Study of radium behavior in contact with the cementitious phase CSH

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ABSTRACT

Radium-226 is an important radionuclide with respect to the long-term safety of repositories for low and intermediate level radioactive wastes, as well as deep geological repositories for high level radioactive waste and spent nuclear fuel. To evaluate its mobility in the engineered barrier system of a repository, the sorption of radium on Calcium-Silicate-Hydrates (CSH), which form the major hydration phases in cementitious materials, was studied. Radium sorption to CSH was found to be very fast, leading to steady state between solid and liquid phase after less than four days. The dependency of the equilibrium distribution ratios on radium concentration, the calcium to silicon ratio in CSH, liquid to solid ratio, and temperature was investigated, and estimates of apparent activation energy, reaction enthalpy, entropy and Gibbs energy of the sorption process were derived. Radium sorption on CSH can be described by linear isotherms with R_d *values mostly in the order of* 10^4 *L/kg. Radium sorption was found to be an exothermic and spontaneous reaction probably governed by chemical reaction rather than diffusion. As expected, the presence of EDTA at low concentrations led only to a small decrease in radium sorption, due to the strong competition of dissolved calcium for EDTA complexation. A comparison of the sorption behavior of various alkaline earth elements used as chemical analogues for radium confirmed the significant difference in the* R_d *values with sorption on CSH decreasing in the order Ra > Ba > Sr.*

Keywords: radium sorption, isotherm, enthalpy, entropy, Gibbs energy, activation energy

INTRODUCTION

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Cementitious materials such as concrete and mortar have a wide spectrum of applications in nuclear waste management, for example, as construction and backfill materials in near-surface repositories and geological disposal facilities for radioactive wastes, for solidification of low- and intermediate-level wastes, and in specific waste containers. Cementitious materials are important barriers in repositories for low- and intermediate-level radioactive wastes, where ^{226}Ra can be one of the contaminants of concern. Moreover, they are also intended for use as structural support and plugs, or in some cases, also as backfill material and buffer, in deep geological repositories for high-level radioactive waste and spent nuclear fuel [1–3]. Regarding the direct disposal of spent nuclear fuel, ^{226}Ra is one of the most important contributors to dose in the long term, due to the large amount of ^{238}U present [4].

For the assessment of the long-term safety of a repository, the retardation mechanisms of radionuclides on cementitious materials within the engineered barriers need to be understood [5,6]. In general, the uptake and retention of radionuclides in cementitious materials can be attributed to either, (i) precipitation of sparingly soluble pure phases, (ii) incorporation into existing or newly formed phases (e.g., by entrapment or solid solution formation) or (iii) sorption to cement hydration phases or aggregates [1,7,8]. The composition and properties of hydrated cementitious materials can vary significantly, depending strongly on the cement formulation and the mixing and curing processes and conditions [9]; thus affecting the retention behavior of radionuclides. The predominant hydration products in Hardened Cement Pastes (HCP) are amorphous to nanocrystalline Calcium-Silicate-Hydrates (CSH), besides portlandite ($Ca(OH)_2$), AFm (Aluminate Ferrite monosulphate) or ettringite (Aluminate Ferrite trisulphate, AFt). In addition to research on HCP and concrete made from commercial cements, which can provide phenomenological insights into the radionuclide retention capacities of various cement formulations, studies on individual hydration phases can provide further insights into radionuclide retention mechanisms [8,10].

Studies on Ra sorption on cementitious materials are quite rare to date. Due to the ease of working with (inactive) Sr and Ba, which are considered as potential chemical analogues of Ra [11,12], these are more often used in sorption studies, despite there being little evidence for the veracity of such comparisons. Previous studies have shown that the retention of Ra (and other alkaline earth elements such as Ba and Sr) can predominantly be attributed to sorption by CSH phases [10,13,14]. Ra and Sr (and probably also Ba) sorption on CSH phases, and accordingly on HCP, is probably governed by cation exchange of e.g., Ra^{2+} vs. Ca^{2+} on edge and planar silanol groups of the CSH phases [12,15,16]. These groups are deprotonated under the alkaline conditions in cementitious systems and their negative charge neutralized e.g. by Ca. The exchange proceeds as described for Ra in Eq. (1)

$$\text{Ca-CSH} + Ra^{2+} \Leftarrow\Rightarrow \text{Ra-CSH} + Ca^{2+}. \tag{1}$$

The uptake of alkaline earth elements on pure CSH phases is higher compared to commercial cementitious materials [10,13,15]. The range of distribution ratios (R_d values) of Ra for pure CSH phases was determined to be in the order of 10^2 to 10^4 L/kg depending on the Calcium to Silicon (C/S) ratios of CSH, with higher R_d values at lower C/S [10,15]. R_d's for ^{226}Ra on CSH with C/S ratios of 1.4 and 0.9 are in the order of 10^3 and 10^4 L/kg, respectively. R_d values for Sr on CSH were determined in several studies [12,17]. Here, the R_d values were also found to depend on the C/S ratios and to be significantly lower than those for Ra – R_d values on CSH with C/S = 1.4 are about 100 L/kg and up to 10^3 L/kg for C/S = 0.9. Ba sorption on CSH was reported in [18], where the R_d values were in the range of 10^3 to 10^4 L/kg for C/S ratios of about 0.9; by analogy to Ra and Sr, the R_d for higher C/S ratios can be expected to be lower.

Repositories for highly radioactive heat-producing wastes will feature elevated temperatures over a significant period after closure. In particular, in the case of early canister failure, radionuclides may come in contact with aqueous systems at elevated temperatures. Thus, it is necessary to study (i) the effect of temperature on the cementitious material itself and (ii) on the sorption of radionuclides. Changes in the radionuclide retention capacity of cementitious materials at elevated temperatures might be caused by changes in radionuclide solubility and speciation as a function of temperature, changes in the phase assemblage of the HCP, recrystallization effects and changing surface properties of the solids, or due to changes in the chemical process of the sorption itself [19,20]. Investigations of Sr sorption on hydrothermally altered cementitious materials (at temperatures up to 70°C) indicated a decrease in Sr sorption with increasing alteration temperature [21]. However, to our knowledge there are no studies so far addressing temperature effects on Ra sorption to cementitious materials or other solids.

Organic materials are present in some nuclear waste streams, e.g. as paper, gloves, over-clothing, flasks, filters, seals, cables, ion exchange resins, oils or detergents (e.g. EDTA, NTA) etc., and can potentially influence the performance of the disposal system, especially in the context of low and intermediate level waste disposal [22–24]. In cementitious materials such as concrete, organic materials are directly present as part of the cement matrix, since additives like plasticizers and superplasticizers added to allow for enhanced workability are generally based on organic compounds, which can influence the speciation and sorption properties of cements (e.g., [25,26]). Moreover, there may also be organic materials that get into the repository unintentionally. The source of these organic materials can be microorganisms and small plants in storage tunnels, organic material entering through ventilation together with building materials, or human activity [27]. All these organic materials, and in particular their degradation products, can affect the migration and mobility of radionuclides in a nuclear waste repository, as the formation of organic complexes in solution with some radionuclides of interest can (i) increase radionuclide solubility, and (ii) decrease radionuclide sorption [28]. Moreover, the organic degradation products may sorb to the cementitious materials thus reducing the number of surface sites available for radionuclide sorption, or may form substances with suitable properties to capture radionuclides [27].

