Development of a sorption data base for the cementitious near-field of a repository for radioactive waste*

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The migration of radionuclides within a repository for radioactive waste is retarded due to interaction with the engineered barrier system. Sorption processes play a decisive role in the retardation of radionuclides in the repository environment, and thus, the development of sorption data bases (SDBs) is an important task and an integral part of performance assessment. The methodology applied in the development of a SDB for the cementitious near-field of a repository for long-lived intermediate-level waste is presented in this study. The development of such a SDB requires knowledge of the chemical conditions of the near-field and information on the uptake process of radionuclides by hardened cement paste. The principles upon which the selection of the “best available” laboratory sorption values is based are outlined. The influence of cellulose degradation products, cement additives and cement-derived colloids on the sorption behaviour of radionuclides is addressed in conjunction with the development of the SDB.

1 Introduction

The migration of radionuclides in a repository environment is retarded due to their interaction with engineered and natural barriers such as the cementitious materials in the near-field and the host rock. The retardation of radionuclides by these matrices is controlled by chemical reactions occurring at the solid-liquid interface. Thus, the role of sorption processes is decisive and one of the pillars upon which safety assessments for waste repository systems are built [1]. The development of well-documented sorption data bases (SDBs) is regarded as being an integral part in the performance assessment (PA) studies performed within the framework of the Swiss waste management programme. Over the past several years SDBs have been developed and updated in our laboratory, including SDBs for the cementitious near-field [2-4], for bentonite [5] and potential host rock formations such as granite, marl and Opalinus clay [6-10].

Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of low- and intermediate level (L/ILW) and long-lived intermediate level (ILW) radioactive wastes. Cement is used to condition the waste materials and to construct the engineered barrier systems. The retardation of safety-relevant radionuclides by cement is taken into account in PA studies because the source term for radionuclide migration into the host rock is determined by a combination of solubility and sorption constraints in the cementitious near-field. The main focus of the present article is the methodology lying behind the development of a SDB. As an example, the conceptual approach and procedures applied for setting up a SDB for the cementitious near-field of a repository for long-lived intermediate-level waste (ILW) is described. Details of

*) Acknowledgements: We would like to thank Drs. I. Hagenlocher and B. Schwyn (Nagra) for their constructive comments and continuous support of this work. The work was partially financed by the National Cooperative for the Disposal of Radioactive Waste (Nagra).

the selection process for individual elements and a list of the sorption values selected for the SDB are reported by Wieland and Van Loon [4].

2 Sorption data bases

The main objectives of the SDB work are to select and document the sources of sorption data used and the procedure upon which the selection process is based, and 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 [2]. In addition to the above it has been realised that the following aspects are essential to the quality of SDBs:

First, the usefulness of sorption data critically depends on the availability of complete sets of experimental data for the materials of interest, including measurements of isotherms, studies on the dependence of sorption values on the solid to liquid (S/L) ratio, and on how well the experimental conditions are defined. Single-point measurements in which sorption has been determined for one set of conditions and at one concentration are viewed as being considerably less useful than sorption data deduced from measurements carried out under different experimental conditions. Moreover, it has been realised that an understanding of sorption mechanisms is required to strengthen the credibility of the sorption values selected in SDBs. For this purpose, macroscopic studies (i.e., wet chemistry experiments) should be complemented by advanced spectroscopic (e.g., X-ray absorption fine structure (XAFS) spectroscopy, time-resolved laser fluorescence spectroscopy (TRLFS)) and microscopic techniques (e.g., transmission electron microscopy coupled with energy dispersive spectrometry (TEM/EDS)) to improve the current knowledge of sorption processes on an atomic/molecular level.

Secondly, continuity between different compilations of SDBs is required to identify gaps in our knowledge and to design future experimental research programmes. It is evident that a continuous feedback from experimental sorption studies to the SDB work and input from PA studies are essential to increase the quality of sorption data and to improve our system understanding of the repository environment. For this reason, SDB updates have been made and are foreseen to be made in the future as required in the context of PA studies for the Swiss disposal concepts. The intention is always to base updates on the previous version of a particular SDB, and only include new information and data leading to (potentially) significant changes to, or re-appraisals of, the sorption data themselves, or the procedures for obtaining or modifying them.

