interactions. Both processes are favourable to colloid removal via colloid aggregation and filtration, i.e. attachment to the surface of backfill material, respectively, under the conditions of a cementitious near field.
Cement phases are not stable under environmental conditions and undergo chemical degradation at decreasing pH (Berner 1988, Harris et al. 2002, Schweizer 1999). Non-stoichiometric dissolution of C-S-H-type gels with a C/S ratio >1 was observed in the pH range 10.5 – 12.5, indicating transformation of C-S-H phases with high C/S ratios into phases with lower C/S ratios (Berner 1988, Rahman et al. 1999, Harris et al. 2002). In contrast, dissolution was stoichiometric for C-S-H phases with C/S = 0.8 in the same pH range. C-S-H phases are chemically unstable in solution below about pH 10 and start dissolving (Schweizer 1999). This finding suggests that C-S-H-type colloidal matter is chemically not stable in groundwater of the host rock formation. Note that this is further true for other kinds of cementitious colloidal materials formed in the near field, in particular calcium-aluminate-type colloidal matter, while carbonate-type colloids are considered to be chemically stable in the cementitious near field and the host rock. Therefore, it is conceivable that complete dissolution of C-S-H-type near-field colloids occurs at the interface between the cementitious near field and the host rock due to the large pH gradient. Hence, it is anticipated that the dissolution of C-S-H type colloids frees up radionuclides at the interface between the cementitious near field and the host rock that are associated with the C-S-H-type colloidal matter by adsorption or incorporation.

4.3.3 Effect of colloids on radionuclide uptake

The influence of C-S-H-type colloids on radionuclide mobilisation in the cementitious near field of a L/ILW repository is discussed in detail elsewhere (Wieland et al. 2004). The impact of colloids on radionuclide mobilisation was found to be small due to the low concentration of colloids in the cementitious near field. The amount of radionuclides bound onto colloidal matter further depends on the distribution ratio (R_d), which is radionuclide-specific. For example, the uptake of Sr by C-S-H was found to be much weaker than that of trivalent lanthanides (e.g., Nd(III), Eu(III)) or tetravalent actinides (such as Th(IV)) (Tits et al. 2003a, Tits et al. 2006a). Furthermore, reversibility of the uptake process onto C-S-H phases is radionuclide-specific. For example, Sr binding to C-S-H was found to be a largely reversible process which could be modelled in terms of an ion exchange process on C-S-H phases (Tits et al. 2006a). In contrast, uptake of strongly sorbing radionuclides, such as Eu(III) and Nd(III), occurs via Ca replacement in the structure of C-S-H phases thus implying irreversible bonding of trivalent lanthanides (and trivalent actinides by analogy) (Tits et al. 2003a, Mandaliev et al. 2009, Mandaliev et al. 2010a,b).

It is expected that cement-type colloidal matter only plays a minor role in radionuclide migration from the near field into the far field for two reasons: Firstly, the concentration of colloids is very low in the cementitious near field and therefore radionuclide mobilisation in the near field by cementitious colloids is weak. Secondly, cement-type colloidal matter dissolves at the interface between the near-field or the far field altered by the highly alkaline pH plume and the far field, thus releasing radionuclides associated with cement-type colloids. Note, however, that calcium-carbonate-type colloidal matter may be chemically stable both under near field and groundwater conditions. This type of colloids could facilitate radionuclide migration across interface between the near field and the host rock. Nevertheless, their impact on radionuclide migration is expected to be limited because radionuclide uptake by calcium carbonate is weaker than uptake by C-S-H-type solid materials for most radionuclides (Curti 1999, Bradbury et al. 2010).
The reduction of radionuclide uptake by HCP in presence of dispersed colloids can be expressed in terms of a sorption reduction factor (Wieland 2001, Wieland & Van Loon 2002). The distribution ratio \( R_{d,\text{eff}} \) in presence of colloids is given by:

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

\( R_d \) denotes the distribution ratio of the radionuclide onto HCP (immobile material) in the absence of colloids (m\(^3\)/kg). \( R_c \) is the distribution ratio of the metal between the colloidal phase and solution (m\(^3\)/kg), and \( m_c \) is the concentration of colloids in the fluid (kg/m\(^3\)). The effect of colloids on radionuclide uptake is expressed in terms of a sorption reduction factor, \( F_{\text{red}} \) (\( F_{\text{red}} = R_d/R_{d,\text{eff}} \)), by analogy with the impact of complexing ligands on radionuclide uptake. The sorption reduction factors listed in Tab. 6.3 are accepted as derived earlier by Wieland & Van Loon (2002).

### 4.4 Radionuclide retention under saline near-field conditions

#### 4.4.1 Saline groundwater of host rock

The planned Swiss L/ILW repository could be located in a geological formation with elevated chloride concentrations of the groundwater. The Cl\(^-\) concentration of cement pore water is generally low (range typically \( \leq 10^{-3} \) M) due to the limited inventory of stable chloride in commercial cements (maximum 0.01 wt.-\%). The Cl\(^-\) concentration of pore water from the Effingen Member, which is a potential host rock, was determined to be 565.9 mmol/kg H\(_2\)O (Tab. 4.2). Therefore, the Cl\(^-\) concentration in the pore water of the cementitious near field could be significantly enhanced after ingress of saline groundwater from the Effingen Member. This calls for more detailed considerations on the mineralogy of hydrated cement at elevated Cl\(^-\) concentration in order to assess potential impacts on the retention of radionuclides under these conditions.

Groundwater from Effingen Member and seawater have similar chemical compositions (Tab. 4.2). Therefore, a preliminary assessment of the influence of saline groundwater on the mineralogy of HCP can be made on the basis of existing knowledge on the long-term durability of cementitious materials in the submerged zone of seawater.

Permeability of concrete seems to be the most important factor determining the long-term durability of cement paste (Mehta 1991). Durability of concrete is seen as the ability of concrete to resist weathering action, chemical attack, and abrasion while maintaining its desired engineering properties (Glasser et al. 2008). For instance, microcracking and expansion due to physical effect of pressure from salt crystallization will increase the permeability and allow deleterious chemical interactions between seawater and the hydrate assemblage of HCP. Modern marine structures are built with concrete mixtures that are relatively impermeable and therefore less vulnerable to chemical attack. In contrast, older structures built with relatively permeable concrete were found to be susceptible to various types of chemical attack in seawater, e.g. interaction with \( \text{SO}_4^{2-} \) and Cl\(^-\). Hence, low permeability concretes are used for marine constructions with the aim of minimizing steel corrosion promoted by chloride and sulphate attack.

The corrosion of concrete by seawater is the result of the simultaneous action of the major ions Na\(^+\), Mg\(^{2+}\), \( \text{SO}_4^{2-} \) and Cl\(^-\). Brucite (\( \text{Mg(OH)}_2 \)) and aragonite (\( \text{CaCO}_3 \)) were found to be the initial products formed by the action of Mg\(^{2+}\) and dissolved carbonate in seawater (Mehta & Haynes
The layers of brucite overlain by aragonite may form a surface skin which significantly reduces permeability of concrete. The latter process protects concrete from further alteration by seawater and advocates the long-term durability of HCP in contact with seawater (Mehta 1991, Al-Amoudi 2002). Monitoring of the long-term durability of concrete in marine environments and the resulting knowledge from field practice, however, is based on observations made over a very short period of time compared to the time scale involved in connection with assessments of the long-term safe disposal of radioactive waste in cement-based environments. Hence, more detailed considerations are needed with the aim of assessing durability of concrete in a repository environment over geological times scales, in particular with a view to possible phase transformations in cement paste over longer periods of time, and possible effect on the immobilization of radionuclides.

Tab. 4.2: Major composition and geochemical parameters of cement pore water (Berner 2009), Effingen groundwater (Mäder 2009, Table 7-8) and seawater (DOE 1994, Stumm & Morgan 1981).

<table>
<thead>
<tr>
<th>Elements/species</th>
<th>Cement pore water [mmol/kg H$_2$O]</th>
<th>Effingen Member [mmol/kg H$_2$O]</th>
<th>Seawater (35 ‰ salinity) [mmol/kg seawater]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>5 – 114</td>
<td>374.1</td>
<td>469.07</td>
</tr>
<tr>
<td>K</td>
<td>1 – 180</td>
<td>1.99</td>
<td>10.21</td>
</tr>
<tr>
<td>Ca</td>
<td>2.5 – 22</td>
<td>60.51</td>
<td>10.28</td>
</tr>
<tr>
<td>Mg</td>
<td>$10^{-4}$ – $10^{-3}$</td>
<td>45.30</td>
<td>53.08</td>
</tr>
<tr>
<td>Sr</td>
<td>0.1 – 1</td>
<td>0.812</td>
<td>0.090</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1 – 2</td>
<td>565.9</td>
<td>545.9</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>1 – 10</td>
<td>11.5</td>
<td>28.2</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>0.1</td>
<td>0.428</td>
<td>2.06</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td>54556</td>
<td>53600</td>
</tr>
<tr>
<td>Other parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>12.5 – 13.3</td>
<td>7.305</td>
<td>7.5 – 8.4</td>
</tr>
<tr>
<td>Ionic strength (molal)</td>
<td>0.07 – 0.294</td>
<td>0.677</td>
<td></td>
</tr>
</tbody>
</table>

4.4.2 Influence on the cement matrix

Elevated concentrations of Na$^+$, Mg$^{2+}$, SO$_4^{2-}$ and Cl$^-$ in the inflowing saline groundwater are expected to have an influence on the mineral composition of cementitious materials in a way similar to actions observed in contact with seawater. Thermodynamic scoping calculations showed that increasing amounts of Mg added to a cementitious system causes the formation of brucite (Mg(OH)$_2$) and small amounts of hydrotalcite (Wieland & Berner 2011). In addition, seawater is considered to promote the degradation of the C-S-H phases and by ultimate conversion to magnesium silicate hydrates (M-S-H phases) (Skalny et al. 2002). Note that poorly crystalline M-S-H phases exhibit structural properties similar to those of C-S-H phases (Skalny et al. 2002). At present, however, conversion of C-S-H to M-S-H phases cannot be taken into account in thermodynamic modelling for lack of thermodynamic data. Nevertheless,
it is expected that conversion of C-S-H to M-S-H phases might occur in contact with Mg-rich saline groundwater from the Effingen Member to a limited extent only due to preferential formation of the thermodynamically stable Mg(OH)$_2$ under hyper alkaline conditions.

The amount of C-S-H phases to be converted to M-S-H phases can be estimated on the basis of mass balance considerations. To this aim, the mass of HCP per m$^3$ cavern is assumed to be 350 kg/m$^3$ while the porosity is 20% (Schwyn et al. 2003). The portion of C-S-H phases (MW: 194 g/mol) in HCP corresponds to ~ 45 wt.% (= 812 moles per m$^3$ cavern), which corresponds to ~ 1420 moles Ca in C-S-H phases (C-S-H: CaO$_{1.75}$SiO$_2$.2H$_2$O). It is further estimated that each replacement of saline groundwater per m$^3$ cavern (= 200 L) yields ~ 9 moles Mg. Complete conversion of C-S-H to M-S-H phases would last over ~ 160 water exchange cycles on the assumption that the total amount of Mg is available for C-S-H conversion, thus ignoring the formation of Mg(OH)$_2$, and assuming a stoichiometric (1:1) substitution of Ca by Mg in C-S-H phases. Note that one water exchange cycle is expected to last several thousand years in a diffusion-controlled repository system (Schwyn et al. 2003).

Conversion reactions further alter the mineral composition of cement-based material exposed to SO$_4^{2-}$ containing groundwater (Skalny et al. 2002, Glasser et al. 2008). Sulphate ions react with ionic species of the cement pore solution to precipitate ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O) and, at high SO$_4^{2-}$ concentrations, gypsum (CaSO$_4$·2H$_2$O). Furthermore, the formation of thaumasite (CaSiO$_4$·CaCO$_3$·CaSO$_4$·15H$_2$O) was observed in cementitious materials containing significant amounts of calcium carbonate, sources of calcium silicate and excess sulphate and humidity (Schmidt et al. 2008, Lothenbach et al. 2010). Note that thaumasite contains no aluminium. Precipitation of thaumasite is expected to occur preferentially at the interface between the cementitious near field and the host rock dominated by high concentrations of SO$_4^{2-}$ and CO$_3^{2-}$. In the main body of the cementitious near field, however, the CO$_3^{2-}$ inventory associated with hydrated cement is limited (~ 1 wt.% of hydrated cement), which further limits thaumasite formation. Therefore, excess sulphate is expected to predominately precipitate as ettringite at the given SO$_4^{2-}$ concentrations of saline groundwater from the Effingen Member (Tab. 4.2) as gypsum was found to precipitate only at very high SO$_4^{2-}$ concentrations (Glasser et al. 2008, Lothenbach et al. 2010). Formation of ettringite requires an additional Al source, which is AFm present in the paste. As a consequence, ingress of SO$_4^{2-}$ rich groundwater from the Effingen Member might gradually convert AFm phases to ettringite.

The background chloride concentration in cement pore water is a few millimolar at the maximum due to the limited concentration of stable chloride in commercial cements (limits impact on steel corrosion) (Wang et al. 2009 and references therein). Chloride interacts with C-S-H phases of hydrated cement, and further reacts with the aluminate phases of the paste to form Friedel's salt (3CaO·Al$_2$O$_3$·CaCl$_2$·10H$_2$O (Nielsen et al. 2005, Balonis et al. 2010). Nielsen et al. (2005) suggested that the solid-liquid distribution of chloride occurs between the pore solution, C-S-H phases and an AFm solid solution phase consisting of Friedel's salt (AFm-Cl$_2$) and calcium monocarboaluminate (AFm-CO$_2$). Birnin-Yauri & Glasser (1998) showed that aqueous chloride concentrations above 2 mM are required to convert hydroxy AFm (AFm-OH$_2$) to Friedel's salt. The latter phase is considered to be a selective binder of chloride in the paste (Taylor 1997) and proved stable over a wide range of chloride concentrations from > 2 mM to over 3 M (Birnin-Yauri & Glasser 1998, Balonis et al. 2010). Formation of calcium oxychlorides, which could act as an additional "sink" for chloride, was observed to occur in the concentration range > 3 M (Glasser et al. 2008).

The AFm phases present in hydrated cements are important storage minerals for water molecules and anions such as OH$^-$, Cl$^-$, CO$_3^{2-}$, SO$_4^{2-}$, and Si(OH)$_4$O$^-$ (Glasser & Kindness 1999). These phases are further responsible for the immobilization of safety-relevant anions, such
SeO$_4^{2-}$ and I$^-$ (Baur & Johnson 2003, Aimoz et al. 2012a). Chloride was found to readily displace OH$^-$, SO$_4^{2-}$, and CO$_3^{2-}$ anions in the AFm phases (Birni n-Yauri & Glasser 1998, Glasser & Kindness 1999, Balonis et al. 2010). In CO$_3^{2-}$-containing cements, such as the HTS cement used for the solidification of radioactive waste in Switzerland, chloride binding by AFm phases occurs predominantly due to the formation of a solid solution between calcium mono-carboaluminate and Friedel’s salt (Nielsen et al. 2005, Balonis et al. 2010). The only miscibility gap was observed at low Cl$^-$ concentrations (Baloni et al. 2010). Detailed structural studies further showed the formation of two polymorph of the solid solution series at ambient temperature: a rhombohedral structure over the entire domain of the solid solution and a metastable monoclinic structure at higher Cl$^-$ contents (Mesbah et al. 2011).

Several authors noted that the tricalcium aluminate (C$_3$A) content of cement could play a key role in Cl$^-$ uptake by cementitious materials (Mehta 1991, Rasheeduzzafar et al. 1992, Hussain et al. 1995, Yuan et al. 2009). Increasing C$_3$A content was found to increase the Cl$^-$ binding capacity of cement (Suryavanshi et al. 1995, Yuan et al. 2009) whereas evidence was provided that C$_4$AF could be involved in chloride binding by hydrated cement (Glasser et al. 2008 and references therein). Hence, increasing C$_3$A contents (and presumably C$_4$AF) give rise to increasing amounts of calcium aluminate phases formed in hydrated cement, which might increase the capacity for chloride binding. Note that the C$_3$A content of sulphate resistant Portland cements (SRPC), such as HTS cement, is typically lower than in OPC while the C$_4$AF content is higher in SRPC. The Cl$^-$ binding capacity was found to be moderate in SRPC and at any rate lower than in OPC (Suryavanshi et al. 1995). This indicates that the Cl$^-$ binding of cement pastes caused by AFm is limited due the limited amount of AFm-type phases formed, particularly in SRPC.