The main aim of this study was to investigate the equilibrium R_d values of the sorption of radium to CSH as the main Ra-sorbing phase in cementitious materials and their temperature dependency, and to determine the related thermodynamic quantities. Moreover, for the first time the influence of organic ligands on Ra sorption to cementitious materials was evaluated using EDTA as an example, since it can form strong complexes with alkaline earth elements [29]. Furthermore, the use of Ba and Sr as analogue elements to assess the retention of ^{226}Ra was explored further.

MATERIALS AND METHODS

Materials

CSH

Synthetic CSH phases with different C/S ratios (i.e. 0.9, 1.0, 1.2 and 1.4) were prepared following the procedure of [30] as described in detail in [10]; i.e. synthesized from CaO (produced from ignited $CaCO_3$), amorphous fumed SiO_2 and deionized H_2O in an inert gas atmosphere. The structure of the synthesized phases was confirmed by X-Ray Diffraction analysis, which revealed the presence of small amounts of $CaCO_3$ in the samples. All synthesized CSH phases contained significant amounts of water (more than 50% by weight), which was taken into account in the preparation of the sorption experiments.

Radionuclides

The isotopes of interest, i.e., ^{226}Ra, ^{90}Sr and ^{133}Ba were studied to compare the sorption isotherms of the different alkaline earth elements on CSH. Radioactive isotopes of Sr and Ba were used to avoid potential problems in the data analysis due to the ubiquitous presence of natural isotopes of these elements in cementitious materials. In the experiments focused on the temperature dependency of Ra sorption to CSH, ^{223}Ra (commonly used in radiotherapy) was used as substitute for ^{226}Ra. ^{223}Ra is predominantly an α emitter (half-life = 11.43 days) that decays to ^{219}Rn with a final decay product of ^{207}Pb. The radon isotope ^{219}Rn has a half-life of only 4 seconds. The advantage of the much shorter half-life of ^{219}Rn compared to ^{222}Rn is that it is safer to work with. The isotope ^{223}Ra was obtained as the product Xofigo (radium-223 dichloride in solution) used for the treatment of prostate and bone cancer in hospitals.

Methods

Sorption experiments

The sorption of Ra (and Ba and Sr) to CSH was investigated using batch type experiments carried out in plastic ampoules under inert gas atmosphere in a glove-box (N_2 atmosphere, < 50 ppm CO_2), as CSH is sensitive to carbonation in the presence of atmospheric CO_2. After the required reaction time and centrifugation (5,000 rpm, 10 min), samples of the liquid phase were taken and analyzed for the remaining radionuclide activity in solution.

The required equilibration times were determined in kinetic experiments. The kinetic experiments were performed with CSH with a C/S ratio of 1.0 at Liquid to Solid (L/S) ratios of 250 and 500 L/kg at temperatures of 22, 50 and 80°C (these data were also used for the estimation of activation energies) and with C/S ratio 1.2 at L/S = 500 L/kg and 22°C in the presence and absence of Na_2EDTA (Ethylene Diamine Tetraacetic Acid disodium salt dihydrate, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, hereinafter referred to as EDTA), respectively. The experiments confirmed that a duration of 4 days (96 h) was appropriate to achieve close-to-equilibrium steady state, i.e. virtually zero concentration changes of the radionuclide activity in solution (cf. [13]) in all experimental setups.

For studying the temperature dependency of the Ra sorption, CSH with C/S ratios of 1.0 and 1.2 were used. The sorption experiments were carried out at 22 and 80°C in solutions saturated with the respective CSH phase for 4 days, using L/S ratios varying between 100 to 1,000 L/kg (6 mL of liquid phase) and initial ^{223}Ra concentrations of approx. $2.5 \cdot 10^{-12}$ mol/L. The pH of the equilibrium solutions prepared were determined to be 10.7 (CSH 1.0) and 10.5 (CSH 1.2), using a combined pH electrode (Radiometer Analytical).

CSH with a C/S ratio of 1.2 was used to determine the effect of the presence of EDTA on Ra sorption. The experiments were performed in the same way as described above (i.e., with respect to duration, L/S, c(^{223}Ra)) at room temperature (22°C), using an EDTA concentration of $5 \cdot 10^{-5}$ mol/L.

To investigate the effect of the aging of CSH phases on their sorption properties, the sorption of ^{223}Ra on CSH C/S = 1.2 of different ages (freshly prepared, age 3 months, and age 12 months; no special treatment applied, material stored as powder in a glove box) at the same conditions as mentioned above (regarding duration, L/S, c(^{223}Ra), temperature) was compared.

For comparison of the sorption of Ra (^{226}Ra), Sr (^{90}Sr) and Ba (^{133}Ba) to CSH with various C/S ratios (0.9, 1.2 and 1.4), experiments were performed using an L/S ratio of 200 L/kg with radionuclide concentrations in the range of $4 \cdot 10^{-10}$-$8 \cdot 10^{-7}$ mol/L, which were achieved in the cases of Sr and Ba by the addition of a carrier ($Sr(OH)_2$ and $Ba(OH)_2$, respectively). These sorption studies were performed at room temperature and lasted for three weeks (approx. 500 hours).

Analysis of radionuclides

Ra and Ba isotopes in the liquid phase were measured by gamma spectroscopy mostly with HPGe detectors (^{226}Ra: HPGe detector system, type: EGC 35 195 R, EurisysMesures, spectrometer system obtained from EG & G Ortec, GammaVision® Model A66 B32 software version 5.20, ^{223}Ra: HPGe detector system, type GEM40P4 with Ortec DSPEC jr 2.0, Maestro software version 7.0, or NaI(Tl) well type detector; ^{133}Ba: HPGe detector, PGC 2018, DSC: detector system GmbH, Gamma W for Windows version 2.55); for ^{90}Sr Liquid Scintillation Counting (LSC) was used (1220l Quantulus, Perkin Elmer, Winq software version 1.2).

Due to the relatively short half-life of ^{223}Ra, the observed decrease of radioactivity in the liquid phase caused by the Ra uptake on the solid cementitious material had to be decay corrected. Furthermore, the sorption on the walls of the experimental vials was determined across all conditions and included during evaluation of the experiments. The sorption on walls was found to be about 10% of the initial radionuclide activity. Based on parallel determinations of large number of experiments on radium sorption on CSH, sorption on the ampoule walls and analysis of all possible sources of measurement error, the average error of the obtained sorption data was set to 10%.

Evaluation of sorption data

The uptake of the radionuclides by CSH is characterized here in terms of the distribution ratio, R_d, between liquid and solid phases, calculated according to Eq. (2)

$$R_\mathrm{d} = \frac{A_\mathrm{init} - A_\mathrm{t}}{A_\mathrm{t}} \cdot \frac{V}{m}, \tag{2}$$

where A_init is the initial activity concentration of the radionuclide in solution, and A_t corresponds to the activity concentration at time t, respectively, both in the unit of activity (Bq), V (L) is the volume of the liquid phase, and m (kg) the mass of solid phase used in the experiment.

Besides calculation of R_d values, the data were evaluated using sorption isotherms. In previous work [13], the sorption of radium on various cementitious materials (i.e. HCP and concrete prepared from CEM I, CEM II and CEM III) in low concentrations (≈10^{-12} mol/L) was described using Langmuir isotherms. However, the sorption of radium on CSH is, according to the literature [10,15] and previously obtained results in [13], fairly constant for different L/S ratios (100-1,000 L/kg). Therefore, it is more appropriate to use a simpler description with a linear isotherm by employing a K_d-model (Eq. (3)), especially when dealing with very low radionuclide concentrations. This isotherm is defined as

$$q = K_d \cdot c, \tag{3}$$

where q (mol/kg) is the equilibrium concentration in the solid phase, c (mol/L) is equilibrium concentration in the liquid phase and K_d (L/kg) is the distribution coefficient, dimensionally identical to the distribution ratio R_d.