SDBs are based on quantitative information regarding material and nuclide inventories and pore water chemistries. They include nuclide-specific information, such as sorption values for the safety-relevant radionuclides on the barrier-specific materials and assessments of the potential influence of disturbing factors affecting the sorption behaviour.

2.1 Repository-specific information

The development of the SDB for the near-field of the ILW repository requires quantitative knowledge of the nuclide inventories in the waste, the composition of the near-field pore water, the element inventories of hardened cement paste (HCP) and the organic materials present in the waste matrix as well as the colloid concentrations in the pore water.

Near-field: The present design of the Swiss ILW repository foresees a cavern with a total length of about 200 m for waste emplacement which is located in the Opalinus clay formation (OPA). Waste packages are placed in this cavern in containers made of concrete. The wastes are conditioned with cement or cementitious binders. Voids between packages, containers and within the cavern are backfilled with a gas-permeable mortar composed of quartz and HCP. Estimates of the masses and volumes of the various components of the near-field are required to deduce fundamental quantities such as the mass of HCP and organics in the repository and the porosity of the near-field (Table 1). HCP has a high sorption capacity and selective binding properties for cations and anions [11], and thus, is regarded as being the most relevant sorbing material for the development of a SDB for a cementitious near-field. Mass balance calculations reveal that HCP is present in the repository in significant quantities (Table 1). Organics may have an influence on the uptake of radionuclides by HCP due to their potentially complexing properties. Quantification of the porosity is required to estimate the volume of pore water in contact with HCP.

Nuclide inventories: The safety-relevant radionuclides present in the various types of Swiss ILW wastes include actinides and their daughters with significant half-lives, as well as fission and activation products. The radioelements expected to be present at significant concentrations are listed in Table 2 and grouped according to their chemical properties. In addition the dominant oxidation state under reducing repository conditions are indicated. Note that, in general, solubility limits and the extent of sorption are strongly influenced by the oxidation state of a radioelement. Moreover, speciation of radionuclides is controlled by pH, Eh and the concentration of complexing ligands. Therefore, knowledge of the pore water composition was required for the development of the SDB.

Table 1. Mass and volume of major components in the cementitious near-field of a representative volume (144.4 m³) for the present design of the planned Swiss repository for ILW waste.

Component	Mass [kg]	Mass [wt. %]
HCP	65800	24
Cementitious binders	7400	2.7
Steel	12000	4.4
Waste	4700	1.7
Gravel/quartz aggregates	177500	65
Cellulose	6.6	0.002
Bitumen	650	0.2
Pore volume		31 vol. %

Table 2. Safety-relevant radioelements including expected valence states under the reducing conditions relevant to the planned Swiss repository for ILW waste.

Group I and II elements	H(HTO), Cs(I), Be(II), Ca(II), Sr(II), Ra(II)
Transition elements (first and second series)	Fe(II/III), Co(II), Ni(II), Zr(IV), Nb(V), Mo(VI), Tc(IV), Ru(III,0), Pd(II), Ag(I)
Group IV, V, VI and VII elements	C(IV), Sn(IV), Pb(II), Sb(V), Se(IV/-II), Po(II), Cl(-I), I(- I)
Lanthanides and actinides	Pm(III), Sm(III), Eu(III), Ac(III), Th(IV), Pa(V), U(VI), Np(IV), Pu(IV), Am(III), Cm(III)