The uptake of Cl$^-$ by C-S-H phases is considered to take place by chemisorption (Beaudoin et al. 1990, Viallis et al. 1999, Hill et al. 2006, Sugiyama 2008). At C/S ratios above 1.2 the C-S-H surface is positively charged (Viallis-Terrisse et al. 2001, Jönsson et al. 2004, Pointeau et al. 2006b). This suggests that Cl$^-$ binding prevails on C-S-H phases with high C/S ratio whereas Cl$^-$ uptake by C-S-H with low C/S ratio, and therefore negatively charged surfaces, is expected to be limited. In-house sorption studies with $^{36}$Cl on C-S-H phases showed Cl$^-$ uptake by a C-S-H phase with C/S = 1.65 while no uptake at all was observed by a C-S-H phase with C/S = 0.7 (Tab. 4.1). Although the maximum proportion of Cl$^-$ bound per unit mass of solid material is lower for C-S-H than for Friedel’s salt, the binding potential of C-S-H phases with a high C/S ratio should not be ignored as it is the most abundant constituent (~ 50 wt.-%) of fresh cement paste. In contrast, uptake of Cl$^-$ by C-S-H phases with low C/S ratio is expected to be negligibly small.

C-S-H phases seem to be chemically stable up to the reported NaCl concentration of 1 M as no evidence for congruent C-S-H dissolution indicated by an enhanced Si release to solution over time was observed (Hill et al. 2006). However, changes in the chemical composition of C-S-H phases were reported due to an increase in the Ca concentration in solution with increasing NaCl concentration. A Ca-Na ion exchange process was invoked to explain this finding (Hill et al. 2006, Sugiyama 2008). Alkali metal ions in solution are considered to replace Ca ions in the C-S-H gel with low C/S ratios giving rise to an increase in the Ca concentration in saline waters. In contrast, at the higher C/S ratios where both calcium hydroxide and C-S-H gels are present, ionic strength dependence of calcium hydroxide solubility is considered to control the Ca concentration in solution. To summarize, NaCl solutions may interact with C-S-H phases in two ways: 1) Non-specific chemisorption of Cl$^-$ onto C-S-H, and 2) Na uptake by C-S-H phases with a low C/S ratio via a Ca-Na ion exchange process.
The present survey of literature shows that saline groundwater inflowing from the Effingen Member will interact with hydrated cement, thus giving rise to possible changes in the mineral composition of the cement paste over time. Nevertheless, the resulting sequence of mineral alteration and the mineral composition of hydrated cement are significantly different from those expected during the course of the degradation stages in contact with non-saline groundwater. The impact of elevated Mg$^{2+}$ and SO$_4^{2-}$ concentrations of the saline groundwater will be limited because 1) Mg$^{2+}$ may predominately precipitate as Mg(OH)$_2$ under the hyper alkaline conditions of a cementitious near field while partial conversion of C-S-H phases to M-S-H phases is acknowledged, and 2) the slightly elevated SO$_4^{2-}$ concentration may cause small amounts of secondary ettringite to precipitate due to the limited Al inventory that is available for ettringite formation in hydrated cement. Hence, the main effect on the mineral composition of HCP is attributed to the high NaCl concentrations in saline groundwater from the Effingen Member.

The high Cl$^-$ concentration is expected to cause the conversion of AFm phases, primarily calcium monocarboaluminate present in calcium-containing cements to Friedel's salt. In addition, a small portion of Cl$^-$ may be bound onto C-S-H phases with high C/S ratios while Cl$^-$ has no influence on the C-S-H structure. Furthermore, the chemical composition of C-S-H phases with low C/S ratios may change due to replacement of Ca$^{2+}$ by Na$^+$ in the C-S-H structure. Nevertheless, it is believed that the exchange process only influences the Ca/Na ratio of the C-S-H phase while the chemical stability of the C-S-H phases is not affected even under highly saline conditions.

In summary, AFm phases may be depleted from hydrated cement over time in contact with NaCl rich saline groundwater from the Effingen Member while C-S-H phases are expected to be chemically stable. Partial exchange of Ca$^{2+}$ by Na$^+$ in the structure of C-S-H phases might take place, which, however, is not expected to significantly change the sorption capacity of C-S-H for metal cations. Furthermore, partial conversion of C-S-H phases to M-S-H phases by the action of Mg$^{2+}$ might only occur in the long run due to the large amount of C-S-H phases in cement paste compared to Mg which is supplied by the ingress of saline groundwater. The formation of small quantities of secondary ettringite is expected as the SO$_4^{2-}$ concentration in saline pore water of the Effingen Member is slightly enhanced compared to that in cement pore water.

The binding capacity of HCP for Cl$^-$ is determined on the one hand by the amount AFm phases that can be converted to Friedel's salt, and on the other hand by the amount C-S-H phases, which can sorb Cl$^-$ on the surface. The Cl$^-$ binding capacity attributable to the conversion of AFm phases into Friedel's salt is limited by the rather small amount of AFm phases in HCP. Cl$^-$ binding to C-S-H phases is considered to be very low on the assumption that C-S-H phases with low C/S ratios will prevail as a consequence of Ca-Na replacement under saline conditions. Hence, the large portion of Cl$^-$ is expected to remain dissolved in the pore solution. This suggests that Cl$^-$ could act as complexing ligand for metal cations which, in principle, could have an influence on radionuclide retention by HCP in highly saline pore water. Furthermore, Cl$^-$ acts as competitive ion for the other anions. The impact of elevated Cl$^-$ concentration on radionuclide uptake by HCP is discussed in the following section.

### 4.4.3 Influence on radionuclide uptake

The appraisal of sorption values for safety-relevant radionuclides under saline conditions has been made on the following assumptions:

- Precipitation of small amounts of secondary ettringite has no effect on the sorption properties of cement paste
- Na-Ca ion exchange process may reduce the C/S ratio of C-S-H phases
• C-S-H phases with low C/S ratios are the main constituent of cement paste exposed to saline groundwater from the Effingen Member

• Partial replacement of Ca by Mg in C-S-H phases may occur which gives rise to the formation of M-S-H phases

• Complete conversion of AFm phases (e.g. calcium monocarboaluminate, calcium monosulphoaluminate) to Friedel's salt may take place over time

• The largest portion of Cl\(^-\) taken up by cement paste will be associated with Friedel's salt

• Cl\(^-\) dissolved in the pore water of the cementitious near field may form chloro complexes with metal cations and acts as competing ion thus reducing the uptake of the other anions by HCP

The effect of high salinity groundwater on radionuclide retention can be assessed in view of the above considerations. No separate sorption values are assigned to the different stages of the cement degradation. Sorption reduction caused by the presence of highly saline groundwater was imposed on the lowest sorption value assigned to unperturbed HCP in either stage I or II of the cement degradation (Tab. 6.1). Sorption values for HCP under saline conditions are listed in Tab. 6.4.

**Formation of metal chloro complexes**

Thermodynamic modelling was carried out to determine the species distribution of metal cations at elevated Cl\(^-\) concentrations ([Cl\(^-\)] = 0.11 M and 1.3 M) at pH = 11.07 (Thoenen 2012). It was observed that the formation of aqueous chloro complexes changes the speciation of only very few radionuclides at pH = 11.07. For example, the speciation of Ag is dominated by AgCl, AgCl\(_2\), AgCl\(_3\)\(^-\), and AgCl\(_4\)\(^3-\) complexes. For other metal cations, such as Zr, Sn, Pb and in particular all the actinides, hydroxo complexes are thermodynamically more stable than chloro complexes and therefore determine the species distribution even at the highest Cl\(^-\) concentration. As a consequence of the above, a sorption value of zero is retained for Ag on hydrated cement under saline conditions. For the other radionuclides, however, the effect of elevated Cl\(^-\) concentration on the uptake by cement paste is considered to be negligibly small in the pH range > 11.

**Trivalent and tetravalent actinides**

Substantial evidence was presented that the C-S-H phase is the cement phase controlling the uptake of actinides by HCP. Uptake of actinides by cement paste altered due to the ingress of saline groundwater is expected to be high although the C/S ratio might be reduced (Na-Ca exchange) and the amount of C-S-H phases might be slightly reduced due to enhanced ingress of Mg\(^{2+}\) thus partially converting C-S-H phases into M-S-H phases or magnesium silicates. Note, however, that strong interaction is also anticipated with M-S-H phases as it was observed that actinides generally sorb strongly onto oxide-type minerals under highly alkaline conditions. Therefore, the sorption values of actinides are, in principle, expected to be similar in value for both cement paste altered by non-saline or saline groundwater (i.e. \(R_d \geq 100 \text{ m}^3/\text{kg}\)). It is assumed that C-S-H phases are the only sorbing cement mineral in the altered cement paste while its amount could be reduced due to conversion to M-S-H phases over time. Hence, a cautious approach is taken in the current appraisal of actinide uptake by HCP under saline conditions by assuming that the sorption values for actinides on cement paste which is altered upon interaction with saline groundwater (Tab. 6.4) are a factor 10 lower compared to the earlier selected values for cement paste degraded by non-saline groundwater (Tab. 6.1).
The above reduction in radionuclide uptake is further adopted for the other strongly sorbing metal cations that are expected to be predominantly taken up by the C-S-H phases in cement paste, such as Zr(IV), Nb(V), Sn(IV), Tc(IV), and Pb(II) (Tab. 6.4).

**Alkaline and earth-alkaline metal cations**

The alkali (Na, K) concentration of cement-type pore water in the near field determines the extent of Cs⁺ interaction with HCP (see Section 4.1.15). Furthermore, both competition with alkalis and Ca²⁺ is considered to control Sr²⁺ and Ra²⁺ uptake by cement paste. The Na concentration of the near-field pore water is expected to increase due to ingress of saline groundwater compared to that of a stage I pore water (Tab. 4.2). Hence, the concentration of alkalis and Ca may be enhanced in cementitious materials altered by saline groundwater. As a consequence, the sorption value for Cs⁺ under saline conditions is reduced by a factor of 2 (Tab. 6.4) compared to that selected for radionuclide uptake in stage I of the cement degradation (Tab. 6.1) as the Na concentration is a factor of two higher in saline groundwater than in stage I pore water. Similarly, uptake of Sr²⁺ and Ra²⁺ by cement paste is expected to be lower under saline conditions than in stage II of the cement degradation due to the high Na and Ca concentrations of the Effingen Member groundwater. For this reason, a proportional reduction (Factor of 6) is recommended for Sr²⁺ and Ra²⁺ uptake by cement paste under saline conditions (Tab. 6.4).

**Anions**

The safety-relevant species showing anionic sorption behaviour are Cl⁻, I⁻, MoO₄²⁻ (Mo(VI)), SeO₃²⁻ (Se(IV)), SeO₄²⁻ (Se(VI)), and TcO₄⁻ (Tc(VII)).

Cl⁻ is bound in the cement matrix by forming a solid solution between calcium monocarboaluminate and Friedel's salt and by chemisorption onto C-S-H phase with high C/S ratios (see Section 4.4.2). In contrast, in-house studies showed that I⁻ is predominantly taken up by AFm phases by forming a solid solution with calcium monosulphoaluminate (Aimoz et al. 2012b). The latter study further suggests that solid solution formation with calcium hemicarboaluminate could be an alternative uptake process. Se(IV) is sorbed by calcium monosulphoaluminate, ettringite and the C-S-H phase while Se(VI) is preferentially taken up by ettringite (Ochs et al. 2002, Baur & Johnson 2003, Zhang & Reardon 2005). Sorption studies with Mo(VI) resulted in only scarce information on the uptake-controlling cement phases in the cement paste. Solid solution formation with ettringite is believed to be the uptake-controlling mechanism for Mo(VI) (Zhang & Reardon 2003). Experimental information on the uptake-controlling mechanism for Tc(VII) on cement paste is currently lacking.

Sorption values of the above anions are estimated on the basis of our current understanding of the uptake mechanisms in combination with mass balance considerations. In the case of Cl⁻ complete conversion of AFm phases in the cement paste (~ 8 wt.-% in HTS cement, Lothenbach & Wieland 2006) to Friedel's salt is expected at a Cl⁻ concentration of 0.566 mol/kgH₂O (Tab. 4.2). Uptake of Cl⁻ by C-S-H with a low C/S ratio is ignored in this study.

The amount of Cl⁻ bound by Friedel's salt is estimated at 0.274 mol Cl⁻ per kg cement paste using the proportions of Cl⁻ bound as reported in Balonis et al. (2010) (Friedel's salt: 12.33 wt.-% Cl⁻ per mass of solid phase). The distribution ratio of ³⁶Cl can be estimated on the assumption that isotopic exchange between ³⁶Cl and stable Cl⁻ occurs. The latter process implies that the partitioning of ³⁶Cl between the cement paste and pore water corresponds to that of stable Cl⁻ and further that all the stable Cl⁻ ions bound in Friedel's salt are accessible to isotopic
exchange. The distribution ratio of stable Cl\(^-\) is given by the ratio of bound Cl\(^-\) (0.274 mol Cl\(^-\) per kg cement paste) and the concentration of Cl\(^-\) in saline groundwater (0.576 mol Cl\(^-\) per L solution). Thus, the resulting \(R_d\) value amounts to \(4.8 \times 10^{-4}\) m\(^3\)/kg, which is about an order of magnitude less than the value recommended for both stages of the cement degradation under non-saline conditions (Tab. 6.4).

Uptake of \(\Gamma\) by AFm phases, i.e. calcium monosulphoaluminate and calcium hemicarbo-aluminate, is considered to be the controlling mechanism in cement paste. In contact with groundwater from the Effingen Member, complete conversion of the AFm phases to Friedel's salt is anticipated in cement paste. Zero sorption is assigned to \(\Gamma\) uptake by hydrated cement under saline conditions (\(R_d = 0\)) because no significant \(\Gamma\) uptake was observed by Friedel's salt and by a C-S-H phase with C/S ratio = 0.75 at elevated Cl\(^-\) concentration due to strong Cl\(^-\) – I\(^-\) competition (Tab. 6.4).

Several studies have suggested an uptake of SeO\(_3^{2-}\) and SeO\(_4^{2-}\) by ettringite and AFm phases (Hassett et al. 1990, Gougar et al. 1996, Ochs et al. 2002, Baur & Johnson 2003, Zhang & Reardon 2005, Cornelis et al. 2006). Selenite (Se(IV)) was suggested to be bonded onto ettringite, calcium monosulphoaluminate and C-S-H phases by surface adsorption (Baur & Johnson 2003). In-house sorption studies using \(^{75}\)Se(IV) radiotracer further revealed moderate uptake by AFm phases and C-S-H phases while uptake by ettringite was found to be low (Tab. 4.1). Interestingly, high Se(IV) uptake was also observed by Friedel's salt. Selenate (Se(VI)) which is the dominant species under oxidizing conditions was found to sorb only weakly to ettringite (Baur & Johnson 2003) while other studies considered direct substitution into the structure of ettringite due to partial or full replacement of SO\(_4^{2-}\) as the dominant mechanism for SeO\(_4^{2-}\) uptake (Hassett et al. 1990, Ochs et al. 2002, Zhang & Reardon 2005). Further appraisal of SeO\(_3^{2-}\) and SeO\(_4^{2-}\) retention by cement paste under saline conditions was made on the following assumptions: 1) Ettringite persist under the given conditions while calcium monosulpho-aluminate converts to Friedel's salt, and 2) both Se species may sorb onto ettringite while uptake by C-S-H phases with low C/S ratio is conceivable solely for Se(IV). A nominal distribution ratio (\(R_d = 10^{-4}\) m\(^3\)/kg) is assigned to both species, thus taking into consideration that the main sorbing cement phases (ettringite, C-S-H phases) might persist even under saline conditions. However, a cautious approach is taken by assuming only weak uptake. Therefore, uptake of Se(IV,VI) by cement paste is expected to be less under saline conditions than non-saline conditions due to elevated Cl\(^-\) concentration (Tab. 6.4).

Several studies have suggested strong interaction of MoO\(_4^{2-}\) with ettringite (Zhang & Reardon 2005, Cornelis et al. 2008). Note that zero sorption was considered in the case of Mo(VI) for all stages of the cement degradation for lack of well-supported sorption measurements (Tab. 6.1). Zero sorption is retained under saline conditions.

Pertechnetate (TcO\(_4^{-}\)) is the dominant species of Tc under oxidizing conditions. This species was found to sorb weakly onto cement paste whereas the controlling mechanism has not yet been unravelled. It is conceivable that ettringite or AFm phases are the cement minerals responsible for Tc(VII) binding in cement paste, thus suggesting an uptake mechanism similar to that proposed for the other oxyanions. Nevertheless, conclusive information is still lacking, which justifies \(R_d = 0\) (Tab. 6.4).
4.5 Radionuclide retention in SMA-1/LMA-1 waste compartments

Nagra’s disposal concept developed for L/ILW and ILW foresees to divide the waste sorts into two groups: SMA-1/LMA-1 and SMA-2/LMA-2 waste (Nagra 2008a). The main property of SMA-1/LMA-1 waste is that no detrimental effects on radionuclide retention in the cementitious near field occur. In particular this implies that (Kosakowski et al. 2014):

- Complexing ligands will be present in the pore water of the cementitious near field at concentration levels that do not enhance radionuclide mobility.
- Inventories of organic materials will not exceed levels, which could have a detrimental effect on radionuclide retention caused by carbonation of the cement paste as a consequence of the degradation of these organic materials (CO₂ production).
- Inventories of reactive metals, such as Fe and Al, will not exceed levels, which could significantly change the mineral composition of the cement paste due to the reaction of corrosion products with cement minerals.