Thermodynamic evaluation

The influence of the temperature on the sorption of ^{223}Ra is described using the apparent activation energy E_A (J/mol) and changes in enthalpy ΔH (J/mol) and entropy ΔS (J/mol·K). Enthalpy and entropy were obtained from the linear dependence of lnK_d as a function of $1/T$ – Eq. (4)

$$ln\, K_d = -\left({}^{\Delta H}/_{R}\right) \cdot {}^{1}/_{T} + {}^{\Delta S}/_{R}\,, \tag{4}$$

where R is the gas constant (8.314 J/mol·K) and T (K) is temperature. Equation (4) is derived based on the van't Hoff equation for low concentrations of a given component in the liquid phase, if the quantity K_d can be considered constant in time (thermodynamic relations for the change of Gibbs energy were used to derive the equation) [31].

The Gibbs energy (or the Gibbs free energy or free enthalpy) ΔG (J/mol) describing isobaric and isothermal processes can be determined based on the changes in entropy and enthalpy according to Eq. (5)

$$\Delta G = \Delta H - T\Delta S. \tag{5}$$

Apparent activation energies of Ra sorption to CSH were derived via the Arrhenius equation by plotting lnk as a function of $1/T$ – Eq. (6)

$$lnk = lnA - {}^{E_A}/_{RT}\,, \tag{6}$$

where k (s^{-1}) is a kinetic coefficient and A (L/mol·s) is the frequency factor. The kinetic coefficients were determined in the course of the evaluation of kinetic experiments with one of the following models of possible rate-controlling processes: mass transfer (or two-film model) (DM), Film Diffusion (FD), Diffusion in Inert layer (ID) and Chemical Reaction (CR) [see Supplemental Table S1]. A detailed derivation of the models can be found in [32] and [33], respectively. All models are also described in detail in [13]. The decreasing Ra concentrations in the aqueous phase, -dc/dt, were compared to the values computed with the individual kinetic models after each experimental time-step. The best model was selected using the parameter *Goodness-of-Fit* (GoF, GoF = χ^2/*degrees of freedom*, described in detail in [13]), for the GoF, it holds that the value should be as low as possible, preferably 0.1 < GoF < 20 [34].

Determining the change in reaction enthalpy, i.e. whether the reaction is endothermic or exothermic, is important for the design of operating systems, where it is necessary to ensure the removal of reaction heat. Otherwise, there is a risk of damage not only to the equipment itself, but also to the change in reaction conditions and the composition of the reaction products. The change in Gibbs energy is an essential criterion for assessing the natural direction of a given reaction. Activation energy represents the minimal amount of energy needed to complete a chemical reaction. Many particles have sufficient energy to react, but some reactions must be initiated by supplying energy (e.g. heat) or with a catalyst.

Speciation calculations

To aid interpreting the batch sorption experiments in presence of EDTA, the aqueous speciation of the components in solution and saturation indices of relevant phases were calculated using the geochemical code PhreeqC Ver. 3.5.0 [35]. The ThermoChimie v.10d thermodynamic database (Consortium Andra – Ondraf/Niras – RWM; [36,37]) was used for the thermodynamic modelling. Data for the $Ra(EDTA)^{2-}$ complex were taken from [29]. The activities of aqueous species were calculated using the specific ion interaction (SIT) approach (cf. [38–40]). The equilibrium constants and the ion interaction coefficients used in the thermodynamic calculations are included in [Supplemental Tables S2 and S3].

RESULTS AND DISCUSSION

Effects of temperature on radium sorption

Distribution ratios and sorption isotherms

Kinetic experiments confirmed that 4 days is sufficient to reach steady state for ^{223}Ra sorption onto CSH for both C/S ratios at all temperatures.

In the equilibrium experiments with the CSH with C/S 1.0, the R_d values were determined at 22 and 80°C (evaluated in Fig. 1, top left, as a function of L/S). The values for the temperature of 22°C vary in the range of 35,500 to 60,600 L/kg, with an average value of $R_{d(22°C)}$ = 44,838 ±4,605 L/kg (Table 1). These values are two to twenty times higher than published ones (e.g. [10,14,15]), which is probably due to the use of the higher radium concentrations in the aforementioned publications, namely in the order of 10^{-10}-10^{-6} mol/L. R_d values determined at 80°C were in the range of 41,500 to 49,500 L/kg, with an average value of $R_{d(80°C)}$ = 45,176 ±4,640 L/kg (Fig. 1, top left). The R_d values for both temperatures can be considered comparable within the experimental error and measurement uncertainty. What is important is the change in the gradient (i.e. steepness) between the ^{223}Ra isotherms of temperatures 22 and 80°C (cf. Fig. 1, top right), which indicates a reduction of sorption capacity with temperature, thus suggesting an exothermicity of the sorption reaction. This corresponds to the previously determined sorption behavior of ^{223}Ra on real cementitious materials [13], where a significant change in the shape of the isotherms with temperature was observed. Linear isotherms were obtained by fitting the experimental data with the K_d-model (Eq. (3)) using the linear regression method. The slopes of these lines give the following K_d values: $K_{d(22°C)}$ = 50,933 ±4,158 L/kg and $K_{d(80°C)}$ = 42,324 ±1,858 L/kg (Table 1), which, in contrast to the average R_d values, unambiguously confirm that $K_{d(22°C)} > K_{d(80°C)}$.

The same comparison was performed for the 3 months old CSH C/S 1.2 material with similar conclusions. The R_d values determined at 22°C were in the range of 15,500 to 29,700 L/kg, with an average value of $R_{d(22°C)}$ = 21,706 ±2,887 L/kg. This value is approximately four times higher than the value published in [14] for CSH with the same C/S ratio. R_d values determined at 80°C were in the range of 8,500 to 20,500 L/kg, with an average value of $R_{d(80°C)}$ = 15,823 ±2,105 L/kg (Fig. 1, bottom left). Also in this case, the significant change in the slope of the ^{223}Ra isotherms at temperatures 22 and 80°C (cf. Fig. 1, bottom right) is observed. The K_d-model determines the K_d to be $K_{d(22°C)}$ = 26,028 ±2,677 L/kg and $K_{d(80°C)}$ = 9,065 ±1,066 L/kg, which is in quite good agreement with the average R_d value (Table 1).

The R_d values of CSH C/S 1.2 are lower than the values of C/S 1.0 (cf. Table 1), which is in agreement with previous research [10,14,15]. What is more, in the comparison of the isotherms at the same temperature for two C/S ratios of CSH, the sorption capacity increases with lower C/S ratio as the isotherm for C/S 1.0 is steeper for both temperatures. The same finding was obtained in the comparison of sorption of Ra, Ba and Sr on CSH with different C/S ratios mentioned below.

From Fig. 1 (right), the important finding is that the isotherms for 80°C in general lie below the isotherms for 22°C – i.e. the sorption capacity is reduced with the changing slope of the isotherm with increasing temperature. This indicates the exothermic character of the sorption reaction, i.e., the decrease in the value of the equilibrium constant with temperature. This difference between the isotherms can lead to the assumption that the rate controlling process is dependent on temperature. It should be noted that the reduction in sorption capacity due to higher temperature, unfortunately, is not apparent from a comparison of the determined R_d values (cf. Table 1) probably due to the uncertainty of the measurement.

This uncertainty can be related to the very low concentration of ^{223}Ra in solution ($\leq 10^{-12}$ mol/L), which can lead to uncertainty itself or anomalous behavior shown as the $R_{d(80°C)} > R_{d(22°C)}$ in some cases in Fig. 1.