Pore water composition: Model calculations of “reference” cement pore waters (CPW) for the cementitious near-field of the planned Swiss ILW repository were performed using available models previously developed within the framework of PA studies and used to predict the degradation of cement materials and the evolution of CPW compositions [12-14]. A pH value ranging between 12.5 and 13.3 and an Eh value of, at maximum, -230 mV were predicted based on these model calculations [15]. The redox potential results from calculations assuming magnetite as the dominant Fe bearing phase and an upper limit of 10^{-7} M for dissolved Fe(II,III) in CPW. A pH of about 13.3 corresponds to the composition of a CPW in the early stage of cement degradation (stage I) which is dominated by alkali hydroxides (NaOH and KOH) released from the cement matrix. A pH of about 12.5 is obtained for the stage II of cement degradation where the chemical composition of the alkali-depleted CPW is controlled by the solubility of portlandite ($[\text{Ca}]_{\text{tot}}$ at $\sim 2 \cdot 10^{-2}$ M). Note that three stages of the chemical degradation of cement materials can be distinguished in the course of the lifetime of a repository caused by the interaction of HCP with infiltrating groundwater [13, 16]. The last stage of cement degradation where the buffering capacity of the portlandite is exhausted and the pH drops continuously is however expected to be of minor relevance to a cementitious repository in OPA due to low hydraulic conductivity of the host rock.

Cement materials: Previous studies have indicated that the cement composition has only a second order effect on radionuclide sorption [2 and references therein]. Therefore, differences in the chemical compositions of HCP prepared from various types of cement mixes are currently ignored. An important feature of HCP however is the presence of trace element impurities. Cement clinker is manufactured by blending a calcareous material such as limestone or chalk with an argillaceous one such as shales or clays. These constituents contain impurity elements at trace levels, which are eventually present in the clinker product or HCP after hydration. It is worth noticing that the concentrations of stable isotopes may be significant in CPW and exceed the concentrations of radioisotopes added to CPW for uptake studies by orders of magnitudes.

2.2 Sorption values

Uptake processes: The pool of sorption data available in the open literature originates primarily from batch-type sorption experiments in which a known quantity of a

radiotracer is added to a known mass of crushed HCP in contact with a known volume of CPW of known composition. The partitioning of the radionuclide between the mobile and immobile phase can be described in terms of a distribution ratio, R_d , (also denoted as “sorption value”) given by:

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

It should be noted that the determination of R_d values does not require information on the speciation of the sorbing and dissolved cations and anions as well as the binding mechanism involved. Nevertheless, information on the uptake mechanism is required and is used to strengthen the credibility of the sorption values recommended in SDBs.

Cation and anion binding by cementitious materials can be classified into particular uptake mechanisms [17, 18]: 1) Precipitation or surface precipitation, i.e., the formation of a solid phase of pure or mixed composition without forming a solid solution (e.g., in the form of metal (hydr)oxides or mixed hydr(oxides)), 2) Solid-solution formation and co-precipitation, i.e., incorporation of foreign ions in the structure of a solid phase by precipitation or diffusion into an existing solid phase, and 3) Specific and non-specific adsorption, i.e., the formation of covalent bonds between the sorbing species and the solid surface (inner-sphere surface complexation) or replacement of one adsorbed, readily exchangeable ion by another (ion exchange, outer-sphere complexation). Often the different mechanisms cannot clearly be distinct from each other, and the classes given above represent limiting cases of radionuclide uptake. Moreover, the state of knowledge of the different type of uptake processes on a microscopic level and the thermodynamic descriptions of these processes are generally not well advanced.

The main aim of our experimental studies on cement systems is to gain mechanistic information on uptake processes. For this purpose spectroscopic investigations using XAFS or TRLFS are carried out in conjunction with macroscopic sorption studies to elucidate the physico-chemical processes on the atomic/molecular level and to identify the cement phases responsible for the uptake [e.g., 19, 20]. In addition, macroscopic sorption studies must be designed and carried out so as to improve our knowledge on the chemical processes. For example, the lack of information on trace element inventories in the cement matrix may give rise to uncertainties in the interpretation of uptake processes at trace levels. Note that the presence of trace element impurities, which are inherently associated with the cement matrix, are an important feature of cementitious systems. The inventories of stable isotopes in a repository may significantly exceed the radioisotope inventories of the waste matrix [4]. In this case the partitioning of a radionuclide between the mobile and immobile phase occurs via isotopic exchange irrespective of how the corresponding stable isotope is associated with the cement matrix. Moreover, stable isotope concentrations are relevant in conjunction with solubility limits, which are determined by the free concentration of an element (stable and unstable isotopes) rather than the concentration of the radioisotope alone. For example, it was observed that the concentration of stable Ni in CPW is controlled by a solubility-limiting process via a Ni phase in the cement matrix [4, 19].