Changes in the mineral composition of the cement paste occur mainly due to ingress of groundwater (saline, non-saline) from the host rock, thus causing the degradation of hydrated cement with time, or possibly due to interactions between cement and aggregates (internal degradation) (Kosakowski et al. 2014). The former process is adequately considered by assigning three stages of the cement degradation. For performance assessment, radionuclide retention in the SMA-1/LMA-1 compartments of the cementitious near field can be estimated using:

- Sorption values for the respective stage of the cement degradation under non-saline conditions (Tab. 6.1) or sorption values selected for saline conditions (Tab. 6.4).
- Potential sorption reduction caused by cementitious colloids present in the near field (Tab. 6.3).

4.6 Radionuclide retention in SMA-2/LMA-2 waste compartments

Contrary to SMA-1/LMA-1 waste the main property of SMA-2/LMA-2 waste is that detrimental effects on radionuclide retention could occur. These effects are mainly caused by the large inventory of complexing ligands in some SMA-2/LMA-2 waste forms, which requires potential impact of these ligands on radionuclide uptake by hydrated cement to be considered in terms of sorption reduction factors.

Additional detrimental effects could be caused by the presence of large inventories of organic or metallic materials (aluminium, steel). Carbonation of cement paste during the course of the degradation of organic materials and the anoxic corrosion of aluminium and steel could give rise to changes in the mineral composition of hydrated cement that could affect radionuclide retention in the cementitious near field.

4.6.1 Sorption reduction by complexing ligands

Ethylenediaminetetraacetic acid (EDTA), cyanide (CN⁻), ammonia (NH₃), gluconic acid (GLU) and isosaccharinic acid (ISA) are considered to be the most important complexing ligands of radionuclides in a cement-based repository (Schwyn et al. 2003). Nitrates/nitrites are oxidizing agents, which might have an influence on the redox potential. The maximum concentrations of the complexing ligands in the near field were estimated on the basis of the MIRAM-08 inventories (Nagra 2008b) and listed in Tab. 4.3 for the L/ILW and ILW repositories. The
maximum concentrations estimated on the basis of the MIRAM-12\textsuperscript{7} inventories were found to be comparable to those estimated with MIRAM-08 for most ligands. Comments have been added in those cases where MIRAM-08 and MIRAM-12 data deviated. In addition to the above components of the waste matrix, degradation products of polymeric organic materials (rubber, plastics etc.) and bitumen as well as concrete admixtures and degradation product of acidic ion-exchange resins could be potentially complexing ligands of radionuclides.

Tab. 4.3: Maximum concentration of complexing ligands in near-field pore water.

<table>
<thead>
<tr>
<th>Material</th>
<th>L/ILW maximum concentration [mol/L]</th>
<th>ILW maximum concentration [mol/L]</th>
<th>Concentration limit * [mol/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA</td>
<td>0.027</td>
<td>n.a.</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Cyanide</td>
<td>0.13</td>
<td>0.42</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>Ammonia**</td>
<td>0.67</td>
<td>0.042</td>
<td>0.1</td>
</tr>
<tr>
<td>Gluconic acid</td>
<td>$4.9 \times 10^{-6}$</td>
<td>$7.5 \times 10^{-6}$</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>Isosaccharinic acid</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$10^{-4}$</td>
</tr>
</tbody>
</table>

* Concentration limits used to differentiate between SMA-1/LMA-1 and SMA-2/LMA-2 waste groups as reported by Kosakowksi et al. (2014) and Schwyn (2008), except for gluconic acid and for ammonia which was selected based on the study of Van Loon & Hummel (1999b) and thermodynamic calculations reported by Thoenen (2013) ($0.1$ M for all radionuclides except $10^{-4}$ M for Ag).

** Complexation by ammonia is only relevant in stage III of the cement degradation.

n.a. = not applicable

The sorption reduction factors recommended for PA are listed in Tab. 6.5. The contribution of each complexing agent is discussed in the following sections.

4.6.1.1 Nitrate/Nitrite

In contrast to MIRAM-08 (Nagra 2008b), the currently assumed inventory (MIRAM-12) does not contain nitrate/nitrite in significant amounts because the form of some reprocessing waste from France has changed. Thus, the effect of these compounds on metal complexation has not been assessed in this study in contrast to the previous SDB (Wieland & Van Loon 2002).

4.6.1.2 EDTA

The maximum EDTA concentration in the near-field pore water was estimated to be 0.027 M for some L/ILW waste sorts (MIRAM-12), which is above the recommended limit of $10^{-3}$ M. Hummel (1993) showed that under alkaline conditions EDTA has an effect on the speciation of only very few cations, in particular Ni and Pb. Bradbury & Van Loon (1997) assigned a sorption reduction factor of 5 to Pb which is retained in this study. For Ni it is expected that the solubility limit may be enhanced in presence of EDTA. According to Hummel (1993) an

\textsuperscript{7} At the time this report went into press, MIRAM-14 was released. Based on a preliminary assessment, it is expected that the differences between MIRAM-12 and MIRAM-14 do not have an impact on the discussion in this report.
influence on actinide complexation (e.g. U, Np, Pu) is only expected if [EDTA] > [Ca], under near neutral pH conditions. It is unlikely that such conditions prevail in cementitious environments.

### 4.6.1.3 Cyanide

CN⁻ is present in the waste as Prussian Blue (Fe⁴⁺₄[Fe⁶⁺(CN)₆]₃) which is used as caesium ion exchanger in decontamination processes for liquid waste. Prussian Blue readily dissolves in alkaline solution (Hummel 2001, Schwyn et al. 2003). Free cyanide is released if hexa-cyanoferrate (Fe(CN)₆⁴⁻) further decomposes. However, the compound is expected to be stable in the dark even under alkaline conditions (pH > 8) which limits the concentration of free cyanide. High CN⁻ concentrations may only result for very few waste forms on the assumption that hexacyanoferrate decomposes and further that biotic or abiotic decomposition of free cyanide can be excluded. At the given maximum concentration CN⁻ has an effect on the speciation of only a very limited number of radionuclides, i.e. Ni, Co and Ag (Hummel 2004). For Ni and Co it is expected that the solubility limit may slightly be enhanced in the presence of free CN⁻. In the case of Ag, however, any influence of CN⁻ on radionuclide uptake can be ignored as zero sorption is assumed.

### 4.6.1.4 Ammonia and amines

Spent ion exchange resins are considered to be the main source of NH₃ and amines (methylamine, dimethylamine and trimethylamine). Radiolytic degradation is an important process, which generates ammonia, amines, other nitrogen-containing ligands along with low-molecular weight carboxylic acids (Van Loon & Hummel 1995). Complexation with carboxylic acids under the alkaline conditions of a cementitious near field can be ignored (Hummel 1993, Hummel & Van Loon 1999). Ammonia forms strong complexes with "soft" cations, such as Ag (Van Loon & Hummel 1999b). Any influence of ammonia on sorption reduction is not relevant to Ag as zero sorption is assumed. Presence of ammonia (representing also the amines) has an effect on Ni and Co speciation at high NH₃ concentration under alkaline conditions (Thoenen 2013). However, an effect on the uptake and solubility of these radionuclides is only expected for stage III of the cement degradation (pH ~ 11) (Tab. 6.5).

### 4.6.1.5 Gluconic and isosaccharinic acids

Gluconic acid (GLU) and isosaccharinic acid (α/β-ISA) are considered to be the most important complexing ligands present in a cement-based repository. Both compounds have similar poly-hydroxy-type chemical structures (Glaus et al. 2004).

**Appearance in the waste**

The majority of waste forms will contain gluconic acid, which is used as a water-reducing agent and retarder during waste solidification. Adsorption of GLU onto HCP can be modelled in terms of a Langmuir isotherm. Partitioning between solid and liquid phase determines the aqueous GLU concentration in the pore water. In some waste forms, the GLU concentration slightly exceeds the limit of 10⁻⁵ M acceptable for SMA-1/LMA-1 waste (max. 2 × 10⁻⁵ M) which, in principle, suggests a small effect on the complexation of safety-relevant radionuclides or representative analogues, respectively, by GLU in SMA-2/LMA-2 waste.
A few waste forms contain cellulose which degrades under alkaline conditions. The maximum loading in some of these waste packages is about 7% of the HCP mass (Wieland & Berner 2011). The main degradation products of cellulose are $\alpha$- and $\beta$-isosaccharinic acids (Van Loon & Glaus 1998). The kinetics of cellulose degradation and hence the formation of ISA is still disputed due to significant discrepancies observed in the rate constants determined from short- and long-term degradation experiments with those deduced from degradation studies at elevated temperature.

The concentration of ISA in the near-field pore water was estimated by considering adsorption of ISA onto HCP which was modelled using the simplified one-site Langmuir isotherm as reported in Bradbury & Van Loon (1997). Sorption reduction caused by high concentrations of $\alpha$-ISA (ISA > $10^{-4}$ M) in some waste forms has to be considered in terms of appropriate sorption reduction factors (Tab. 4.3).

The influence of ISA and GLU on the uptake of earth-alkaline (e.g. Sr) and transition metals (e.g. Ni) is considered to be negligibly small in the concentration range of interest (ISA $\leq 4 \times 10^{-3}$ M; GLU $\leq 2 \times 10^{-3}$ M). ISA and GLU could have an effect on the uptake of transition metals by cementitious materials as indicated from complexation studies and sorption measurements on resins (Warwick et al. 2003, Warwick et al. 2006). However, sorption studies with Ni on HCP in presence of ISA showed that sorption reduction caused by the formation of aqueous Ni-ISA complexes occurs solely at ISA concentrations $> 10^{-2}$ M (Wieland et al. 2000). No effect was observed below this limit.

The studies of Warwick et al. (2003, 2006) indicate that ISA could have an effect on U(VI) adsorption onto resins due to the formation of aqueous U(VI)-ISA complexes. Nevertheless, the effect on U(VI) uptake was even smaller than that on Co and Ni uptake (Warwick et al. 2006). The latter finding, in view of the experimental data on Ni uptake by HCP in presence of ISA (Wieland et al. 2000), suggests that the effect of ISA on U(VI) uptake by HCP can be ignored.

**Influence of GLU and ISA on the uptake of tri- and tetravalent actinides by hydrated cement**

Sorption studies with actinides on cementitious materials in presence of ISA and GLU allowed the influence of the ligands on radionuclide retention to be determined (Holgersson et al. 1998, Tits et al. 1998, Wieland et al. 2002, Tits et al. 2002, Tits et al. 2005). Figs. 4.3 and 4.4 summarise published and recent in-house data on Eu(III) and Th(IV) uptake by HCP and C-S-H phases under the conditions relevant to a cementitious near field. Details of the corresponding experimental protocols are given in Section 3.2 and in literature (Wieland et al. 2002). The in-house studies revealed that the experimental window for sorption studies with strongly sorbing tracers in the presence of complexing ligands, such as studies on Eu(III) and Th(IV) uptake by cementitious materials in the presence of ISA and GLU, is limited due to the following constraints: 1) The minimal, statistically significant radionuclide activity that can be determined under the given experimental conditions (or the maximum sorption value that can be determined, respectively) (see further details in Sections 4.1.18 and 4.1.19), and 2) the stability of the cementitious materials at increasing ligand concentrations (Wieland et al. 2002). In the latter study it was demonstrated that HCP dissolves at high ISA concentrations, presumably due to the formation of Ca-ISA complexes (Vercammen et al. 1999). In a similar manner, GLU is expected to have an influence on the stability of HCP as GLU is known to form weak complexes with Ca$^{2+}$ (Schubert & Lindenbaum 1952). The dissolution of HCP or C-S-H phases, respectively, is considered to be a side reaction, which limits the maximum ligand concentration that can be used in sorption studies at the given solid content (broken lines in Figs. 4.3 and 4.4).
Thus, all experimental data displayed in Figs. 4.3 and 4.4 were determined under experimental conditions where the dissolution of HCP and C-S-H could be excluded as prevailing side reaction.

Fig. 4.3: Uptake of europium and thorium by HCP and C-S-H in presence of GLU at pH = 13.3.

Broken and dotted lines: Calculated stability limit of HCP expressed in terms of % CaO present in HCP (right scale). Shaded area: Estimated uncertainty range of the sorption values.

Fig. 4.4: Uptake of europium and thorium by HCP and C-S-H in presence of ISA at pH = 13.3.

Broken and dotted lines: Calculated stability limit of HCP expressed in terms of % CaO present in HCP (right scale). Shaded area: Estimated uncertainty range of the sorption values.

Sorption reduction factors in presence of GLU

Bradbury & Van Loon (1997) selected a GLU concentration of $10^{-4}$ M as being the upper limit for an undisturbed cementitious system, implying that GLU has no adverse effect on radionuclide uptake by hydrated cement below this limit. Note that the limit was selected on the basis of earlier in-house sorption measurements with safety-relevant radionuclides on C-S-H phases (Tits et al. 1998). It is worth recalling that Tits et al. (1998) reported only a limited set of experimental data from sorption kinetics and sorption isotherm measurements at pH = 13.3 on a C-S-H phase with a C/S ratio = 1.09. Schwyn (2008) further recommended $10^{-4}$ M as threshold for the classification of SMA-1/LMA-1 waste in earlier PA studies. Additional sorption measure-
ments with Eu(III) and Th(IV) on C-(A)-S-H and HCP were carried out in the past (Fig. 4.3). These data reveal that the critical GLU concentration for Eu(III) and Th(IV) uptake by HCP, which has no detrimental effect on radionuclide uptake, ranges in value between $\sim 10^{-5}$ M GLU for Th(IV) and $\sim 10^{-4}$ M GLU for Eu(III) in cementitious systems (Fig. 4.3).

Tits et al. (2002, 2005) showed that GLU concentrations below $10^{-7}$ M had no detectable influence on the uptake of Eu(III) and Th(IV) by calcite while sorption reduction occurred above this threshold value due to the formation of Eu(III)-GLU and Th(IV)-GLU complexes in solution. Note that the corresponding concentration limit for ISA was determined to be about $10^{-7}$ M by the same authors. The sorption measurements reported earlier by Tits et al. (1998) suggested that the critical GLU and ISA concentrations might be higher in cementitious systems than on calcite, presumably due to sorption of ternary complexes. For example, an aqueous GLU concentration of $10^{-4}$ M was found to have no effect on Eu(III) and Th(IV) uptake by C-S-H which is significantly above the limit ($10^{-7}$ M) observed on calcite.

Recent in-house investigations reveal a strong influence of GLU on Np(IV) adsorption onto ion exchange resins in the pH range between 11 and 13.3 in presence and absence of Ca (Rojo et al. 2013). In the latter study sorption reduction was observed at a GLU concentration above $\sim 3 \times 10^{-6}$ M (Fig. 4.5). It is expected that this limit will be higher in cementitious systems due to the formation of ternary complexes. In view of the new information that is available, it is recommended to reduce the upper limit of GLU in SMA-1/LMA-1 waste from $10^{-4}$ M to $10^{-5}$ M.

**Fig. 4.5:** Uptake of Np(IV) by ion exchange resin in presence of GLU in the pH range 11 - 13.3 (Rojo et al. 2013).

Sorption reduction caused by GLU complexation can be neglected for all radionuclides except the trivalent actinides and lanthanides, and the tetravalent actinides (Tab. 4.4). Sorption reduction factors for the latter radionuclides have been selected as follows:

**Trivalent lanthanides and actinides:** Tits et al. (2005) investigated the influence of increasing concentrations of GLU on Eu(III) and Am(III) uptake by calcite. The authors showed (Figure 6 in Tits et al. 2005) that the influence of GLU on Eu(III) and Am(III) uptake is different.
Stability of the aqueous Eu(III)-GLU 1:1 complex was found to be higher than that of the corresponding Am(III) complex, thus resulting in a difference in the sorption reduction factor between trivalent lanthanides and actinides by about an order of magnitude. We accept an order of magnitude difference between the sorption reduction factor for trivalent lanthanides and actinides. At the maximum GLU concentration of $2.0 \times 10^{-5}$ M a sorption reduction factor of 10 is assigned to Eu(III) uptake by HCP on the basis of the available experimental data (Fig. 4.4). This value is further accepted for all lanthanides (Tab. 4.4). A sorption reduction factor of 1, indicating no effect on uptake by HCP, is assigned to Am(III) and the other trivalent actinides taking into account weaker complexation of trivalent actinides with GLU (Tab. 4.4).