Other source of uncertainty can be related to the significant volume of water present in the CSH (more than 50%) despite correction for water weight, because the water content can influence the homogeneity of the material. This is more pronounced in experiments where rather small amounts of CSH are used (i.e. higher L/S, especially L/S = 1,000 L/kg).

In general, the K_d-model (compared to Langmuir or Freundlich isotherm) is used for the linear isotherm description, which is the case in the region of very low concentrations, despite its simplicity. The knowledge of the sorption isotherm, especially the relevant model, is one of the data needed to characterize the sorbent and the system as a whole. These data are needed for example in the design of technological parameters of the sorption process.

Derivation of thermodynamic quantities of radium sorption to CSH

The entropy and enthalpy of sorption of ^{223}Ra on CSH C/S 1.0 and C/S 1.2 were estimated from the K_d values resulting from the application of the K_d-model as described in Eq. (4) and shown in Fig. 2 (left). The Gibbs energies were determined for the temperatures used (22 and 80°C) according to Eq. (5)

(cf Table 2). The thermodynamic quantities determined from the experimental measurement of sorption cannot directly be assigned to a particular sorption mechanism.

The values of change in entropy (Table 2) are generally very small, but positive, for both C/S ratios. These values were used for the determination of the change of Gibbs energy together with values of the change in enthalpy. Enthalpy change values are negative, which corresponds to an exothermic reaction. Based on the experimental determination for only 2 different (and relatively similar) C/S ratios, no statement on the dependence of these quantities on C/S is given here. The change in values of Gibbs energy is generally very small, but negative. It can therefore be assumed that the sorption process is spontaneous. On the other hand, a small effect of temperature on the Gibbs energy is evident here, since the absolute value of change in Gibbs energy increases with temperature. When comparing ΔG for two different C/S ratios, it is also not possible to reach a clear conclusion, as the data are comparable within experimental error.

In [10], the values of enthalpy and entropy change of exchange of Ra from solution with an interlayer Ca in CSH were estimated from DFT calculations (Density Functional Theory) for three C/S ratios. The values for C/S 1.0 (ΔH = -10.8 kJ/mol, ΔS = 83.8 J/mol·K [10]) are comparable to the values given in Table 2. However, value of Gibbs energy presented in [10] for C/S 1.0 is ΔG = 14.2 kJ/mol, which does not correspond to the obtained results (negative ΔG) or the assumption of spontaneity of the chemical process, though, this value is determined with an error estimate of 20 kJ/mol. Besides, in [10] a clear decrease of enthalpy and Gibbs energy change with decreasing C/S was observed, which was only partly confirmed here, as the values are more likely comparable. What must be noted is that the values in [10] are determined by the different method (DFT modelling) for a specific ion exchange process.

The kinetic dependencies of the sorption of ^{223}Ra on CSH C/S 1.0, L/S 250 and 500 L/kg for 3 temperatures (22, 50 and 80°C) were evaluated with different kinetic models. The model describing diffusion in an inert layer (ID) was determined as the most appropriate based on the values of GoF.

Activation energies for Ra sorption were determined for L/S 250 and 500 L/kg as described in Eq. (6) and shown in Fig. 2 (right). Although equilibrium experiments do not show a dependence on L/S, the kinetic experiments cannot be evaluated independently of L/S because the kinetics curves for different L/S cannot be averaged. However, this does not necessarily mean that a dependence of E_A on L/S can be described since we compare only two values of the estimate of this quantity. Fig. 2 (right) shows that the kinetic coefficient determined at 50°C and L/S = 250 L/kg was not used, since in this case the coefficient of the ID model was deemed unsuitable with respect to the GoF value. Nevertheless, kinetic coefficients obtained from the ID model were used for the evaluation of the following apparent activation energy values: $E_{A(L/S\ 250)}$ = 24.5 ±3 kJ/mol and $E_{A(L/S\ 500)}$ = 67.6 ±9 kJ/mol. These values suggest both diffusion (lower E_A) and chemical reaction (higher E_A) as rate-controlling process, respectively. However, the boundary between these controlling processes in terms of E_A values is not exactly clear (generally from experience it can range from 15 to 30 kJ/mol, occasionally 40 kJ/mol). Thus, taking into account the significant change in the slope of the isotherms with temperature, it can be assumed that the rate-controlling process is probably a chemical reaction, which is generally more influenced by temperature than diffusion.

Effects of CSH aging on radium sorption

The radionuclide sorption properties of CSH in cementitious barrier materials can be subject to changes over time, e.g. due to recrystallization processes and changes in C/S ratios (i.e. decrease in C/S) due to leaching processes caused by groundwaters [41,42]. To address changes in Ra sorption by CSH due to isochemical aging processes, sorption experiments with CSH (C/S ratio 1.2) of different ages were performed. In Fig. 3 (left), the sorption isotherms for ^{223}Ra are shown for the three investigated materials. A significant difference in the distribution ratios R_d was observed for the CSH of different ages, with R_d values increasing with the age of the material leading to steeper linear isotherms. Thus, the material evidently changes over time, which can be caused, for example, by a slow degradation of the CSH material, which is assumed to be placed in an inert atmosphere in a glove box. However, neither the box nor the storage containers are completely airtight. Thus, contact with atmospheric CO_2 and conversion to $CaCO_3$ may probably occur, leading to a decrease in C/S ratio and consequently to an increase of sorption.

The isotherms presented in Fig. 3 (left) show an increase of the R_d values with increasing age of material, the average R_d's are: $R_{d(0\ m)}$ = 14,716 ±1,619 L/kg, $R_{d(3\ m)}$ = 21,706 ±2,887 L/kg and $R_{d(12\ m)}$ = 31,193 ±4,311 L/kg. K_d values obtained from the evaluation with the K_d-model are (cf. Fig. 3, left. Table 1): $K_{d(0\ m)}$ = 15,653 ±1,560 L/kg, $K_{d(3\ m)}$ = 26,028 ±2,677 L/kg and $K_{d(12\ m)}$ = 29,541 ±1,288 L/kg. A more pronounced change in sorption properties can be seen during the first three months than during further aging from month 3 to month 12. Besides the increase of R_d or K_d with age of the material it is evident that the individual data points of the younger material (age 0 month) are more widely scattered around the isotherms, whereas at higher age, the data points fit much better to the proposed linear isotherm. This also contributes to the assumption that the material changes over time.

This phenomenon of increasing Ra sorption with ageing of CSH over the timescale of several months may provide also and explanation for an apparent inconsistency observed when comparing ^{226}Ra – as well as ^{90}Sr and ^{133}Ba (Table 1) - sorption on CSH with different C/S ratios (0.9, 1.2 and 1.4). Here, despite the generally assumed decrease of R_d with increasing C/S (cf. [10,12,15,18]), the R_d values for C/S = 1.2 were lower than those for C/S = 1.4 (Fig. 3, right, Table 1). This might be due to the fact that the materials with C/S 0.9 and 1.4 were already several months old, while the material with C/S 1.2 was freshly prepared and its Ra (Sr and Ba) sorption capacity was therefore lower than for CSH 1.2 of similar age as the other two materials.