Selection hierarchy: Judgements on the quality and validity of published sorption values and selection of the “best available” sorption values are the main considerations upon which SDB work is based. The data used are from sorption studies published in the open literature and from in-house measurements. The knowledge gained from in-house studies allows the quality and validity of the published sorption values to be evaluated and judged in a more detailed and exact manner.

The development of SDBs for the cementitious near-field are based on the guiding principles discussed in Bradbury and Sarott [2]. In this work it was noted that many factors play an important role in the choices made and that “expert judgement” is an important component in SDB work. The main guiding principles are “transparency” and “traceability” in the selection process. A “selection hierarchy” is set up based on the degree of confidence in the data from the various sources. For the current SDB work the sequence of priorities given to the various data sources are: 1) In-house sorption data, 2) Data published in the open literature, 3) Sorption values deduced based on chemical analogy. First priority is given to in-house measurements. These data result from studies carried out under experimental conditions relevant to the “in situ” situation, and in particular, they are usually deduced from a large data set rather than from single-point measurements. A high level of confidence can be assigned to such data sets which yield a consistent picture of sorption under various experimental conditions, e.g., by changing the concentration range of radionuclides (isotherm) or changing the solid to liquid (S/L) ratio of the system. Second priority is given to those sorption data published in the open literature, which have been determined under well defined experimental conditions and, in particular, conditions relevant to the “in situ” repository conditions. Finally, reliable sorption data for a particular radioelement are often not available. In this case the option is to select a chemical analogue for which sorption data are available or to assign a nominal sorption value based on the chemical properties anticipated for the element of interest. For example, Th(IV) is often taken as an appropriate chemical analogue for the tetravalent actinides for which sorption data are often lacking. Assessment of the sorption of an element is often made feasible by using systematic investigations on the relationship between the chemical properties of metal cations and their sorption behaviour on metal(hydr)oxides [e.g., 21, 22]. In these cases, the tendency of metal cations to adsorb on the surface of the solids was found to correlate with the stability constants of the aqueous mono-hydroxo complexes (i.e., the first hydrolysis constant). Fig. 1 shows that the measured R_d values in cement systems tend to increase with increasing charge-to-size ratio of the metal cations (z = effective cation charge, d = M-O interatomic distance based on the ionic radii reported by Shannon and Prewitt [23]). It is noteworthy that the charge-to-size ratio is a measure of the polarising effects of cations on anionic counter-ions [24]. This parameter was successfully used by Baes and Mesmer [25] to group the first hydrolysis constants of metal cations. The trends revealed in Fig. 1 allow internal consistency of the selected sorption values to be checked and, moreover, allow nominal R_d values to be estimated for those radioelements for which sorption data are lacking.

Fig. 1. Sorption values for selected elements on HCP displayed as a function of the charge-to-size ratio (z/d); z is the cation charge, d is the M-O interatomic distance, which is the sum of the ionic radii based on data published by Shannon and Prewitt [23]. The sorption values were determined under CPW conditions corresponding to the early stage of cement degradation.

2.3 Influence of organics and colloids

The presence of complexing ligands and colloids in CPW can have an adverse effect on the immobilisation of radionuclides in the near-field. The formation of water-soluble complexes in the case of organics and the association of radionuclides with colloidal matter can, in principle, reduce radionuclide uptake by HCP. Sources of organics are bitumen and cellulose present in the waste matrix, and organic additives blended with cement used for the construction of the engineered barrier.