**Tetravalent actinides and other tetravalent metal cations:** The influence of GLU on Th(IV) uptake was found to be negligibly small at GLU concentrations $\leq 2.0 \times 10^{-5}$ M (Fig. 4.3). It is expected that this is further true for the other tetravalent actinides on the basis of chemical analogy as well as for Zr(IV) and Sn(IV).

**Penta- and hexavalent actinides:** The influence of GLU on the uptake of Pa(V), Np(V), Pu(V) and U(VI) by HCP is expected to be limited on the basis of lacking evidence for significant GLU complexation at GLU concentrations $\leq 2.0 \times 10^{-5}$ M.

**Sorption reduction factors in presence of ISA**

Th(IV) and Eu(III) were found to form strong complexes with ISA under alkaline conditions (Vercammen et al. 2001). Thus, sorption reduction caused by ISA complexation can be neglected for all radionuclides except the trivalent actinides and lanthanides, the tetravalent metal cations, i.e. actinides and Zr(IV) and Sn(IV), and the penta- and hexavalent actinides (Tab. 4.4).

At ISA concentrations $\leq 10^{-4}$ M the influence on radionuclide uptake by HCP is considered to be negligibly small. Hence, the limit used in the previous SDB (Bradbury & Van Loon 1997) is accepted in this study. Sorption reduction has to be taken into account for SMA-2/LMA-2 waste where ISA can reach maximum concentrations in solution up to $3.7 \times 10^{-3}$ M. Sorption reduction factors are estimated as follows:

**Trivalent lanthanides and actinides:** A sorption reduction factor of 10 is considered in the case of Eu(III) (and by analogy for the trivalent lanthanides and actinides) on the basis of the available experimental evidence (Fig. 4.4). Note that Tits et al. (2005) showed that the influence of ISA on the uptake of Eu(III) and Am(III) by calcite is similar. This implies comparable thermodynamic stability of Eu(III)-ISA and Am(III)-ISA complexes which justifies selection of the same sorption reduction factors for trivalent lanthanides and actinides (Tab. 4.4).

**Tetravalent metal cations:** The influence of ISA on the uptake of Sn(IV) and Zr(IV) by HCP is expected to be weak due to limited thermodynamic stability of Zr(IV)-ISA and Sn(IV)-ISA complexes. Nevertheless, a possible effect on the Zr(IV) and Sn(IV) uptake by HCP is considered at the maximum ISA concentration of $3.7 \times 10^{-3}$ M (sorption reduction factor = 10). In contrast, the influence of ISA on the uptake of the tetravalent actinides is strong (Fig. 4.4). On the basis of the experimental data with Th(IV) (Fig. 4.4) it is anticipated that an increase in the ISA concentration from $10^{-4}$ M to $3.7 \times 10^{-3}$ M gives rise to a reduction in the $R_d$ value by about two orders of magnitude (sorption reduction factor = 100). The same value is adopted for Np(IV), Pu(IV) and U(IV) based on chemical analogy.
Penta- and hexavalent actinides: The influence of ISA on the uptake of Pa(V), Np(V), Pu(V) and U(VI) is expected to be weak. A possible effect on uptake by HCP is considered by assigning a nominal sorption reduction factor $= 10$ at the maximum ISA concentration of $3.7 \times 10^{-3}$ M.

Tab. 4.4: Recommended sorption reduction factors in presence of GLU and ISA.

<table>
<thead>
<tr>
<th>Metal cation</th>
<th>ISA</th>
<th>GLU</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lesssim 10^{-4}$ M</td>
<td>$10^{-4}$ M – $3.7 \times 10^{-3}$ M</td>
<td>$\lesssim 10^{-5}$ M</td>
</tr>
<tr>
<td>Zr(IV), Sn(IV)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Pm(III), Sm(III), Eu(III), Np(III)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Ac(III), Am(III), Cm(III), Pu(III), Pa(IV), Th(IV), U(IV), Np(IV), Pu(IV)</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>Pa(V), Th(VI), U(IV), Np(IV), Pu(IV)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Pa(V), Np(V), Pu(V)</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>U(VI)</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

4.6.1.6 Concrete admixtures

Concrete admixtures are unavoidable components of cements used for the conditioning of radioactive waste and they will be employed for the production of concretes (liner, backfill) during construction of a cement-based deep geological repository. Concrete admixtures improve the workability of cement, influence its physical properties such as compressive strength, durability or setting time, and confer certain beneficial effects to the material. In most cases, concrete admixtures are polymeric organic compounds with an often poorly defined and, owing to proprietary reasons, only partly known composition.

The most important concrete admixtures are polynaphthalene-sulphonic acids, polymelamine-sulphonates, lignosulphonates, gluconic acid and polycarboxylate-ether based molecules. The latter type of compounds are used in modern concrete admixtures. Glaus & Van Loon (2003), Glaus et al. (2004, 2006) investigated the influence of selected concrete admixtures on radionuclide complexation. The experimental studies show that all concrete admixtures with the exception of formerly used gluconic acid and lignosulphonates form only weak complexes with radionuclides. Furthermore, application of modern concrete admixtures (such as polycarboxylate-ether based molecules) in typical dosage (few % relative to HCP) was found to result in concentrations of the polymeric and low-molecular-weight organic ligands in the near-field pore water under the relevant repository conditions (e.g. HCP-to-pore water ratio of $\sim 2$ kg/L) which are expected to have no adverse effect on radionuclide uptake by HCP (Andersson et al. 2008, Wieland et al. 2014). The evidence is that sorption reduction effects caused by concrete admixtures are negligibly small in the cementitious near field. Therefore, sorption reduction caused by concrete admixtures is not taken into account in this study, except for gluconic acid (see Section 4.6.1.5).
4.6.1.7 Organic polymers

Earlier studies showed that the effect of high-molecular-weight polymeric organic materials and their degradation products on radionuclide solubility and sorption is small compared to that of cellulose degradation products (Greenfield et al. 1992, Greenfield et al. 1994). This indicates that polyhydroxy-type carboxylic acids, with structures similar to those of GLU and ISA, are not the dominant products formed in the course of the degradation of polymeric organic materials. In accordance with appraisals made earlier (Bradbury & Sarott 1994, Bradbury & Van Loon 1997) and due to lack of new information it is assumed that an adverse effect of polymeric organic materials and their degradation products on radionuclide complexation, and therefore on radionuclide uptake by HCP, can be ignored.

4.6.1.8 Degradation products of bitumen and acidic ion-exchange resin

Gamma irradiation decomposes strong acidic cation exchange resins while no evidence for decomposition was found in the absence of a radiation field. Sulphate and dissolved organic compounds were found to be the main degradation products while oxalic acid and an unidentified ligand were found to be the most strongly complexing ligands formed upon decomposition of the exchange resin (Van Loon & Hummel 1995, Van Loon & Hummel 1999b). Nevertheless, both ligands are expected to have only a minor effect on radionuclide speciation (in particular Ni) under alkaline near-field conditions due to the limited total concentrations of the ligands in near-field pore water and the formation of strong Ca complexes with both ligands (Hummel & Van Loon 1999). Bradbury & Sarott (1994) concluded that the degradation products from bitumen and ion exchange resins have no significant influence on radionuclide uptake by hydrated cement.

4.6.2 Influence of cement carbonation on radionuclide retention

L/ILW and ILW will contain high-molecular-weight polymeric organic materials, such as graphite, rubber, plastics, polyvinylchloride, polystyrene, detergents, bitumen, spent ion exchange resin, cellulosic materials and concrete admixtures, and low-molecular-weight monomeric organic compounds, such as EDTA, gluconic acid, oxalic acid, citric acid and tartaric acid. Although microbial activity will be low under the alkaline conditions of a cement-based repository it is assumed that microbially mediated decomposition of organic materials might occur over time. Degradation of organic materials in a repository is expected to predominantly occur via fermentation (methanogenesis) which produces CO$_2$ and CH$_4$. Microbial degradation of organic materials coupled to Fe(III) and SO$_4^{2-}$ reduction is expected to play only a minor role due to the limited inventories of the latter electron-capturing species in the cementitious near field (Wieland & Berner 2011).

The generation of large amounts of CO$_2$ is expected to change the mineral composition of hydrated cement which further influences radionuclide retention. Under the highly alkaline conditions of the near field, CO$_2$ will be present mainly as CO$_3^{2-}$, which reacts with portlandite and C-S-H phases to form CaCO$_3$. In the first place, portlandite reacts with CO$_3^{2-}$. As soon as the amount of portlandite present in the near field has been converted to CaCO$_3$, carbonation of C-S-H is expected to take place. While both reactions give rise to changes in the total volume of solids in the near field, it is expected that only the latter reaction may have an adverse effect on the retention of cationic radionuclides by cement paste.

Conversion of C-S-H phases to CaCO$_3$ might occur if the loading of organic materials is very high in the cementitious near field. This maximum loading can be estimated on the basis of the PA "portlandite criterion", i.e. 2/3 of the total inventory of portlandite in the near field is
allowed to degrade, and on the assumption that the degradation of organic materials occurs via methanogenesis (production of CH₄/CO₂). Complete degradation of portlandite and C-S-H phases might occur in the SMA-2/LMA-2 waste compartment due to high loadings of organic materials. In the case of complete degradation of cement paste in the near field the resulting geochemical conditions are expected to be similar to those in a strongly altered, calcite-rich host rock (Bradbury & Baeyens 1997), i.e. elevated pH of the pore water and CaCO₃ as the dominating solid phase. The sorption values relevant to a calcite-rich system were selected and listed elsewhere (Bradbury & Baeyens 1997, Nagra 2008a, Bradbury et al. 2010).

4.6.3 Influence of metal corrosion products on radionuclide retention

Metallic aluminium and iron are regarded as the only inorganic materials with potentially large impacts on the cement barrier (Wieland & Berner 2011). High inventories of metallic Al loading were found to convert portlandite and ettringite into hydrogarnet, calcium hemicarboaluminate and calcium hemisulphoaluminate solid solutions (Wieland & Berner 2011). Preliminary assessment of the impact of corroding steel causes the transformation of ettringite into hydromagnetite and pyrite under the given reducing conditions of a cementitious near field. Thus, with time, the mineral composition of hydrated cement could change in the presence of large amounts of aluminium and iron in the SMA-2/LMA-2 waste compartment. Detailed assessments of the impact of the resultant changes in the mineralogy of cement paste on radionuclide retention are currently uncertain due to the limited information on the final mineral composition of a cement paste altered by steel corrosion products.
5 Assessment of Diffusion Parameters for Cementitious Materials of the Near Field for Use in Safety Analysis

In safety analysis it is considered that diffusive transport of radionuclides through cementitious barrier under water-saturated conditions could occur (Nagra 2008a). To this aim a provisional assessment of the diffusion parameters for use in SGT-E2 (Sachplan Geologische Tiefenlager-Etappe 2), such as the effective diffusion coefficient, is required. In the following sections the diffusion parameters as used in earlier PA-related studies are briefly discussed and the corresponding appraisal is made with the aim of selecting the parameters for use in provisional safety analysis carried out in the framework of SGT-E2.

5.1 Diffusion of solutes

The migration of radionuclides through hardened cement paste under water-saturated conditions and absence of fractures is controlled by molecular diffusion in the pore water. The theoretical formalism for modelling through- and out-diffusion experiments in cementitious materials was developed elsewhere (Jakob et al. 1999, Jakob 2002, Tits et al. 2003b). In this study, the effective diffusion coefficient for cementitious materials was estimated on the basis of a single porosity-diffusivity relationship (Archie's law) and compared with experimental data.

The definition of diffusion parameters and their relationship as used here are as follows:

\( D_0: \) Molecular diffusion coefficient in free water

Detailed discussion of the determination of \( D_0 \) (= \( D_w \) as used by others) is given elsewhere (Flury & Gimmi 2002). The latter study further reports a compilation of \( D_0 \) values for ionic species. These values typically range between \( 1.1 \times 10^{-9} \) m\(^2\)/s and \( 2.1 \times 10^{-9} \) m\(^2\)/s for most major ions.

\( D_e: \) Effective diffusion coefficient

Diffusion of solutes in porous media is affected by the length of the diffusion path, which is expressed in terms of tortuosity (\( \tau \)) and constrictivity (\( \delta \)). Invoking these terms indicates that the actual travel distance between two points in the porous media may be considerably longer than the Euclidian distance and further the pores may have varying cross sections and dead ends (Flury & Gimmi 2002). Furthermore, additional properties of the media and processes may influence the diffusion process in porous media, such as the viscosity of water in the pores of different size and electrostatic interactions. All of the above factors tend to reduce the diffusivity of ions in porous media compared to bulk water. They can be combined to a single factor, \( f \) (= impedance factor) as they are not discernable separately (Flury & Gimmi 2002 and references therein). This allows \( D_e \) and \( D_0 \) to be related as follows:

\[
D_e = \frac{\delta}{\tau^2} \cdot D_0 \cdot \varepsilon = f \cdot D_0 \cdot \varepsilon
\]

where \( \varepsilon \) denotes the accessible porosity of the porous media [m\(^3\)/m\(^3\)].
The porous-medium diffusion coefficient (or pore diffusion coefficient), $D_p$, is related to the diffusion coefficient in free water as follows:

$$D_p = \frac{\delta}{\tau^2}D_0$$

(7)

The pore diffusion coefficient is related to the effective diffusion coefficient as follows:

$$D_p = \frac{D_e}{\varepsilon}$$

(8)

indicating that $D_p > D_e$.

Archie's law

An empirical equation (= Archie's law) allows the conductivity of rocks to be linked to their porosity (Archie 1942, Wong et al. 1984). This equation was developed in order to describe the electrical conductivity of porous rocks as a function of fluid resistivity and porosity (Archie 1942). Later, the equation was adapted with the aim of linking the effective diffusion coefficient and the accessible porosity (or effective porosity) of porous media (Boving & Grathwohl 2001, Van Loon 2014):

$$D_e = D_0 \cdot a \cdot \varepsilon^m$$

(9)

where $a$ and $m$ are empirical parameters dependent on the pore geometry. The exponent, $m$, corresponds to the cementation factor of sedimentary rocks and varies from 1.3 for unconsolidated sediments such as sand up to 2 in well-cemented (clay-free) sediments while $a$ was found to be approximately equal to one (Boving & Grathwohl 2001). Archie's law was further employed to estimate the permeability or conductivity of concrete using pore parameters (Tumidajski et al. 1996, Nokken & Hooton 2008). It was observed that Archie's law does not represent a unique relationship for all concretes (Nokken & Hooton 2008), such as OPC, blended cements etc., while it can be used for specific concrete mixtures, such as cement pastes prepared from OPC at different w/c (Tumidajski et al. 1996).

5.2 Diffusion parameters used in previous safety analysis studies

In previous PA-related studies, the pore diffusion coefficient, $D_p$, was assumed to range in value between $10^{-10}$ - $10^{-9}$ m$^2$/s while the porosity of the various cementitious built-in components of the L/ILW near field varied from 5 % to 35 % (Nagra 1994). Thus, $D_e$ ranged between $5 \times 10^{-12}$ m$^2$/s and $3.5 \times 10^{-10}$ m$^2$/s. In the framework of the SGT provisional transport calculations of radionuclides in the cementitious near field were based on $D_p = 2 \times 10^{-9}$ m$^2$/s and an average porosity of the near field components of 20 % (Nagra 2008a). This corresponds to $D_e = 2 \times 10^{-10}$ m$^2$/s. The latter value can be compared with diffusion parameters used for modelling the degradation of cement grout and their impact on the geochemistry of the backfill in the framework of the Swedish disposal programme, i.e. $D_e = 10^{-10}$ m$^2$/s for shotcrete/grout ($\varepsilon = 30 \%$) and $1.2 \times 10^{-10}$ m$^2$/s for backfill (Luna et al. 2006) and $D_e = 10^{-11}$ m$^2$/s for grout cement ($\varepsilon = 12.5 \%$) and $6 \times 10^{-10}$ m$^2$/s for backfill ($\varepsilon = 30 \%$) (Grandia et al. 2010). Furthermore, Höglund (2001) reported an effective diffusivity in concrete ranging between $10^{-11}$ m$^2$/s and $10^{-10}$ m$^2$/s. This indicates a lower $D_e$ in less porous cementitious materials prepared at low w/c ratio, such as cement paste, compared to porous backfill. The latter assumption is consistent with earlier findings from diffusion experiments with chloride on cement pastes prepared at different w/c (Jakob et al. 1999).
5.3 Evaluation of diffusion parameters

For the major ions present in a cementitious system \( D_0 \) varies by less than a factor of 2 (1.1 × 10^{-9} \text{ m}^2/\text{s} to 2.1 × 10^{-9} \text{ m}^2/\text{s}) in electrolyte solutions, e.g. 0.1 – 1.0 M NaCl (Flury & Gimmi 2002). An average \( D_0 = 1.5 \times 10^{-9} \text{ m}^2/\text{s} \) was assumed for reactive transport calculations aiming at predicting the evolution of the cement/rock interface in an L/ILW repository. These calculations were carried out in the framework of SGT-E2 (Kosakowski & Berner 2013, Kosakowski et al. 2014). In the latter studies the effective diffusion coefficient was estimated on the basis of Archie's law using the parameters \( a = 1 \) and \( m = 2 \) while a porosity of 20 % was considered for concrete. Note that in these studies the single porosity-diffusivity relationship given by Archie's law was employed for both host rock and concrete for the sake of consistency.