Effects of EDTA on radium sorption to CSH

In Fig. 4 the ^{223}Ra uptake by CSH (C/S = 1.2, age 12 months) in presence and absence of EDTA is depicted. The distribution ratios, $R_d = f(L/S)$, show that the addition of EDTA leads to a slight decrease in Ra uptake (cf. Fig. 4, left). The R_d values determined without EDTA are in the range of 28,400 to 37,000 L/kg, with an average value of R_d = 31,193 ±4,311 L/kg. This value is approximately six times higher than the R_d value published for this C/S ratio in [14]. R_d values determined in the presence of EDTA are in the range of 22,100 to 31,500 L/kg, with an average value of $R_{d(EDTA)}$ = 27,207 ±3,677 L/kg. The evaluation of the isotherms with the K_d-model provides K_d = 29,541 ±1,288 L/kg (in absence of EDTA) and $K_{d(EDTA)}$ = 22,341 ±1,558 L/kg in the system with the organic ligand (cf. Fig. 4, right), which is in quite good agreement with the average R_d values (Table 1). Based on the K_d values, a Sorption Reduction Factor (SRF), defined as

$$\mathrm{SRF} = \frac{K_\mathrm{d}\ without\ organics}{K_\mathrm{d}\ with\ organics}, \tag{7}$$

of 1.3 can be estimated for Ra sorption on CSH due the presence of EDTA.

At the investigated EDTA concentration of $5 \cdot 10^{-5}$ mol/L, the sorption of ^{223}Ra on CSH is only slightly reduced as expressed by the rather small sorption reduction factor, despite the generally strong complexation of radium by EDTA [29]. A comparison with data in [43] shows a generally high variability of sorption reduction factors for various radionuclides (e.g., Pu, Ni, Eu) due to the presence of diverse organic substances (e.g., EDTA, ISA, gluconate) in cementitious systems, with sorption reduction factors varying between unity and several thousands. Generally, the ability of EDTA and other organics to form complexes with radionuclides in a cementitious environment is strongly affected by the high pH and high Ca concentrations, the stability of relevant Ca-organic complexes and the concentration of the organic ligand. Since the stability of the EDTA complexes of alkaline earth elements decreases in the order $\text{Ca-EDTA}^{2-} > \text{Sr-EDTA}^{2-} > \text{Ba-EDTA}^{2-} > \text{Ra EDTA}^{2-}$ [44], an influence of EDTA on the speciation of radium and hence radium sorption is only possible if the EDTA concentration exceeds the concentration of calcium, which is generally high in pore waters of cementitious materials ($[\text{Ca}]_{\text{total}} > 1 \cdot 10^{-3}$ mol/L). In Fig. 5, the calculated speciation of radium ($c_{\text{Ra}} = 1 \cdot 10^{-12}$ mol/L) in a solution containing $1 \cdot 10^{-3}$ mol/L Ca at two EDTA concentrations ($5 \cdot 10^{-5}$ and $5 \cdot 10^{-3}$ mol/L) is shown as function of pH. Two other concentrations of EDTA (0 and $5 \cdot 10^{-4}$ mol/L) were also used for calculations, but the results are similar as in the case of $5 \cdot 10^{-5}$ mol/L for the absence of EDTA, and in the case of $5 \cdot 10^{-4}$ mol/L the result differs from the presented case ($5 \cdot 10^{-5}$ mol/L) only in hundredths of a percent. In alkaline conditions and in absence of EDTA, Ra is present in solution mainly as free Ra^{2+} ion, with increasing contributions of RaOH^{+} with increasing pH. The calculations show that only at an EDTA concentration exceeding the one of Ca, Ra is predominantly present as Ra-EDTA^{2-}; otherwise, the EDTA is complexed almost completely by Ca in the form of the Ca-EDTA^{2-} complex and effectively not available for the complexation of radium [cf. Supplemental Fig. S1]. Additional thermodynamic calculations of the radium speciation in a solution in equilibrium with CSH1.2 (pH 11.3; $c_{\text{Ca}} = 1.82 \cdot 10^{-3}$ mol/L) revealed that at the experimental conditions ($c_{\text{Ra}} = 1 \cdot 10^{-12}$ mol/L), with and without the presence of $5 \cdot 10^{-5}$ mol/L EDTA, 99.5% of the radium are present as Ra^{2+}, with the remaining part represented by RaOH^{+}. Thus, the rather marginal effect of EDTA on the reduction of radium sorption in the experiment is due to the lack of changes in the radium speciation as a consequence of the complexation of virtually all the EDTA by Ca; the observed slight sorption reduction might be caused by small variations in the composition of the solution, ionic strength etc. or a minor change in the solid phase (e.g. Ca leaching), due to the presence of EDTA. In [45] an EDTA concentration of 0.01 mol/L is proposed as no-effect concentration, i.e., the concentration below no sorption reduction occurs, with respect to the sorption of Ra in cementitious systems.

Comparison radium, barium, and strontium sorption to CSH

From previous studies, a decreasing affinity for the sorption of alkaline earth elements to CSH phases in the order Ra > Ba > Sr can be inferred [10,12,15,18], indicating that in particular Sr cannot be used as meaningful analogue for quantification of the Ra uptake in cementitious systems [10,13]. However, in these studies usually only single radionuclides were studied using CSH prepared by slightly different methods and with various C/S ratios and specific surface areas. To overcome these difficulties in comparing the sorption of the alkaline earths, sorption experiments with radium, barium and strontium using the same CSH material as sorbent were performed. In Fig. 6, R_d values for the uptake of ^{226}Ra, ^{133}Ba and ^{90}Sr on CSH (C/S ratios 0.9 and 1.4) are compared (cf. Table 1). This comparison confirms:

1) the distribution ratios of studied radionuclides are independent of the concentration in solution in the investigated concentration range;

2) Ra sorption is strongest with R_d in the range of thousands L/kg (average $R_{d(C/S\ 0.9)}$ = 19,374 ±3,750 L/kg, $R_{d(C/S\ 1.4)}$ = 1,981 ±383 L/kg) and Sr sorption is the weakest at about 10^2 L/kg ($R_{d(C/S\ 0.9)}$ = 293 ±18 L/kg, $R_{d(C/S\ 1.4)}$ = 108 ±7 L/kg), while distribution ratios for Ba show intermediate values in the range from hundreds to thousands L/kg ($R_{d(C/S\ 0.9)}$ = 4,919 ±751 L/kg, $R_{d(C/S\ 1.4)}$ = 636 ±97 L/kg); and

3) for all investigated alkaline earth elements, the sorption to CSH increases with decreasing C/S ratio.

These findings are in good agreement with the literature (see, e.g., for Ra [10,15], for Ba [18] and for Sr [12]).

In the investigated concentration range, the sorption isotherms of all elements reveal a linear shape as shown in Fig. 6 (right). The K_d's obtained from the K_d-model fitting the experimental data are in very good agreement with the average values of R_d, and the values are as follows: radium – $K_{d(C/S\ 0.9)}$ = 19,240 ±387 L/kg, $K_{d(C/S\ 1.4)}$ = 1,818 ±49 L/kg, barium – $K_{d(C/S\ 0.9)}$ = 4,221 ±36 L/kg, $K_{d(C/S\ 1.4)}$ = 572 ±5 L/kg and strontium – $K_{d(C/S\ 0.9)}$ = 309 ±4 L/kg, $K_{d(C/S\ 1.4)}$ = 112 ±1 L/kg.

However, though the sorption behavior of the elements is similar in principle, the use of Ba or Sr to estimate R_d values of Ra, e.g., for safety assessments, does not seem appropriate.