Bitumen: The degradation of bitumen has been studied intensively in the past and it has been shown that only radiolytic degradation is of importance [26]. Oxalate was found to be the main degradation product. The effect of oxalate on the sorption of radionuclides is however negligible for two reasons: 1) Complexes between radionuclides and oxalate are relatively weak, and 2) the concentration of oxalate is small owing to the formation of sparingly soluble calcium oxalate solids [27].

Cellulose: Cellulose is known to degrade in an alkaline environment [28]. Isosaccharinic acid (ISA) was found to be the main degradation product [29]. ISA forms stable complexes, especially with tri- and tetravalent nuclides and can significantly influence the sorption of radionuclides [30-32]. The extent of the effect, however, depends on the ISA concentration in solution. This in turn depends on factors such as the amount of cellulose in the repository, the extent of degradation, the stability of ISA, the formation of sparingly soluble solids and the sorption of ISA onto HCP. An assessment of these factors showed that the main process in regulating the ISA concentration in CPW is the sorption of ISA on HCP [4, 33]. The aqueous ISA concentration was estimated to be below ~

$3 \cdot 10^{-7}$ M based on realistic assumptions concerning the cellulose inventory, the degree of degradation and the extent of sorption under repository conditions [4]. Note that no effect of ISA on the uptake of the safety-relevant radionuclides by HCP has been observed experimentally at this concentration level [30, 32, 34].

Cement additives: Naphtalenesulphonate, melamine formaldehyde, sodium lignin-sulphonate, polycarboxylates and sodium gluconate are regarded as being potentially important complexing ligands present in CPW and, hence, capable of affecting sorption onto HCP. Similar to the case of ISA, the main process in regulating the aqueous concentration of cement additives is sorption on HCP [35]. Due to strong interaction of cement additives with HCP, these organics will be predominantly associated with the solid phase. One of the main problems with cement additives however is that it is presently not known which additives will be used for the construction of the repository. Cement additives cannot be treated generally and their effect on sorption has to be investigated individually on a case by case basis [35].

Cement-derived colloids: A highly permeable mortar is currently favoured as the backfill material for the planned Swiss repository for ILW wastes. The backfill was specially designed to allow the release of gas, which could be generated in the repository due to corrosion, and to ensure mechanical stability by filling of the voids between the waste containers. This material is considered to be a chemical environment with some potential for colloid formation due to its high porosity and because quartz is used as the aggregate material (dissolution of quartz at high pH followed by precipitation of calcium silicate hydrates) [36]. Therefore, colloid-facilitated transport is considered to be a potential migration pathway out of the repository. Extensive experimental studies on colloid stability and colloid inventories under conditions relevant to the cementitious near-field revealed that the concentrations of dispersed colloids are typically below $\sim 10^{-4}$ kg m $^{-3}$ [36, 37]. Under these conditions, however, no effect of colloids on sorption was predicted for weakly to moderately sorbing radionuclides such as Cs(I), Sr(II), Pb(II), Sn(IV) and U(VI) (Fig. 1) with R_d values ≤ 10 m 3 kg $^{-1}$. A minor effect was predicted only in the case of the very strongly sorbing radionuclides such as Eu(III) and Th(IV) (Fig. 1) with R_d values $\gg 10$ m 3 kg $^{-1}$ [36]. These findings indicate that, on the assumption that sorption processes are reversible, the effect of cement-derived colloids on radionuclide mobility in the near-field is negligibly small.

3 Conclusion

Development of a SDB for the cementitious near-field of the planned ILW repository in OPA host rock was required for performance assessment [4]. The main task of this work was to select the “best available” laboratory sorption values for the safety-relevant radionuclides on HCP. The SDB includes relevant site- and nuclide-specific information.

The development of the SDB was based on certain guiding principles, such as traceability and transparency of the selection process, and was supported by detailed documentation of the justifications lying behind the chosen sorption values. The sorption values were selected from in-house data and literature data regarded as being the most relevant to the “in situ” repository conditions. In addition, potential effects of organic ligands

associated with the waste and cement, and colloids present in the near-field pore water on radionuclide uptake by HCP were assessed and quantified.

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