The diffusion parameters listed in Tab. 5.1 are estimated for a concrete with porosity of 20 % (Kosakowski et al. 2014) using Archie's law and parameters reported in literature. The concrete modelled in the study consisted of an OPC CEM I 52.5 N HTS (Lafarge, France) and quartz aggregates. The parameters reported by Tumidajski et al. (1996) and by Nokken & Hooton (2008) were determined from measurements of permeability or conductivity of cement pastes, concrete or mortars, respectively. Tumidajski et al. (1996) used a type 10 Portland cement to prepare cement pastes with different w/c ratios while the mortar samples were prepared using the type 10 Portland cement and Ottawa sand with size fractions < 50 mesh and > 100 mesh. The porosity of the paste samples varied between ~ 10 % and ~ 60 % while the porosity of the mortar samples ranged between ~ 12 % and ~ 15 %. Nokken & Hooton (2008) used a low-alkali ASTM Type I Portland cement to prepare the cement pastes while the concrete mixtures consisted of Type I cement and varying proportions of fine and coarse aggregates. Nokken & Hooton (2008) further investigated cementitious materials, which were made with Type I cement blended with silica fume, fly ash or blast furnace slag. The results reported for the latter mixtures are ignored in the current assessment of diffusion parameters as it was observed that blended cementitious materials have microstructural properties that differ significantly from those of non-blended OPC type materials (Page et al. 1981, McCarter et al. 2000). The parameters deduced by Nokken & Hooton (2008) for cement paste were obtained by determining the conductivity of concrete and using the paste porosity. This approach is only poorly documented and therefore, uncertainties are greater on the resulting diffusivities, which should be used with caution.

Tab. 5.1 reveals that \( D_e \) is expected to range in value between 10^{-11} \text{ m}^2/\text{s} and 10^{-10} \text{ m}^2/\text{s} (\( D_p = 5 \times 10^{-11} \text{ m}^2/\text{s} \) – 5 × 10^{-10} \text{ m}^2/\text{s}) for a concrete with \( \varepsilon = 20 \% \). This is consistent with \( D_e \) of grout cement (\( D_e = 10^{-11} \text{ m}^2/\text{s} \); \( \varepsilon = 12.5 \% \); \( D_p = 8 \times 10^{-11} \text{ m}^2/\text{s} \)) and shotcrete/grout (\( D_e = 10^{-10} \text{ m}^2/\text{s} \); \( \varepsilon = 30 \% \); \( D_p = 3.3 \times 10^{-10} \text{ m}^2/\text{s} \)) used for modelling ion diffusion in cementitious systems in the framework of the Swedish disposal programme (Luna et al. 2006, Grandia et al. 2010). This range can further be compared with measurements of \( D_e \) on cementitious materials reported in literature (Tab. 5.2).

A compilation of \( D_e \) as a function of porosity (Figure 3.2.1.2-3 in Jakob et al. 1999, Figure 8 in Yamaguchi et al. 2009) indicates that \( D_e \) increases with increasing porosity of the cementitious materials. Yamaguchi et al. (2009) observed that the effective diffusivity amounts to \( \sim 5.4 \times 10^{-12} \text{ m}^2/\text{s} \) at \( \varepsilon = 1 \% \) and increases to \( \sim 1.6 \times 10^{-11} \text{ m}^2/\text{s} \) at \( \varepsilon = 30 \% \). The term \( D_0 \times \delta \times \tau^{-2} \) (\( = D_p \); Eq. 7) was further estimated to range between 3.0 × 10^{-10} \text{ m}^2/\text{s} and 2.4 × 10^{-9} \text{ m}^2/\text{s}. Based on an average value of 1.3 × 10^{-9} \text{ m}^2/\text{s}, \( D_e \) is expected to range from 7.0 × 10^{-11} \text{ m}^2/\text{s} for dense cementitious materials (\( \varepsilon = 5 \% \)) to 3.9 × 10^{-10} \text{ m}^2/\text{s} for porous cementitious materials (\( \varepsilon = 30 \% \)). The upper and lower bounds of \( D_e \) are estimated to be 1.5 × 10^{-11} \text{ m}^2/\text{s} (\( \varepsilon = 5 \% \)) and 7.2 × 10^{-10} \text{ m}^2/\text{s} (\( \varepsilon = 30 \% \)). Jakob et al. (1999) report \( D_e \) for chloride to range in value from \( \sim 6 \times 10^{-12} \text{ m}^2/\text{s} \) (w/c ~ 0.25) to \( \sim 2 \times 10^{-10} \text{ m}^2/\text{s} \) (w/c ~ 1.3). Note that \( D_e \) values deduced based
on Archie's law (Tab. 5.1) fall within this range. Note further that $D_e$ is estimated to be $3.0 \times 10^{-12}$ m$^2$/s at very low porosity, which is consistent with the $D_e$ estimated on the basis of Archie's law by Nokken & Hooton (2008).

Tab. 5.1: Diffusivity in concrete ($\varepsilon = 20\%$) estimated with $D_0 = 1.5 \times 10^{-9}$ m$^2$/s on the basis of Archie's law and parameters reported in the literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Archie's law parameters</th>
<th>Material</th>
<th>$D_e$ [m$^2$/s]</th>
<th>$D_p$ [m$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kosakowski &amp; Berner (2013)</td>
<td>($a = 1, m = 2$)</td>
<td>--</td>
<td>$6.0 \times 10^{-11}$</td>
<td>$3.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>Tumidajski et al. (1996)</td>
<td>(1, 2.55)</td>
<td>Cement paste (varying w/c)</td>
<td>$2.5 \times 10^{-11}$</td>
<td>$1.25 \times 10^{-10}$</td>
</tr>
<tr>
<td>Tumidajski et al. (1996)</td>
<td>(1, 2.14)</td>
<td>Mortar (w/c = 0.35)</td>
<td>$4.8 \times 10^{-11}$</td>
<td>$2.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>Nokken &amp; Hoorten (2008)</td>
<td>(0.92, 2.31)</td>
<td>Concrete (w/c = 0.55)</td>
<td>$3.4 \times 10^{-11}$</td>
<td>$1.7 \times 10^{-10}$</td>
</tr>
<tr>
<td>Nokken &amp; Hoorten (2008)</td>
<td>(0.08, 2.42)</td>
<td>Cement paste (varying w/c)</td>
<td>$2.2 \times 10^{-12}$</td>
<td>$1.1 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Tab. 5.2: Literature data for the effective diffusion coefficients of cementitious materials determined from diffusion experiments.

<table>
<thead>
<tr>
<th>Tracer</th>
<th>System</th>
<th>$D_e$ [m$^2$/s]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{134}\text{Cs}^+$</td>
<td>HCP; $\varepsilon = 65%$; w/c = 1.3</td>
<td>$1.3 - 1.8 \times 10^{-10}$</td>
<td>Sarott et al. (1992)</td>
</tr>
<tr>
<td>$^{22}\text{Na}^+$</td>
<td>HCP; $\varepsilon = 65%$; w/c = 1.3</td>
<td>$1.6 \times 10^{-10}$</td>
<td>Tits et al. (2003b)</td>
</tr>
<tr>
<td>HTO</td>
<td>HCP; $\varepsilon = 65%$; w/c = 1.3</td>
<td>$2.9 \times 10^{-10}$</td>
<td>Tits et al. (2003b)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>HCP; $\varepsilon = 65%$; w/c = 1.3</td>
<td>$1.2 \times 10^{-10}$</td>
<td>Jakob et al. (1999)</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>Concrete mixture; $\varepsilon = 44.5%$; w/c = 0.6</td>
<td>$1.2 \times 10^{-11}$</td>
<td>Samson &amp; Marchand (2007)</td>
</tr>
<tr>
<td>HTO</td>
<td>HCP and concrete mixture; $\varepsilon = 7 - 28%$; w/c = 0.4-0.55</td>
<td>$0.3 - 1.1 \times 10^{-11}$</td>
<td>Numata et al. (1990)</td>
</tr>
<tr>
<td>HTO</td>
<td>HCP; w/c = 0.45/0.6/0.75</td>
<td>$1.4 - 8.7 \times 10^{-11}$</td>
<td>Yamaguchi et al. (2009)</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>HCP; w/c = 0.4/0.5/0.6; T = 25°</td>
<td>$0.5 - 1.2 \times 10^{-11}$</td>
<td>Page et al. (1981)</td>
</tr>
</tbody>
</table>
Kamali-Bernard et al. (2009) determined the diffusion parameters of cement pastes and mortars (cement/sand mixture). The authors showed that the diffusion coefficient of mortar is lower than that of cement paste prepared at the same water to cement ratio due to the presence of sand. The authors further observed that leaching directly affects the diffusion coefficient of cement paste and mortar. The effective diffusion coefficients of sound (i.e. unaltered) cement paste and mortar materials were determined to be $7.5 \times 10^{-12}$ m$^2$/s and $4.5 \times 10^{-12}$ m$^2$/s, respectively. $D_c$ increased by a factor of ~20 after leaching portlandite from the cement matrix in both types of cementitious materials. Subsequent leaching of aluminates increased $D_e$ by a factor of ~2 compared to the portandite-leached materials.

The above considerations show that diffusion parameters of cementitious materials deduced based on Archie's law are consistent with experimental data. An effective diffusion coefficient of $6.0 \times 10^{-11}$ m$^2$/s previously used by Kosakowski et al. (2014) for concrete and $6 \times 10^{-10}$ m$^2$/s for backfill (Grandia et al. 2010) are considered to be reasonable estimates of the diffusion parameters for evolving L/ILW and ILW repositories. The effective diffusion coefficient of an unaltered cement paste prepared at low w/c is assumed to be lower than that of concrete. Furthermore, $D_e$ of leached cementitious materials is higher than that of fresh materials (factor of ~20). In the latter case $D_e$ ranges from ~1 to $2 \times 10^{-10}$ m$^2$/s. The diffusion parameters listed in Tab. 5.3 have been estimated in view of the above considerations.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\varepsilon$ [%]</th>
<th>$D_0$ [m$^2$/s] $\times 10^9$</th>
<th>$D_p$ [m$^2$/s] $\times 10^9$</th>
<th>$D_e$ [m$^2$/s] $\times 10^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste (w/c ~ 0.3)</td>
<td>5</td>
<td>1.5</td>
<td>1.1/2.1</td>
<td>0.2</td>
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<tr>
<td>Concrete</td>
<td>20</td>
<td>1.5</td>
<td>1.1/2.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Backfill</td>
<td>30</td>
<td>1.5</td>
<td>1.1/2.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>
## 6 Sorption Summary Tables and Conclusions

Tab. 6.1: Sorption values for unperturbed HCP (m$^3$/kg) in the stages I – III of the cement degradation under oxidizing (oxid.) and reducing (red.) conditions.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<tbody>
<tr>
<td>$^{12}$CO$_3^{2-}$, Co, Ni $^{***}$</td>
<td>Isotopic exchange and solubility limitation (Section 4.1.1 and Appendix 1)</td>
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<tr>
<td>K</td>
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<td>10$^{-4}$</td>
<td>10$^{-4}$</td>
<td>10$^{-3}$</td>
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<td>5 × 10$^{-2}$</td>
<td>5 × 10$^{-2}$</td>
<td>0</td>
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<td>3 × 10$^{-1}$</td>
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<td>10$^{-2}$</td>
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<td>10$^{-1}$</td>
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<td>Np $^{****}$</td>
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<td>Pu $^{****}$</td>
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<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Definitions of the regions of the cement degradation are given elsewhere (Bradbury & Sarott 1994, Kosakowski et al. 2014).

$^{**}$ Experimental uncertainty limits as defined in Section 4.2. In case of two factors reported (e.g. 1.4/3.3): A factor of 1.4 represents the uncertainty on the lower sorption value, while a factor of 3.3 corresponds to the uncertainty on the higher sorption value.

$^{***}$ Solubility limits are reported by Berner (2014).

$^{****}$ Sorption values estimated on the basis of Se(VI), Np(V,VI), Pu(VI) under oxidizing conditions and on the basis of Se(IV), Np(IV) and Pu(IV) under reducing conditions. No sorption data are presently available for Se(-II). Uptake of Np(III) and Pu(III) by HCP is treated in analogy to that of trivalent actinides, e.g. Am(III).
Tab. 6.2: Lower and upper limits of the sorption values (m³/kg) for stages I – III of the cement degradation.

Lower and upper limit as reported by Wang et al. 2009 and Ochs et al. 2010 except where indicated.

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<td>1/5000</td>
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* See Tab. 6.1. Presentation of the data: lower limit/upper limit; limits are only given for those radionuclides listed in Tab. 6.1 with Rd ≠ 0.

** Limits as given in Wang et al. (2009) and Ochs et al. (2010) with the following exceptions: K: limits given for Cs; Zr: estimated limits for stage I; Tc: estimated limits for Tc(VII) (oxid.); Sm, Eu, Ac, Cm: limits corresponding to those given for Am; Pa, Np, Pu: limits corresponding to those given for Th (oxidation state IV) and U(VI).

*** Estimated value (this study).

n.a. Not applicable.
Tab. 6.3: Sorption reduction factors (realistic and upper bound (pessimistic) values), $F_{\text{red}}$, for uptake by HCP in presence of cement-derived near-field colloids assuming a typical colloid concentration of $10^4$ kg/m$^3$.

Sorption reduction factors are listed for the elements with sorption values different from zero. Values were taken from Wieland & Van Loon (2002) for stages I and II and estimated for stage III as given in Wieland & Van Loon (2002).

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<td>1.2/2</td>
<td>1.2/2</td>
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<td>1.2/2</td>
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<td>1.2/2</td>
<td>1/1.3</td>
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<td>1/1.3</td>
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<td>1/1.3</td>
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<td>1/1.3</td>
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<td>1.2/2</td>
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* See Tab. 6.1.

n.a. Not applicable.
Tab. 6.4: Sorption values (m$^3$/kg) for cement degraded in contact with high salinity groundwater under oxidizing (oxid.) and reducing (red.) conditions.

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<td>$10^{-4}$</td>
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<td>$10^{-1}$</td>
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<tr>
<td>Mo</td>
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<tr>
<td>Tc</td>
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<tr>
<td>Eu</td>
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<td>10</td>
</tr>
<tr>
<td>Pb</td>
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<tr>
<td>Pa</td>
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<td>Am</td>
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<tr>
<td>Cm</td>
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* CO$_3^{2-}$: reduced retention; Ni, Co: no significant influence on solubility.
Tab. 6.5: Sorption reduction factors by important complexing ligands present in the pore water for stages I and II of the cement degradation (see Tab. 6.1) under oxidizing (oxid.) and reducing (red.) conditions.

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<tr>
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<tr>
<td>Mo</td>
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</tr>
<tr>
<td>Tc</td>
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* Ligands affecting radionuclide uptake by HCP: CN = Cyanide, ISA = Isosaccharinic acid, GLU = Gluconic acid, EDTA = Ethylenediaminetetraacetic acid; L = unknown readily soluble organic ligand in wood and paper (Bradbury & Sarott 1994, Bradbury & Van Loon 1997).

** Sorption reduction factors for Ni, Co and Pb as reported by Bradbury & Van Loon (1997) for the reference case. For stage III of the cement degradation and waste group 2 sorption reduction by NH₃ and amines affecting Ni and Co has to be taken into account in addition of EDTA, L, and CN.
The present report is an update of SDBs previously published in the framework of the Swiss waste management programme for the safe disposal of low- and intermediate-level radioactive waste in a deep geological repository (Bradbury & Sarott 1994, Bradbury & Van Loon 1997, Wieland & Van Loon 2002) for application in the framework of the Sectoral Plan for Deep Geological Repositories (SGT-Etape 2). The same guiding principles were obeyed as in the previous SDBs, i.e. transparency and traceability of the selection process. Furthermore, the present SDB has been developed with a view to the comprehensive compilations of sorption values recently published in the framework of the PA for the planned near surface disposal facility in Belgium (Wang et al. 2009, Ochs et al. 2010). These data had been subject to an international review process.

Sorption values were selected based on procedures already reported in the earlier SDBs (Bradbury & Sarott 1994, Bradbury & Van Loon 1997, Wieland & Van Loon 2002). The sorption values recommended in the earlier SDBs have been revised if corresponding new information and/or data was available. The basic information and the new data result from a survey of sorption studies published internationally between 2002 and 2013. In contrast to the previous SDBs, emphasis is placed on the documentation and discussion of uptake mechanisms in this report. In the past decade, the use of modern spectroscopic techniques has made it possible to develop a mechanistic understanding of the uptake of radionuclides by cementitious materials.