CONCLUSIONS

The sorption of radium in very low concentrations on CSH was determined in a wide range of conditions (temperature, C/S ratio, L/S ratio, age of material, absence/presence of EDTA). Radium sorption on CSH between 20 and 80°C can be described with a linear isotherm (K_d-model) and radium sorption on CSH decreases as the temperature increases. For the first time, an estimate of activation energy, enthalpy, entropy and Gibbs energy of Ra sorption on CSH was made. Sorption of Ra on CSH has the character of an exothermic and spontaneous reaction taking place in the transition region probably controlled more by chemical reaction rather than diffusion. A significant effect of the age of the solid material on its sorption properties was observed with the R_d values increasing with the age of the material. Only a small reduction of the R_d value of radium sorption in presence of EDTA at concentrations below those of calcium was observed, leading to a sorption reduction factor 1.3, probably due to the limited availability of EDTA for complexation of radium, due to the high affinity of EDTA for complexation with Ca.

Comparison of the sorption of the 3 alkaline earths elements Ra, Ba and Sr on CSH at higher concentration range confirmed the linear sorption of these elements but with significantly different values of the distribution ratios, decreasing in the order Ra > Ba > Sr.

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NOMENCLATURE

A	frequency factor, L/mol·s
A_{init}	initial radionuclide activity, Bq
A_{t}	radionuclide activity at time *t*, Bq
c	radionuclide concentration in solution, mol/L
E_{A}	apparent activation energy, J/mol
F	fraction
G	Gibbs energy, J/mol
H	enthalpy, J/mol
k	kinetic coefficient, s^{-1}
K_{d}	distribution coefficient, L/kg
L/S	Liquid to Solid ratio, L/kg
m	mass, kg
q	radionuclide concentration in the solid phase, mol/kg
R	gas constant, 8.314 J/mol·K
R_{d}	distribution ratio, L/kg
S	entropy, J/mol·K
T	temperature, K
t	time, s

V	volume, L
Δ	difference
χ^2	chi-square value
AFm	Aluminate Ferrite monosulphate
AFt	Aluminate Ferrite trisulphate, ettringite
CEBAMA	CEment BAsed MAterials, European project
CEM I, II, III	CEMent type I, II or III
CORI	Cement-Organics-Radionuclide-Interactions, European project
CR	Chemical Reaction, kinetic model
CSH	Calcium-Silicate-Hydrate
C/S	Calcium to Silicon ratio
DFT	Density Functional Theory
DM	two-film model, kinetic model
EDTA	Ethylene Diamine Tetraacetic Acid
EURAD	European Joint Programme on Radioactive Waste Management
Euratom	European Atomic Energy Community
FD	Film Diffusion, kinetic model
GoF	Goodness-of-Fit
HCP	Hardened Cement Paste

HPGe	High Purity Germanium radiation detector
ID	Diffusion in Inert layer, kinetic model
ISA	ISosaccharinic Acid
LSC	Liquid Scintillation Counting
NTA	NitriloTriacetic Acid
SRF	Sorption Reduction Factor
SÚRAO	Czech Radioactive Waste Repository Authority

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Figure Captions List

Fig. 1	Distribution ratios of ^{223}Ra sorption on CSH C/S 1.0 (top left) and CSH C/S 1.2 (3 months, bottom left) as function of L/S ratio and evaluation of sorption isotherms (right) for 22 and 80°C. The data points presented in Fig. 1 (right) are shown here for two parallel determinations to demonstrate the uncertainty more clearly.
Fig. 2	Plots used for the determination of enthalpy and entropy (left) for sorption of ^{223}Ra on CSH C/S 1.0 and 1.2 for the distribution coefficient obtained from K_d-model. Activation energy (right) of sorption of ^{223}Ra on CSH C/S 1.0 for L/S 250 and 500 L/kg. Presentation of error bars of kinetic coefficient k as lnk is not possible.
Fig. 3	Influence of CSH C/S 1.2 age on ^{223}Ra sorption isotherms (left) - data points refer to two parallel determinations to demonstrate the uncertainty more clearly. Error bars are omitted for the sake of clarity. Comparison of R_d values of ^{226}Ra sorption on CSH with different C/S ratios (right); materials with a C/S ratio of 0.9 and 1.4 were several months old, while C/S 1.2 was freshly prepared.
Fig. 4	Distribution ratios of ^{223}Ra sorption on CSH (C/S = 1.2; age 12 months) with and without presence of EDTA (c = $5\cdot10^{-5}$ mol/L) as function of L/S ratio (left) and evaluation of sorption isotherms (right). The data points presented in Fig. 4 (right) are shown here for two parallel determinations to demonstrate the uncertainty more clearly.
Fig. 5	Calculated radium speciation ($c_{\mathrm{Ra}} = 1\cdot10^{-12}$ mol/L) in a solution containing $1\cdot10^{-3}$ mol/L Ca at two EDTA concentrations ($5\cdot10^{-5}$ and $5\cdot10^{-3}$ mol/L) as function of pH. F refers to fraction, n.b. two vertical axes in the right hand figure.
Fig. 6	Comparison of sorption of ^{226}Ra, ^{133}Ba and ^{90}Sr on CSH with C/S 0.9 and 1.4 in form of the R_d (left) and sorption isotherms (right). Error bars are omitted for the sake of clarity because of the logarithmic scale.

Table Caption List

Table 1	Summary of all observed distribution ratios (average R_d) and K_d obtained using the K_d-model. All R_d and K_d are in (L/kg).
Table 2	Entropy, enthalpy and Gibbs energy of sorption of ^{223}Ra on CSH C/S 1 and C/S 1.2 (age 3 months) calculated for K_d obtained using the K_d-model. As can be seen, the Gibbs energy is calculated for the temperatures used in the experiment.

Fig. 1

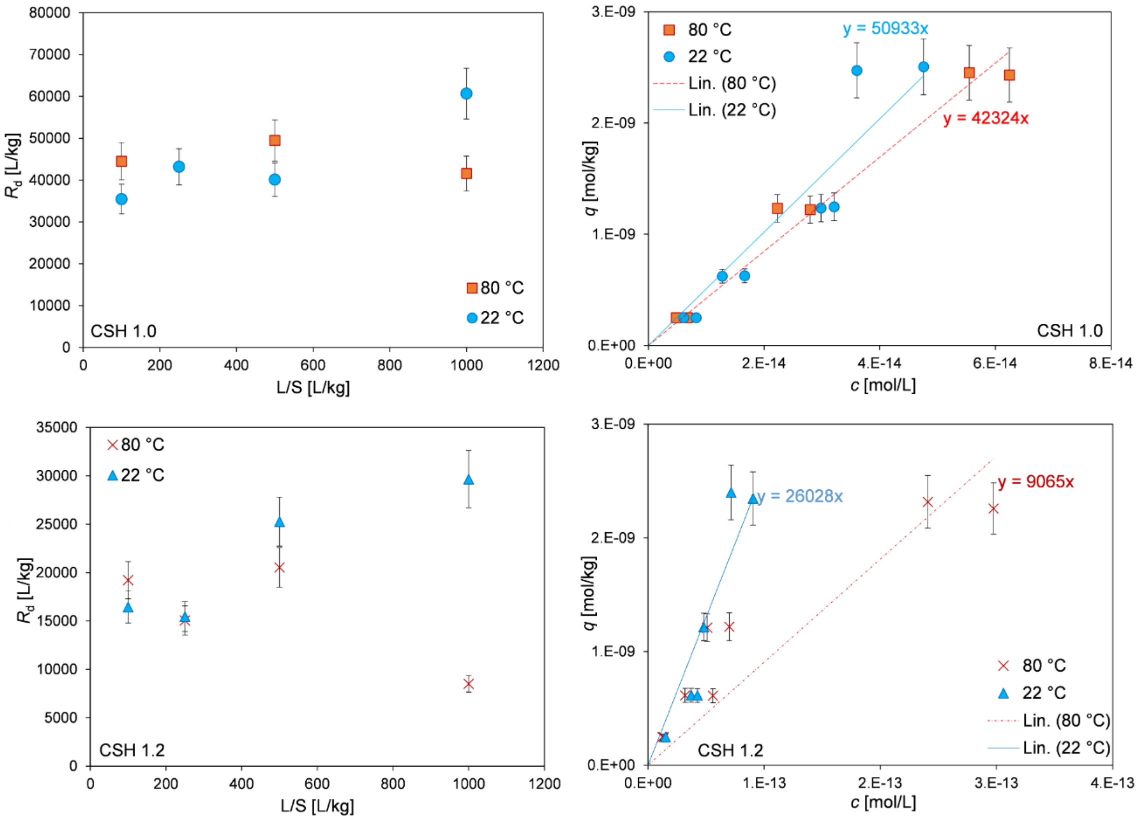
80000
70000
60000
50000
40000
30000
20000
10000
0
R_d [L/kg]
0
200
400
600
800
1000
1200
L/S [L/kg]
CSH 1.0
80 °C
22 °C
3.E-09
2.E-09
1.E-09
0.E+00
q [mol/kg]
0.E+00
2.E-14
4.E-14
6.E-14
8.E-14
c [mol/L]
80 °C
22 °C
Lin. (80 °C)
Lin. (22 °C)
y = 50933x
y = 42324x
CSH 1.0
35000
30000
25000
20000
15000
10000
5000
0
R_d [L/kg]
0
200
400
600
800
1000
1200
L/S [L/kg]
80 °C
22 °C
CSH 1.2
3.E-09
2.E-09
1.E-09
0.E+00
q [mol/kg]
0.E+00
1.E-13
2.E-13
3.E-13
4.E-13
c [mol/L]
y = 26028x
y = 9065x
80 °C
22 °C
Lin. (80 °C)
Lin. (22 °C)
CSH 1.2