The presently available mechanistic understanding of radionuclide uptake by cementitious materials (cement paste, cement phases) in combination with the results from reactive transport modelling allows well-supported appraisal of the sorption values of radionuclides in an evolving cementitious near field to be made. The effect of cement alteration on radionuclide uptake is considered for three characteristic stages of the cement degradation in the case of inflowing non-saline groundwater. The influence of inflowing saline groundwater on radionuclide uptake can be assessed on the basis of our current understanding of the chemical stability of cement phases at high salinity.

Potential effects of important organic and inorganic ligands as well as cement-derived near-field colloids on radionuclide uptake by cement paste can be taken into account in terms of sorption reduction factors.
7 Acknowledgements

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Appendix A: Shared Solubilities

Erich Wieland (PSI)

In the main part of this report (Section 4.1.1) it was noted that the uptake of C (CO\textsubscript{3}\textsuperscript{2-}), Co and Ni by hardened cement paste (HCP) is most probably not controlled by an adsorption-type process. The currently available experimental data rather indicate a solubility-limiting process by Ni and Co containing cement phases and calcite in the case of CO\textsubscript{3}\textsuperscript{2-}. Upper bounds of the concentrations of Ni, Co and CO\textsubscript{3}\textsuperscript{2-} had been predicted on the basis of solubility limits in performance assessment (PA) calculations for intermediate-level waste (Wersin & Schwyn 2004). In this appendix, an approach is proposed which allows \(R_d\) values for Ni, Co and CO\textsubscript{3}\textsuperscript{2-} to be estimated based on their aqueous concentrations in cement-type pore water and their inventories in cement paste and by assuming isotopic exchange as potential retention mechanism. It is worth noting 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 representing sorption processes.

A1 Uptake mechanisms of \(^{59,63}\text{Ni}, ^{60}\text{Co and } ^{14}\text{CO}_3\textsuperscript{2-} by HCP

A1.1 \(^{59,63}\text{Ni and } ^{60}\text{Co}

Experimental evidence has been provided that \(^{63}\text{Ni} \) uptake by HCP should be interpreted in terms of an isotopic exchange process rather than an adsorption process on HCP (Wieland et al. 2000, Wieland & Van Loon 2002) because measured sorption isotherms could not be interpreted in terms of a Langmuir or Freundlich-type sorption isotherm (Wieland et al. 2006). Furthermore, a dependence of the \(R_d\) value for Ni uptake was observed with increasing solid-to-liquid (S/L) ratio (Wieland & Van Loon 2002). Both findings contradict the idea that an adsorption-type mechanism controls Ni uptake by HCP and therefore, a solubility-controlled mechanism was proposed (Wieland et al. 2006).

Spectroscopic investigations further revealed that a mixed Ni-Al layered double hydroxide (LDH) phase might form in cement systems (Scheidegger et al. 2000, Vespa et al. 2006a/b). LDH phases are commonly expressed as \([\text{M}^{II}_{1-x}\text{M}^{III}_x\text{(OH)}_2]^{3+}(\text{An}^-)_x\gamma\text{H}_2\text{O}\) and it has been suggested that Ni\textsuperscript{2+} can partly occupy the M\textsuperscript{II} positions while Al\textsuperscript{3+} fills the M\textsuperscript{III} positions (Vespa et al. 2006a). Charge-balancing anions may be CO\textsubscript{3}\textsuperscript{2-}, Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-} or NO\textsubscript{3}\text{-}. It should be noted that Johnson & Glasser (2003) determined the solubility product of Ni-Al LDH phase which was found to be similar to that of Ni(OH)\textsubscript{2} under alkaline conditions. On the basis of the solubility data reported for Ni\textsubscript{4}Al\textsubscript{2}(OH)\textsubscript{12}CO\textsubscript{3}2H\textsubscript{2}O by Johnson & Glasser (2003), the aqueous Ni concentration is expected to be higher (\(\sim 3 \times 10^{-6} \) M at pH 12.5; Berner 2014) than experimentally observed (range: \(\sim 2 \times 10^{-8} \) M to \(\sim 10^{-7} \) M at pH = 13.3 (Wieland et al. 2006, Engelsen et al. 2010)). The above finding reveals that the chemical nature of the LDH phase formed in cement paste, which controls Ni solubility and consequently the retention of radionickel in cementitious systems, is still poorly known. Improvements in thermodynamic calculations of the experimentally determined Ni concentrations in cementitious systems can be made only if the relevant solubility data for the Ni containing cement phase become available. In this study the empirical approach proposed earlier by Wieland & Van Loon (2002) is used to predict \(^{59,63}\text{Ni} \) retention by HCP on the basis of experimentally determined concentrations for stable Ni in cement pore water and isotopic exchange of \(^{59,63}\text{Ni} \) ("shared solubility").
Wieland & Van Loon (2002) further suggested chemical analogy between Co and Ni with regards to their retention in cement paste. Similarities in the chemical behaviour of Ni and Co in cementitious systems emerge from measurements of the aqueous concentrations of stable Ni and Co as a function of the solid-to-liquid (S/L) ratio of HCP suspensions (Wieland, unpublished data). It was observed that, similarly to Ni, the partitioning of stable Co between cement paste and pore solution cannot be interpreted in terms of an adsorption-type process using reported sorption values (Idemitsu et al. 1991). The latter finding rather suggests that a solubility-limiting process in combination with isotopic exchange might control $^{60}$Co retention in cementitious systems. Furthermore, Vespa et al. (2007) provided some evidence for the presence of a solubility-limiting Co phase in cement paste.

A1.2 $^{14}$CO$_3^{2-}$

The predominant inorganic $^{14}$C species is $^{14}$CO$_3^{2-}$, which may either (co)precipitate as CaCO$_3$ or sorb onto cement phases of HCP. Isotopic exchange with calcium carbonate minerals is commonly regarded as the most important process of $^{14}$C immobilization. In addition, isotopic exchange might occur with CO$_3^{2-}$ bound in calcium monocarboaluminate (Ca$_4$Al$_2$(CO$_3$)(OH)$_{12}$·5H$_2$O) or hemicarbonate (Ca$_4$Al$_2$(CO$_3$)$_{0.5}$(OH)$_{13}$·5.5H$_2$O). Furthermore, $^{14}$CO$_3^{2-}$ sorption to C-S-H phases was proposed by Noshita et al. (1996). The authors observed an increase in $^{14}$CO$_3^{2-}$ uptake by HCP that contains increasing amounts of SiO$_2$. The SiO$_2$ added reacted with portlandite to form additional C-S-H phases which gave rise to an increase in the $K_d$ value of $^{14}$CO$_3^{2-}$. At the present time, conclusive evidence is lacking whether isotopic exchange with CO$_3^{2-}$ containing cement phases (monocarbonate, hemicarbonate, calcite) or adsorption onto C-S-H phases is the prevailing mechanism of $^{14}$CO$_3^{2-}$ interaction with HCP.

Bradbury & Sarott (1994) discussed possible modes of $^{14}$C immobilization in the cementitious near field. These authors suggested that $^{14}$CO$_3^{2-}$ isotopic exchange with solid calcite (CaCO$_3$) in cement paste might control $^{14}$CO$_3^{2-}$ retention (Bradbury & Sarott 1994). An isotopic exchange-based uptake mechanism implies that $^{14}$CO$_3^{2-}$ is bound in the CaCO$_3$ structure, and that uptake is largely controlled by the recrystallization process of CaCO$_3$ (Curti 1999). Isotopic exchange of $^{14}$CO$_3^{2-}$ on finely divided calcite in cement paste was demonstrated by Allard et al. (1981) and Bayliss et al. (1988), but the process was found to be slow in laboratory experiments. Nevertheless, over the time scale of a repository, recrystallization of calcite may be effectively retarding $^{14}$CO$_3^{2-}$. The kinetics of the recrystallization process is affected by site-specific factors in the cementitious near field, including the grain size of calcite, the mass fraction of calcite in cement, pH saturation degree, and the S/L ratio. Pointeau et al. (2003) carried out laboratory studies on the isotopic exchange of $^{14}$CO$_3^{2-}$ on calcite. These authors provided further experimental evidence for the isotopic exchange reaction of $^{14}$CO$_3^{2-}$ while the aqueous CO$_3^{2-}$ concentration is controlled by calcite solubility. Pointeau and co-workers presented an empirical relationship, which allows the fraction of calcite available for isotopic exchange to be estimated as a function of the particle size of calcareous aggregates (Wang et al. 2009). In this study the "shared solubility" approach is applied to estimate $^{14}$CO$_3^{2-}$ retention in the cementitious near field, i.e. by considering the replacement of CO$_3^{2-}$ by $^{14}$CO$_3^{2-}$ in the CaCO$_3$ structure according to isotopic exchange and control of the aqueous CO$_3^{2-}$ concentration by calcite solubility. Furthermore, only CaCO$_3$ present in cement paste is considered to control $^{14}$CO$_3^{2-}$ retention in the near field.
It should be noted that CaCO₃ precipitation also occurs at the interface between the cementitious near field and the host rock due to diffusion-controlled mixing of Ca rich pore water emanating from the alkaline near field and CO₃²⁻ rich pore water intruding from the host rock formation, which further increases the amount of calcite in the cementitious near field (Bradbury & Sarott 1994). Note that the possibility of calcite formation at the interface between the near field and the host rock is not taken into account in this study.

**A1.3 Operational Rd values**

Retention of $^{59,63}$Ni, $^{60}$Co and $^{14}$CO$_3^{2-}$ in the cementitious near field is based on the following assumptions: Firstly, the radioisotopes ($^{59,63}$Ni, $^{60}$Co, $^{14}$CO$_3^{2-}$) distribute between pore water and cement paste in the same way as the stable isotopes (Ni, Co, CO$_3^{2-}$). The proposed approach is in accordance with an earlier methodology used to estimate the $R_d$ value for $^{14}$CO$_3^{2-}$ in the cementitious near field (Bradbury & Sarott 1994). Note that the stable elements Ni and Co and the species CO$_3^{2-}$ are inherent constituents of cement paste (Tab. 2.3, Section 2.2.3). In the case of Ni and Co it is assumed that Ni and Co are taken up by HCP to form a solid solution, such as a LDH-type phase that controls the aqueous Ni and Co concentrations in the pore water, while CO$_3^{2-}$ is controlled by calcite solubility. Secondly, the aqueous concentrations of the stable isotopes and the radioisotopes correspond to those of the aqueous concentrations in equilibrium with HCP. In the case of Ni and Co it is assumed that the aqueous concentrations increase with increasing Ni and Co inventory of HCP as the solubility limit seems to be dependent on the stoichiometric composition of the solid solution. For example, Wieland et al. (2006) showed that the aqueous Ni concentration slightly increases from $\sim 8 \times 10^{-8}$ M to $\sim 10^{-6}$ M if the Ni loading of HCP increases from $\sim 3.2 \times 10^{-4}$ mol/kg to $\sim 2$ mol/kg (pH = 13.3). Note that the aqueous Ni concentration controlled by Ni(OH)$_2$(cr) solubility is $3 \times 10^{-6}$ M at pH = 12.54 (Berner 2014). The latter value is considered to be the upper bound for the Ni concentration in cementitious systems. In the case of Co it is assumed that the solubility limit is lower than that of Ni in accordance with solubility limits for the two elements recommended by Berner (2014). The aqueous Co concentration controlled by the solubility of Co(OH)$_2$ is $6 \times 10^{-7}$ M at pH = 12.54 (Berner 2014). In the case of CO$_3^{2-}$, the aqueous CO$_3^{2-}$ concentration is fixed by calcite solubility.

An operational distribution ratio ($R_d$) for stable Ni, Co and CO$_3^{2-}$ uptake by HCP can be estimated as follows:

$$
R_d = \frac{m_{cem} \cdot f}{m_{aq}} \left( \frac{V_{sol}}{M_{cem}} \right) \quad [m^3/kg] \quad (A1)
$$

$m_{cem}$: number of moles of an element (stable isotope) in the repository associated with HCP [mol]

$m_{aq}$: number of moles of the element (stable isotope) in pore water at equilibrium [mol]

$V_{sol}$: total volume of pore water in the cavern [m$^3$]

$M_{cem}$: total mass of cement in the cavern [kg]

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

The basic system parameters of a SMA repository ($M_{cem}$, $V_{sol}$), which are based on the current design, are summarized in Tab. A1-1. The input data used to estimate an operational distribution ratio for $^{59,63}$Ni, $^{60}$Co and $^{14}$CO$_3^{2-}$ are listed in Tab. A1-2.
For fresh, i.e. not eluted HCP the operational distribution ratio $R_d$ can be directly calculated with the measured concentration of an element in HCP ($c_{cem}$, mol/kg) and the concentration of this element in solution in equilibrium with HCP ($c_{aq}$, mol/L).

$$R_d = \frac{c_{cem} f}{c_{aq}} \quad [\text{m}^3/\text{kg}] \quad (A2)$$

The proportion of the stable isotope inventory accessible to isotopic exchange, $f$, depends on the recrystallization rate of the solid. For example, Wieland et al. (2006) showed that only a small portion of the inventory of stable Ni in the cement matrix is accessible to the isotopic exchange reaction with $^{63}$Ni (range ~ 2 – ~ 5 %) after 30 days reaction time. Pointeau et al. (2003) derived a relationship between the grain size of calcite crystals and the fraction of $\text{CO}_3^{2-}$ available for isotopic exchange. For an average particle size of ~ 10 µm the accessibility factor was determined to be 0.5 % after 140 days reaction time. Uncertainties are associated with the parameters used for calculating the $R_d$ value, in particular the Ni and Co concentrations in cement pore water. Therefore, realistic and upper bound values are considered in the case of Ni and Co retention (Tab. A1-2)

Tab. A1-1: Characteristic parameters of the L/ILW (SMA) repository per metre cavern length (Nagra 2008, Table A3.2-1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Notation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total volume [m$^3$/m]</td>
<td>$V_{tot}$</td>
<td>110</td>
</tr>
<tr>
<td>Average porosity [-]</td>
<td>$\varepsilon$</td>
<td>0.2</td>
</tr>
<tr>
<td>Total volume of solution* [m$^3$/m]</td>
<td>$V_{sol}$</td>
<td>22</td>
</tr>
<tr>
<td>Mass of HCP [kg/m]</td>
<td>$M_{cem}$</td>
<td>$3.85 \times 10^4$</td>
</tr>
</tbody>
</table>

* $V_{sol} = \varepsilon V_{tot}$
Tab. A1-2: Input data used to estimate distribution ratios for \(^{59,63}\text{Ni}\), \(^{60}\text{Co}\) and \(^{14}\text{CO}_3^{2-}\) on HCP.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Notation</th>
<th>\text{Ni}</th>
<th>\text{Co}</th>
<th>\text{CO}_3^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation (A2)</td>
<td>(c_{\text{cem}})</td>
<td>3.2 \times 10^{-4}</td>
<td>5.6 \times 10^{-5}</td>
<td>0.11</td>
</tr>
<tr>
<td>Concentration of stable element in HCP [mol/kg] *</td>
<td>(c_{\text{aq}})</td>
<td>(10^{-7})</td>
<td>(2 \times 10^{-8})</td>
<td>(4.46 \times 10^{-5}) (pH = 13.1) (8.04 \times 10^{-6}) (pH = 12.54)</td>
</tr>
<tr>
<td>Concentration of element in solution in equilibrium with HCP [mol/L] **</td>
<td>(f)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Accessibility factor</td>
<td>(c_{\text{aq}})</td>
<td>(3 \times 10^{-6})</td>
<td>(6 \times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>Upper bound for (c_{\text{aq}})</td>
<td>(m_{\text{em}})</td>
<td>12.32</td>
<td>2.16</td>
<td>4.2 \times 10^{3}</td>
</tr>
<tr>
<td>Total inventory of stable element in HCP [mol/m] ***</td>
<td>(m_{\text{aq}})</td>
<td>(2.2 \times 10^{3})</td>
<td>(4.4 \times 10^{4})</td>
<td>(9.8 \times 10^{-4}) (pH = 13.1) (1.8 \times 10^{-3}) (pH = 12.54)</td>
</tr>
<tr>
<td>Total inventory of stable element in solution [mol/m] ****</td>
<td>(m_{\text{aq}})</td>
<td>(6.6 \times 10^{-2})</td>
<td>(1.3 \times 10^{-2})</td>
<td></td>
</tr>
<tr>
<td>Upper bound for (m_{\text{aq}}) total inventory of stable element in solution [mol/m] ****</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Assuming the following concentrations in unhydrated cement: Ni = 24.3 ppm and Co = 4.28 ppm (Tab. 2.3; Section 2.2.3). The CaCO\(_3\) of HCP corresponds to 1.1 wt.-% (Tab. 2.2; Section 2.2.2). Note that 1 kg unhydrated cement corresponds to \(\approx\) 1.3 kg HCP prepared at w/c = 0.4.

** Aqueous Ni concentration in line with those reported by Wieland & Van Loon (2002), Wieland et al. (2006) and Engelsen et al. (2010). Aqueous Co concentration estimated to be a factor of 5 lower than that of Ni in line with differences in the solubility of the two radionuclides (Berner 2014) and in accordance with unpublished measurements of the Co concentration in pore water squeezed from HCP. Carbonate concentrations as given in Kosakowski et al. (2014) and Berner (2014).

*** \(m_{\text{cen}} = M_{\text{cen}}\cdot c_{\text{cem}}\)

**** \(m_{\text{aq}} = V_{\text{aq}}\cdot c_{\text{aq}}\)

Estimating an operational \(R_d\) value on the basis of Eq. (A1) requires that both the concentration of the element in HCP and in solution do not change significantly over time. A comparison of the total inventories of stable Ni, Co and CO\(_3^{2-}\) in HCP with their concentrations in cement pore water (Tab. A-2) shows that after about 1000 exchange cycles of the near-field pore water the inventories of the stable isotopes in HCP will decrease by \(\approx\) 18 % in the case of Ni, \(\approx\) 20 % in the case of Co and by \(\approx\) 5 % in the case of CO\(_3^{2-}\) (pH = 12.54) indicating that, under the given conditions, the distribution ratio will not significantly change with time. Assuming the upper bound of aqueous concentrations for Ni and Co (Tab. A1-2), however, a reduction in the distribution ratios of the two radionuclides is expected to be significant (> 50 %) already after 100 exchange cycles. Note that within 100'000 years less than 2 pore volumes are expected to be exchanged in the concrete of a repository in Opalinus Clay and about 130 pore volumes in the Palfris Formation (Kosakowski et al. 2014).
The operational \( R_d \) values calculated according to Eq. (A-1) are listed in Tab. A1-3. The lower bounds of the \( R_d \) values for \(^{59,63}\text{Ni} \) and \(^{60}\text{Co} \) have been estimated using the upper bounds for the aqueous Ni and Co concentrations. The accessibility factors are arbitrarily set to \( f = 0.1 \) in the case of \(^{59,63}\text{Ni} \) and \(^{60}\text{Co} \) and to \( f = 0.01 \) in the case of \(^{14}\text{CO}_3^{2-} \). Note that the selected values expected to be valid in the long run are only slightly higher than those determined in short-term experiments, i.e. \( f = 0.02 \) – \( 0.05 \) for \(^{63}\text{Ni} \) (and Co by analogy) (Wieland et al. 2006) and \( f = 0.005 \) for \(^{14}\text{CO}_3^{2-} \) (Pointeau et al. 2003). To calculate the values listed in Tab. A1-3 only stable isotopes are used. Thus, radioisotopes are conservatively neglected.

Tab. A1-3: Estimated \( R_d \) values for \(^{59,63}\text{Ni} \), \(^{60}\text{Co} \) und \(^{14}\text{CO}_3^{2-} \) in the L/ILW (SMA) repository.

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>( R_d ) value [m(^3/kg)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{59,63}\text{Ni} )</td>
<td>0.32 0.01</td>
</tr>
<tr>
<td>(^{60}\text{Co} )</td>
<td>0.28 0.009</td>
</tr>
<tr>
<td>(^{14}\text{CO}_3^{2-} )</td>
<td>0.14 0.02</td>
</tr>
</tbody>
</table>

* Estimated with Eq. (A1) using \( m_{aq} = 2.2 \times 10^{-3} \) and \( f = 0.1 \) for Ni, \( m_{aq} = 4.4 \times 10^{-4} \) and \( f = 0.1 \) for Co, and \( m_{aq} = 1.8 \times 10^{-1} \) and \( f = 0.01 \) for \(^{14}\text{CO}_3^{2-} \).

** Estimated with Eq. (A1) using \( m_{aq} = 6.6 \times 10^{-2} \) and \( f = 0.1 \) for Ni, \( m_{aq} = 1.3 \times 10^{-2} \) and \( f = 0.1 \) for Co, and \( m_{aq} = 9.8 \times 10^{-1} \) and \( f = 0.01 \) for \(^{14}\text{CO}_3^{2-} \).

Note that on the assumption of isotopic exchange with the total stable Ni, Co and \(^{14}\text{CO}_3^{2-} \) inventories in the near field, i.e. \( f = 1 \), the \( R_d \) values listed in Tab. A1-3 would increase by an order of magnitude (\( R_d = 3.2 \) and \( 2.8 \) m\(^3/kg\)) in the case of Ni and Co and by two orders of magnitude (\( R_d = 12 \) m\(^3/kg\)) in the case of \(^{14}\text{CO}_3^{2-} \).

### A1.4 Comparison with literature data

#### A1.4.1 \(^{59,63}\text{Ni} \) and \(^{60}\text{Co} \)

From batch sorption data Pilkington & Stone (1990) determined a distribution coefficient of \( 0.1 \) m\(^3/kg\) for Ni uptake by cement paste although, as stated by the authors, there are considerable experimental uncertainties associated with the sorption data. This value was recommended in the earlier sorption database for a L/ILW (SMA) repository (Bradbury & Van Loon 1997) as the value was in good agreement with in-house measurements (0.2 m\(^3/kg\); Sarott 1996) and with the earlier sorption data published by Hietanen et al. (1984), which reported \( K_d \) values ranging between 0.03 and 0.15 m\(^3/kg\) for Ni on concrete. Holgersson et al. (1998) determined slowly increasing distribution coefficients for Ni on cement paste. After 2 months of equilibration time the \( K_d \) value was reported to be \( 0.04 \) m\(^3/kg\). Wieland et al. (2006) determined an \( R_d \) value of \( 0.15 \) m\(^3/kg\) on pristine HCP, that is in absence of stable Ni added in batch-type sorption experiments carried out at a S/L ratio of \( 2.5 \times 10^{-2} \) kg/L.

Jakob et al. (1999) reported through-diffusion data of Ni on HCP which allowed \( K_d \) values to be estimated. In the latter study, steady state was not reached within the experimental times (400 – 800 days) and therefore, the assumption of equilibrium sorption was not fully justified.
Inclusion of sorption kinetics allowed better fitting of the data and resulted in $K_d$ values ranging from 0.02 to 0.04 m$^3$/kg. This is a factor 5-10 lower than the values obtained in the batch sorption experiments using the same cement (Sarott 1996, Wieland et al. 2000). From multi-tracer diffusion studies in cementitious systems performed with several radiotracers, Holgersson et al. (1998) concluded that discrepancies between batch sorption and diffusion data can generally be explained by the effect of matrix diffusion, which is usually not taken into account in the modelling of diffusion data. However, in case of the Ni diffusion studies (which were performed for about 1 year) the authors observed no clear-cut difference between diffusion through fractures and matrix diffusion. Holgersson et al. (1998) determined a $K_d$ value of 0.04 m$^3$/kg from the diffusion experiments, which is in agreement with the batch sorption data determined by the same author.

Experimental data for Co are scarce. Idemitsu et al. (1991) estimated $K_d$ values from in-diffusion experiments carried out on several kinds of water-saturated concretes, which were reported to range in value between 0.005 and 0.015 m$^3$/kg.

**A1.4.2 14CO$_3^{2-}$**

Allard et al. (1981), Hietanen et al. (1984), Bayliss et al. (1988), Matsumoto et al. (1995), Noshita et al. (1996) and Pointeau et al. (2003, 2008) reported sorption measurements with $14$CO$_3^{2-}$ on cement pastes and concrete. In general, strong uptake was observed with $R_d$ values ranging between $\sim$ 0.7 m$^3$/kg and $\sim$30 m$^3$/kg. The distribution ratio was found to depend on the degradation stage of cement and the S/L ratio of the cementitious system. For stage II of the cement degradation Wang et al. (2009) selected an $R_d$ value (best estimate) of 5 m$^3$/kg (lower limit: 2 m$^3$/kg, upper limit: 20 m$^3$/kg) while slightly lower values were selected for stage I of cement degradation (best estimate: 2 m$^3$/kg, lower limit: 0.7 m$^3$/kg, upper limit: 3 m$^3$/kg).

**A1.5 Discussion and recommendation**

The estimated distribution ratios based on the various approaches, i.e. values estimated on the basis of "shared solubility", batch sorption measurements and diffusion experiments, vary between $\sim$ 0.02 and $\sim$ 3.2 m$^3$/kg in the case of Ni. The highest values are obtained from the assumed analogous behaviour of radioactive and stable, cement-based Ni ($f = 1$) and assuming an aqueous Ni concentration of $10^{-7}$ (R$_d$ $\sim$ 3.2 m$^3$/kg). Calculated values are lower assuming isotopic exchange with 10% of the inventory of stable Ni and an aqueous Ni concentration of $10^{-7}$ M (R$_d$ $\sim$ 0.32 m$^3$/kg). Lowest R$_d$ values are obtained using an accessibility factor $f = 0.1$ and an aqueous Ni concentration of $3 \times 10^{-6}$ M (R$_d$ $\sim$ 0.01 m$^3$/kg; Tab. A1-3). The lower limits further agree with $K_d$ values derived from diffusion experiments (Holgersson et al. 1998, Jakob et al. 1999). As pointed out in the latter studies the obtained retardation values for Ni strongly depend on the experimental initial and boundary conditions in batch and diffusion experiments. The data obtained from diffusion studies further suggest very slowly increasing uptake of Ni with time and therefore an increasing $K_d$ value with time.

The measurements of stable Ni concentrations in cement pore waters reported by Wieland & Van Loon (2002) show that Ni uptake is governed by a solubility-limiting process and that isotopic exchange of active Ni with cement-derived Ni is a plausible uptake mechanism. The latter process, which is likely to be slow, would result in estimated distribution ratios $> 1$ m$^3$/kg if the total inventory of stable Ni were accessible ($f = 1$). The batch sorption experiments performed by Pilkington & Stone (1990), Sarrot (1996) and Wieland et al. (2006) indicate $R_d$ values ranging between 0.1 and 0.2 m$^3$/kg. Under the assumption of slow isotopic exchange, these data may reflect "intermediate" pseudo-stationary conditions in which the active Ni "sees" only a small fraction of the inactive Ni pool.
Based on the above discussion and with a view to the currently existing uncertainties in connection with Ni uptake by HCP, \( R_d = 0.3 \text{ m}^3/\text{kg} \) is recommended as a "best estimate" (Tab. A1-4). This value is similar to that selected for the previous sorption database (Bradbury & Sarott 1994, Bradbury & Van Loon 1997) (\( R_d = 0.1 \text{ m}^3/\text{kg} \)). A lower limit of 0.01 \( \text{m}^3/\text{kg} \) is assigned on the basis of the diffusion data of Holgersson et al. (1998) and Jakob et al. (1999). Finally, the upper limit is set to 3 \( \text{m}^3/\text{kg} \), which accounts for substantial isotopic exchange with cement-based Ni (\( f = 1 \) in Eq. A-1).

In the case of Co the estimated distribution ratios obtained from the various approaches vary between \( \sim 0.009 \) and \( \sim 2.8 \text{ m}^3/\text{kg} \). Note that the highest values result from the assumed analogous behaviour of radioactive and stable, cement-based Co (\( f = 1 \) in Eq. A1) and assuming an aqueous Co concentration of \( 2 \times 10^{-8} \text{ M} \) (\( R_d \sim 2.8 \text{ m}^3/\text{kg} \)). Calculated values are lower on the assumption that isotopic exchange with only 10% of the inventory of stable Co occurs (\( f = 0.1 \) in Eq. A1) and that the aqueous Co concentration is \( 2 \times 10^{-8} \text{ M} \) (\( R_d \sim 0.28 \text{ m}^3/\text{kg} \)). Lowest \( R_d \) values are estimated using an accessibility factor \( f = 0.1 \) and an aqueous Co concentration of \( 6 \times 10^{-7} \text{ M} \) (\( R_d \sim 0.009 \text{ m}^3/\text{kg} \)). The lower limit further agrees with \( K_d \) values derived from in-diffusion experiments as reported by Idemitsu et al. (1991) (\( K_d = 0.005 \) and 0.015 \( \text{m}^3/\text{kg} \)). On the basis of the currently available information \( R_d = 0.3 \text{ m}^3/\text{kg} \) is recommended as a "best estimate" (Tab. A1-4). This value is similar to that selected for the previous sorption database (Bradbury & Van Loon 1997) (\( R_d = 0.1 \text{ m}^3/\text{kg} \)). A lower limit of 0.01 \( \text{m}^3/\text{kg} \) is assigned in accordance with the diffusion data reported by Idemitsu et al. (1991). Finally, the upper limit is set to 3 \( \text{m}^3/\text{kg} \), which accounts for substantial isotopic exchange with cement-based Co (\( f = 1 \) in Eq. A1). The recommended values for Ni and Co further account for the chemical analogy between Ni and Co.

The \( R_d \) value for \( ^{14}\text{CO}_3^{2-} \) estimated on the basis of isotopic exchange with \( \text{CO}_3^{2-} \) bound in calcite depends on the accessibility factor. For \( f = 1 \), i.e. if the total \( \text{CO}_3^{2-} \) inventory is accessible to isotopic exchange an \( R_d \) value of 12 \( \text{ m}^3/\text{kg} \) is obtained. \( R_d \) value = 0.12 \( \text{ m}^3/\text{kg} \) is estimated on the assumption that only 1% of the \( \text{CO}_3^{2-} \) inventory is accessible (\( f = 0.01 \) in Eq. A1). Note that sorption measurements with \( ^{14}\text{CO}_3^{2-} \) on HCP gave \( R_d \) values ranging between \( \sim 0.7 \text{ m}^3/\text{kg} \) and 30 \( \text{ m}^3/\text{kg} \) (Wang et al. 2009). A cautious approach is taken by recommending \( R_d = 0.1 \text{ m}^3/\text{kg} \) as "best estimate" (lower limit: 0.01 \( \text{m}^3/\text{kg} \), upper limit: 1 \( \text{m}^3/\text{kg} \)).

Tab. A1-4: Recommended \( R_d \) values for \( ^{59,63}\text{Ni} \), \( ^{60}\text{Co} \) und \( ^{14}\text{CO}_3^{2-} \) in the L/ILW (SMA) repository.

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>( R_d ) value [( \text{m}^3/\text{kg} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{59,63}\text{Ni} )</td>
<td>0.3</td>
</tr>
<tr>
<td>( ^{60}\text{Co} )</td>
<td>0.3</td>
</tr>
<tr>
<td>( ^{14}\text{CO}_3^{2-} )</td>
<td>0.1</td>
</tr>
</tbody>
</table>
A1.6 References


Appendix B: Sorption Values used for Dose Calculations

Bernhard Schwyn and Veerle Cloet (Nagra)

B1 Introduction

The present report presents sorption values valid in a cementitious near field of an L/ILW and ILW repository. A versatile data base was assembled which is applicable to various conditions potentially prevailing in a cement near field.

The data base accounts for

- different stages of cement degradation (Tab. 6.1 – 6.3),
- the redox state of the safety relevant elements (Tab. 6.1 – 6.5),
- the sorption value range for each element (derived by international expert elicitation, Tab. 6.2),
- the influence of near-field colloids (Tab. 6.3),
- the influence of high salinity porewater in the host rock (Tab. 6.4) and
- the influence of complexing ligands present in some waste sorts (Tab. 6.5)

The present data base does not address the influence of temperature, because the temperature effect is considered to be small (5 – 10 °C) and short-lived (only a few months after repository closure). For the radionuclides $^{59,63}$Ni, $^{60}$Co and $^{14}$C$_{inorg}$ operational sorption values are derived from shared solubilities with stable isotopes in solids, contained in the cement paste. For the corresponding elements no true sorption value can be measured. These operational K$_d$ values are used for the near field of an L/ILW repository for which no solubility limits are included in the dose calculations. For the near field of an ILW repository the shared solubilities are directly used and K$_d$ values for the above mentioned radionuclides are set to zero.

The present Appendix extracts from the extensive sorption data base mentioned above, the adequate sorption value data sets for the near-field conditions expected for an ILW repository in Opalinus Clay and an L/ILW repository in Opalinus Clay, 'Brauner Dogger', Effingen Member or Helvetic Marls). The data extraction presented here considers the requirements of the regulator (ENSI 2010).

Data sets are extracted for waste group 1 and waste group 2. For waste group 1 no increased mobility of the radionuclides by compounds contained in the waste is expected. For waste group 2 sorption values are reduced for some radionuclides due to the influence of certain compounds contained in the waste.

In the main part and in Appendix 1 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. R$_d$ or K$_d$ is also called "sorption value".
Cement degradation

In order to extract the $K_d$ values for the right cement degradation stage the long-term evolution of the repository sited in the above mentioned host rocks needs to be assessed.