Fig. 2

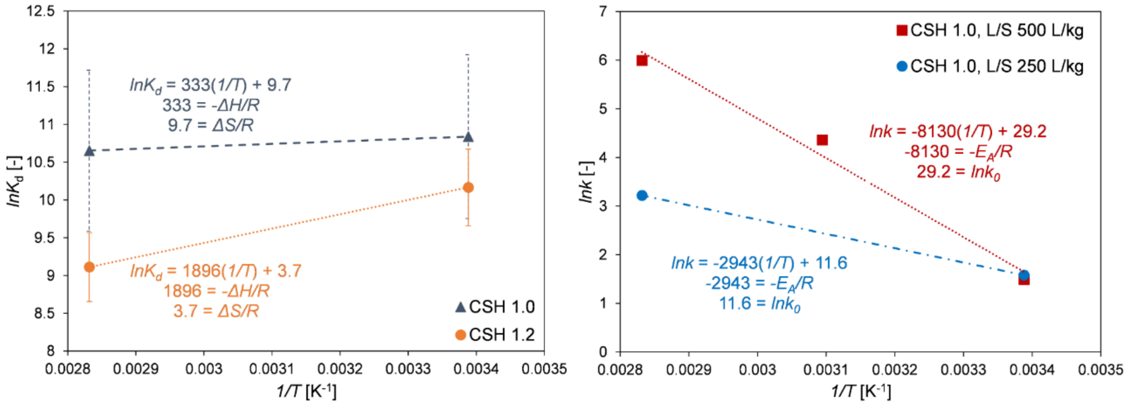
12.5
12
11.5
11
10.5
10
9.5
9
8.5
8
lnK_d [-]
lnK_d = 333(1/T) + 9.7
333 = -ΔH/R
9.7 = ΔS/R
lnK_d = 1896(1/T) + 3.7
1896 = -ΔH/R
3.7 = ΔS/R
▲ CSH 1.0
● CSH 1.2
0.0028
0.0029
0.003
0.0031
0.0032
0.0033
0.0034
0.0035
1/T [K-1]
7
6
5
4
3
2
1
0
lnk [-]
■ CSH 1.0, L/S 500 L/kg
● CSH 1.0, L/S 250 L/kg
lnk = -8130(1/T) + 29.2
-8130 = -E_A/R
29.2 = lnk_0
lnk = -2943(1/T) + 11.6
-2943 = -E_A/R
11.6 = lnk_0
0.0028
0.0029
0.003
0.0031
0.0032
0.0033
0.0034
0.0035
1/T [K-1]

Fig. 3

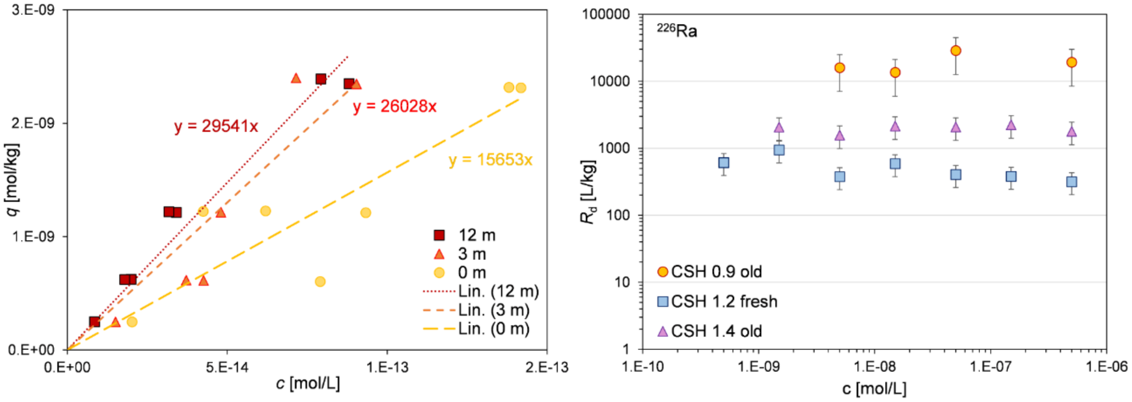
3.E-09
2.E-09
1.E-09
0.E+00
q [mol/kg]
0.E+00
5.E-14
1.E-13
2.E-13
c [mol/L]
y = 29541x
y = 26028x
y = 15653x
■ 12 m
▲ 3 m
● 0 m
Lin. (12 m)
Lin. (3 m)
Lin. (0 m)
100000
10000
1000
100
10
1
R_d [L/kg]
^{226}Ra
● CSH 0.9 old
■ CSH 1.2 fresh
▲ CSH 1.4 old
1.E-10
1.E-09
1.E-08
1.E-07
1.E-06
c [mol/L]

Fig. 4

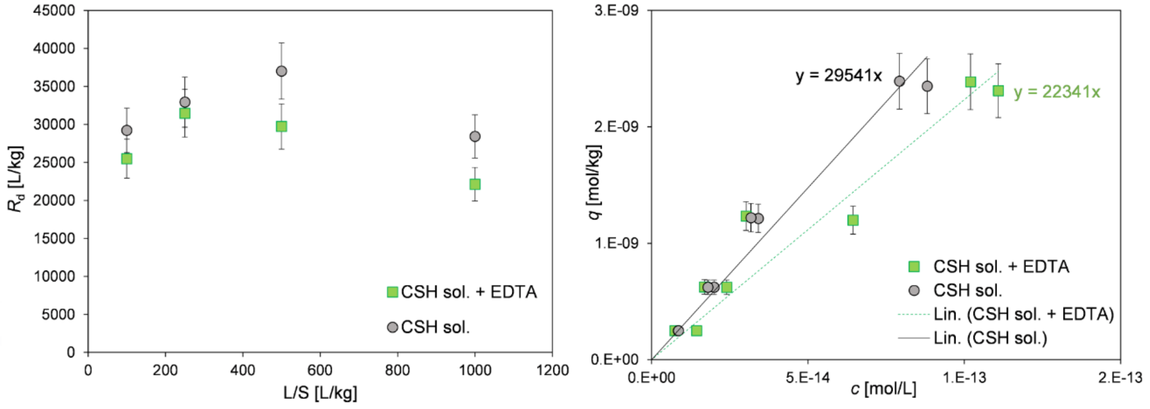
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
R_d [L/kg]
0
200
400
600
800
1000
1200
L/S [L/kg]
CSH sol. + EDTA
CSH sol.
3.E-09
2.E-09
1.E-09
0.E+00
q [mol/kg]
0.E+00
5.E-14
1.E-13
2.E-13
c [mol/L]
y = 29541x
y = 22341x
CSH sol. + EDTA
CSH sol.
Lin. (CSH sol. + EDTA)
Lin. (CSH sol.)