The chemical long-term evolution of the cement in the L/ILW near field depends on the water flux through the near field (and therefore on the flux in the host rock), on the diffusive exchange of water and solutes with the surrounding host rock and, secondarily, on the porewater composition of the host rock. Kosakowski et al. (2014) modelled the portlandite dissolution front migrating into the backfilled emplacement tunnel. The type of tunnel foreseen in the L/ILW repository is K09 (Nagra 2008) with a height of 12.6 m and a width of 10.4 m. For all potential host rocks (Opalinus Clay, 'Brown Dogger', Effingen Member and Helvetic Marls) the migration front is clearly diffusion dominated and advances, dependent on the host rock, not further than 2 metres within 100'000 years.

An interpretation of the modelling result needs to be put in perspective considering the following arguments:

- Most of the cement in the tunnels remains in cement degradation stage II (portlandite present)
- The portlandite depleted regions still contain sorbing C-S-H phases (cement degradation stage III)
- The model neglects an expected clogging at the interface tunnel - host rock which would slow down transport and consequently cement degradation
- The model assumes fully saturated conditions in the tunnels. The tunnels, however, are expected to stay partially saturated for several thousands of years (Papafotiou & Senger 2014). Under such conditions transport in the liquid phase (porewater) and therefore cement degradation is drastically slowed down.

In conclusion, sorption values from stage III are not taken into account for dose calculations for the relevant time span of an L/ILW repository. Unless otherwise stated, the sorption values from stage II are selected for dose calculations.

The conclusions drawn above are also valid for an ILW repository. For the latter a K06 tunnel type is foreseen (Nagra 2008) which has a smaller cross section (height: 11.9 m, width: 7.6 m). As host rock only Opalinus Clay is considered.

**B2 Sorption values for waste group 1**

The data sets used to derive reference values and lower limits for waste group 1 are compiled in Tab. A2-3.

**Basic Reference Values**

In a first step a set of basic reference values is compiled

The values were taken from Tab. 6.1. Generally, the values for cement degradation stage II were taken with the following exceptions:
Cl, Se, Cs

K_d values were conservatively taken from degradation stage I. It is assumed that elements with a small sorption value (<0.1 m^3/kg) in degradation stage I would be washed out before degradation stage II is reached). This rule also applies to K and I, but does not affect the selected K_d, since the values in stage I and II are identical.

14C_{inorg}, 60Co, 59,63Ni

The K_d values of these radionuclides for L/ILW 1 were based on shared solubilities by using equation (A2 in Appendix 1). The inventories and accessibility factors for Ni, Co, and C_{inorg} were taken from Tab. A1-2 in Appendix 1 (see also Tab. A2-1).

Tab.B-1: Inventories of solids in the cement paste and availability for isotope exchange.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>C_{inorg}</th>
</tr>
</thead>
<tbody>
<tr>
<td>c_{cem}</td>
<td>mol/kg</td>
<td>3.20 × 10^{-4}</td>
<td>5.60 × 10^{-5}</td>
</tr>
<tr>
<td>f</td>
<td></td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>c_{cem (available)}</td>
<td>mol/kg</td>
<td>3.20 × 10^{-5}</td>
<td>5.60 × 10^{-6}</td>
</tr>
</tbody>
</table>

However, the solubilities (c_{aq}) for Co and Ni listed in Tab A1-2, which were derived from experimental results, were not used to calculate the K_d values. Instead, the solubilities for Co and Ni as calculated by Berner (2014) were used (Tab. A2-2). As a result, the K_d values for 60Co and 59,63Ni using this procedure are lower than the ones recommended in Tab. A1-4.

Tab. B-2: Solubilities used to calculate K_d in L/ILW 1 (excerpt from Berner 2014).

<table>
<thead>
<tr>
<th>Element</th>
<th>ILW 1</th>
<th>ILW 2 (influence of ISA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference value [mol/kg H_2O]</td>
<td>Upper bound value [mol/kg H_2O]</td>
</tr>
<tr>
<td>C_{inorg}</td>
<td>8 × 10^{-6}</td>
<td>4 × 10^{-5}</td>
</tr>
<tr>
<td>Co</td>
<td>5 × 10^{-7}</td>
<td>2 × 10^{-5}</td>
</tr>
<tr>
<td>Ni</td>
<td>3 × 10^{-6}</td>
<td>2 × 10^{-4}</td>
</tr>
</tbody>
</table>

Pa and U

For the redox sensitive elements Pa and U the values for oxidizing conditions were taken in accordance with the speciation derived by Berner (2014). For the other redox sensitive elements, namely Se (degradation stage I, see above), Tc, Np and Pu, the value for reducing conditions were selected.
Reference values for waste group 1

The reference values to be used for safety calculations for L/ILW 1 and ILW 1 were derived from the basic reference values by considering the formation of colloids. The corresponding realistic sorption reduction factors for reducing conditions in stage II degraded cement were taken from Tab. 6.3.

Since the sorption values for $^{14}\text{C}_{\text{inorg}}$, $^{60}\text{Co}$ and $^{59,63}\text{Ni}$ were derived from isotopic dilution in solids, these values need to be set to zero for ILW 1, where solubility limits (shared solubilities) are considered.

Lower limits of sorption values for waste group 1

As a basis to derive lower limits of sorption values for L/ILW 1 and ILW 1 the following three data sets were compiled:

1. Pessimistic data set:
   The basic reference values were divided by the experimental uncertainty factor $f_E$ taken from Tab. 6.1 on the one hand, and by the pessimistic reduction factors for colloids (Tab. 6.3) on the other hand. Exceptions are the operational $K_d$ values for $^{14}\text{C}_{\text{inorg}}$, $^{60}\text{Co}$ and $^{59,63}\text{Ni}$, which were derived analogously to the basic reference values using the upper solubility limit given by Berner (2014).

2. Lower limit values from Tab. 6.2:
   Values were selected according to the rules used for the basic reference value (see above).

3. Values for high salinity groundwater (Tab. 6.4):
   The same redox conditions for the individual elements were chosen as for the basic reference value (see above).

As lower limit sorption values for L/ILW 1 and ILW 1 the respective minimum of the three data sets was taken.
Tab. B-3: Derivation of sorption values for L/ILW 1, ILW 1.

The minimum of "Pessimistic data set", "Lower limit values, Tab. 6.2" and "High salinity groundwater" is shaded in gray and determines the lower limit L/ILW 1, ILW 1.

<table>
<thead>
<tr>
<th>Element or Radio-nuclide</th>
<th>Basic Reference value [m³/kg]</th>
<th>Colloid factor (real.)</th>
<th>Reference value [m³/kg]</th>
<th>Colloid factor (pess.)</th>
<th>f_P</th>
<th>Pessimistic data set [m³/kg]</th>
<th>Lower limit values, Tab. 6.2 [m³/kg]</th>
<th>High salinity groundwater [m³/kg]</th>
<th>Lower limit L/ILW 1, ILW 1 [m³/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0</td>
<td>n.a.</td>
<td>0</td>
<td>n.a.</td>
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<td>0</td>
<td>n.a.</td>
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<td>0</td>
</tr>
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<td>14C</td>
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<td>1</td>
<td>1.4</td>
<td>1.0 × 10⁻³</td>
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<td>0</td>
</tr>
<tr>
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<td>5.0 × 10⁻⁵</td>
<td>1</td>
<td>1.4</td>
<td>3.6 × 10⁻⁷</td>
<td>1 × 10⁻³</td>
<td>4.8 × 10⁻⁴</td>
<td>4.8 × 10⁻⁴</td>
</tr>
<tr>
<td>K</td>
<td>1.0 × 10⁻⁴</td>
<td>1</td>
<td>1.0 × 10⁻⁴</td>
<td>1</td>
<td>1.4</td>
<td>7.1 × 10⁻⁵</td>
<td>1.0 × 10⁻⁴</td>
<td>7.1 × 10⁻⁵</td>
<td>7.1 × 10⁻⁵</td>
</tr>
<tr>
<td>⁴⁰Co</td>
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<td>n.a.</td>
<td>2.8 × 10⁻⁴</td>
</tr>
<tr>
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<td>0.010</td>
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<td>1.6 × 10⁻³</td>
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<td>0.10</td>
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<td>1.0</td>
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<td>1</td>
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<td>Cs</td>
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<td>1</td>
<td>1.4</td>
<td>3.6 × 10⁻⁷</td>
<td>1 × 10⁻⁴</td>
<td>2.5 × 10⁻⁴</td>
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<td>83</td>
<td>2</td>
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<td>15</td>
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<td>1.0</td>
</tr>
<tr>
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<td>3.0</td>
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<td>2.0</td>
<td>1.0</td>
<td>0.050</td>
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</tr>
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<td>n.a.</td>
<td>1</td>
<td>0</td>
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</tr>
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<td>1 × 10⁻³</td>
<td>8.3 × 10⁻³</td>
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</tr>
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<td>83</td>
<td>2</td>
<td>3.3</td>
<td>15</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
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<td>83</td>
<td>2</td>
<td>3.3</td>
<td>15</td>
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<td>20</td>
<td>1.3</td>
<td>3.3</td>
<td>4.7</td>
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</tr>
<tr>
<td>U</td>
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<td>20</td>
<td>1.3</td>
<td>3.3</td>
<td>4.7</td>
<td>3.0</td>
<td>0.20</td>
<td>0.20</td>
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<td>100</td>
<td>1.2</td>
<td>83</td>
<td>2</td>
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<td>15</td>
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</tr>
<tr>
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<td>83</td>
<td>2</td>
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<td>15</td>
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<td>1.0</td>
<td>1.0</td>
</tr>
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<td>83</td>
<td>2</td>
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<td>15</td>
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<td>1.0</td>
</tr>
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<td>15</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
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n.a.: Not applicable.
B3 Sorption values for waste group 2

The data sets used to derive reference values and lower limits for waste group 2 are compiled in Tab. A2-4. The compilation of the basic reference values is described in section A2.2; the values were taken from Tab. A2-3.

Reference values for waste group 2

The reference values for L/ILW 2 and ILW 2 were obtained by dividing the basic reference values by the corresponding sorption reduction factors for complexing ligands from Tab. 6.5. Sorption reduction due to colloids is not considered since such a reduction is expected only for sorption values higher than the resulting waste group 2 values.

Lower limit values for waste group 2

As a basis to derive lower limit values for L/ILW 2 and ILW 2 the following two data sets were used:

1. Lower limit sorption values for L/ILW 1, ILW 1:
   These values were taken from Tab. A2-3.

2. Pessimistic data set L/ILW 2, ILW 2:
   The basic reference values were divided by the experimental uncertainty factor \( f_e \) taken from Tab. 6.1 on the one hand, and by the sorption reduction factors for complexing ligands (Tab. 6.5) on the other hand. A pessimistic data set is only calculated for those elements that can form complexes with complexing ligands.

As lower limit sorption values for L/ILW 2 and ILW 2 the respective minimum of the two data sets was taken.
Tab. B-4: Derivation of sorption values for L/ILW 2, ILW 2.

The minimum of "Lower limit L/ILW 1, ILW 1" and, "Pessimistic data set" is shaded in gray and determines the lower limit L/ILW 2, ILW 2.

<table>
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<th>Element or Radio-nuclide</th>
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<th>Sorption reduction factor</th>
<th>Reference value [m³/kg]</th>
<th>Lower limit L/ILW 1, ILW 1 [m³/kg]</th>
<th>f_E</th>
<th>Pessimistic data set [m³/kg]</th>
<th>Lower limit L/ILW 2, ILW 2 [m³/kg]</th>
</tr>
</thead>
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<td>0</td>
<td>0</td>
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<td>n.a.</td>
<td>n.a.</td>
<td>0</td>
</tr>
<tr>
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<td>0.028</td>
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<td>n.a.</td>
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<td>1.0 × 10⁻⁵</td>
<td>0</td>
<td>1.4</td>
<td>n.a.</td>
<td>4.8 × 10⁻⁴</td>
<td>7.1 × 10⁻⁵</td>
</tr>
<tr>
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<td>5.0 × 10⁻³</td>
<td>4.8 × 10⁻⁴</td>
<td>1.4</td>
<td>n.a.</td>
<td>4.8 × 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>K</td>
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<td>1.0 × 10⁻⁴</td>
<td>7.1 × 10⁻⁵</td>
<td>1.4</td>
<td>n.a.</td>
<td>7.1 × 10⁻⁵</td>
<td></td>
</tr>
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<td>2.8 × 10⁻⁴</td>
<td>1</td>
<td>2.2 × 10⁻⁴</td>
<td>2.2 × 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>^59,63_Ni</td>
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<td>1</td>
<td>2.1 × 10⁻⁴</td>
<td>1.6 × 10⁻⁴</td>
<td></td>
</tr>
<tr>
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<td>0.03</td>
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<td>n.a.</td>
<td>1.0 × 10⁻⁴</td>
<td></td>
</tr>
<tr>
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<td>0.010</td>
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<td>1.4</td>
<td>n.a.</td>
<td>1.6 × 10⁻⁵</td>
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</tr>
<tr>
<td>Zr</td>
<td>10 10</td>
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<td>1.0</td>
<td>0.10</td>
<td>n.a.</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Nb</td>
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<td>1.0</td>
<td>0.10</td>
<td>1.4</td>
<td>n.a.</td>
<td>0.10</td>
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<tr>
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<td>0</td>
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<td>n.a.</td>
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</tr>
<tr>
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<td>1.0</td>
<td>0.10</td>
<td>1.4</td>
<td>n.a.</td>
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<td>0</td>
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<td>n.a.</td>
<td>0</td>
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<tr>
<td>Sn</td>
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<td>3.3</td>
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<td>0.30</td>
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<tr>
<td>I</td>
<td>1.0 × 10⁻³ 1</td>
<td>1.0 × 10⁻³</td>
<td>0</td>
<td>1.4</td>
<td>n.a.</td>
<td>0</td>
<td></td>
</tr>
<tr>
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<td>5.0 × 10⁻⁴</td>
<td>1.0 × 10⁻⁴</td>
<td>1.4</td>
<td>n.a.</td>
<td>1.0 × 10⁻⁴</td>
<td></td>
</tr>
<tr>
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<td>1.0</td>
<td>3.3</td>
<td>0.30</td>
<td>0.30</td>
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</tr>
<tr>
<td>Eu</td>
<td>100 100</td>
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<td>3.3</td>
<td>0.30</td>
<td>0.30</td>
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<td>0.21</td>
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<td>n.a.</td>
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<td>0.050</td>
<td>1.0 × 10⁻³</td>
<td>1.4</td>
<td>n.a.</td>
<td>1.0 × 10⁻³</td>
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<tr>
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<td>3.3</td>
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<td>0.20</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Pu</td>
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</tr>
<tr>
<td>Am</td>
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<td>1.0</td>
<td>3.3</td>
<td>3.0</td>
<td>1.0</td>
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</tr>
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<td>3.0</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

n.a.: Not applicable.
**B4 Sorption summary table for the L/ILW and an ILW near field**

The sorption values for a cementitious near field to be used for dose calculations within the provisional safety assessments are listed in Tab. A2-5. The values are rounded to one significant figure. According to ENSI (2010) the lower limit value needs to be set to 0 if the corresponding reference value is < 0.001 m³/kg. Affected values are shaded in gray.
Tab. B-5: Sorption values ($K_d$) for the L/ILW and ILW near field (cement).

<table>
<thead>
<tr>
<th>Element or Radionuclide</th>
<th>L/ILW 1, ILW 1</th>
<th>L/ILW 2, ILW 2</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Reference value [m$^3$/kg]</td>
<td>Lower limit value [m$^3$/kg]</td>
</tr>
<tr>
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<td>0</td>
</tr>
<tr>
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</tr>
<tr>
<td>C$_{org}$</td>
<td>$1 \times 10^{-5}$</td>
<td>0</td>
</tr>
<tr>
<td>Cl</td>
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<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>K</td>
<td>$1 \times 10^{-4}$</td>
<td>$7 \times 10^{-5}$**</td>
</tr>
<tr>
<td>$^{60}$Co*</td>
<td>0.01</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^{59,63}$Ni*</td>
<td>0.01</td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Se</td>
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</tr>
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</tr>
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<td>0.1</td>
</tr>
<tr>
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<tr>
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<tr>
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</tbody>
</table>

* For the ILW repository the sorption value must be set to 0 since a solubility limit is considered (isotope exchange).

** According to ENSI (2010) the sorption value must be set to 0.
B5 References


ENSI (2010): Anforderungen an die provisorischen Sicherheitsanalysen und den sicherheitstechnischen Vergleich Sachplan geologische Tiefenlager Etappe 2. ENSI Aktennotiz. AN ENSI 33/75. Eidgenössisches Nuklearsicherheitsinspektorat ENSI, Brugg, Switzerland.