Fig. 5

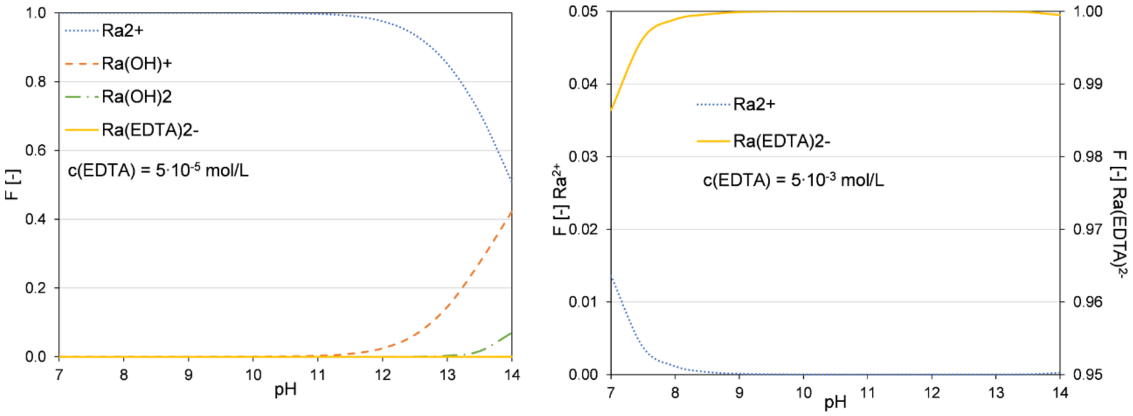
1.0
0.8
0.6
0.4
0.2
0.0
F [-]
Ra2+
Ra(OH)+
Ra(OH)2
Ra(EDTA)2-
c(EDTA) = 5·10^{-5} mol/L
7
8
9
10
11
12
13
14
pH
0.05
0.04
0.03
0.02
0.01
0.00
F [-] Ra^{2+}
1.00
0.99
0.98
0.97
0.96
0.95
F [-] Ra(EDTA)$^{2-}$
Ra2+
Ra(EDTA)2-
c(EDTA) = 5·10^{-3} mol/L
7
8
9
10
11
12
13
14
pH

Fig. 6

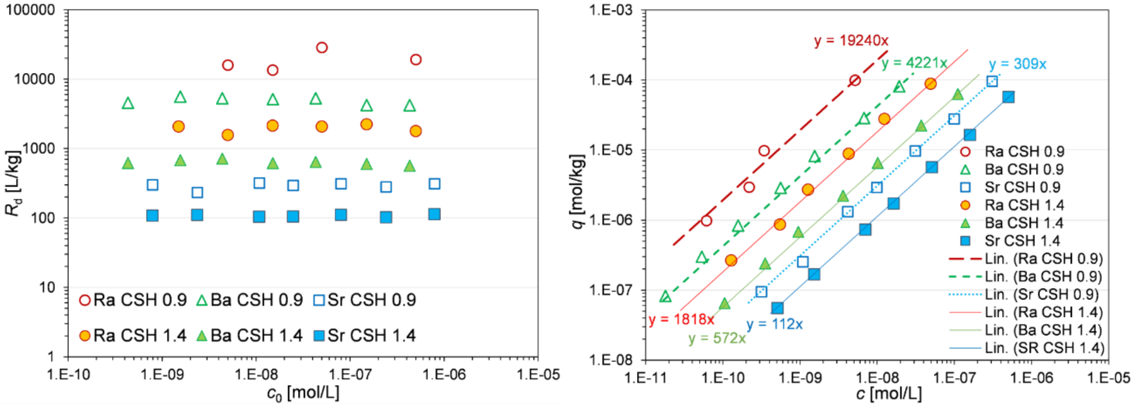
100000
10000
1000
100
10
1
R_d [L/kg]
1.E-10
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
c_0 [mol/L]
Ra CSH 0.9
Ba CSH 0.9
Sr CSH 0.9
Ra CSH 1.4
Ba CSH 1.4
Sr CSH 1.4
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
q [mol/kg]
1.E-11
1.E-10
1.E-09
1.E-08
1.E-07
1.E-06
1.E-05
c [mol/L]
y = 19240x
y = 4221x
y = 309x
y = 1818x
y = 572x
y = 112x
Ra CSH 0.9
Ba CSH 0.9
Sr CSH 0.9
Ra CSH 1.4
Ba CSH 1.4
Sr CSH 1.4
Lin. (Ra CSH 0.9)
Lin. (Ba CSH 0.9)
Lin. (Sr CSH 0.9)
Lin. (Ra CSH 1.4)
Lin. (Ba CSH 1.4)
Lin. (SR CSH 1.4)

Table 1

System	Average R_d	K_d-model
^{223}Ra sorption ($c \approx 2.5\cdot10^{-12}$ mol/L)		
CSH C/S 1.0, 22°C	44,838 ±4,605	50,933 ±4,158
CSH C/S 1.0, 80°C	45,176 ±4,640	42,324 ±1,858
CSH C/S 1.2, 22°C (3 months)	21,706 ±2,887	26,028 ±2,677
CSH C/S 1.2, 80°C (3 months)	15,823 ±2,105	9,065 ±1,066
CSH C/S 1.2, 22°C (12 months)	31,193 ±4,311	29,541 ±1,288
CSH C/S 1.2, 22°C (12 months), EDTA	27,207 ±3,677	22,341 ±1,558
CSH C/S 1.2, 22°C (0 months)	14,716 ±1,619	15,653 ±1,560
Ra × Ba × Sr sorption ($c \approx 10^{-10}$-10^{-7} mol/L)		
Ra CSH C/S 0.9	19,374 ±3,750	19,240 ±387
Ba CSH C/S 0.9	4,919 ±751	4,221 ±36
Sr CSH C/S 0.9	293 ±18	309 ±4
Ra CSH C/S 1.4	1,981 ±383	1,818 ±49
Ba CSH C/S 1.4	636 ±97	572 ±5
Sr CSH C/S 1.4	108 ±7	112 ±1
Ra CSH C/S 1.2 fresh	518 ±100	×
Ba CSH C/S 1.2 fresh	125 ±19	×
Sr CSH C/S 1.2 fresh	32 ±2	×

Due to the use of the model (K_d value) and the average (R_d value), the results in Table 1 are presented as values with more valid numbers than is generally appropriate for experimental results.

Table 2

CSH	Temp. used (°C)	ΔH (kJ/mol)	ΔS (J/mol·K)	$\Delta G_{22°C}$ (kJ/mol)	$\Delta G_{80°C}$ (kJ/mol)
C/S 1.0	22, 80	-2.8 ±1	80.7 ±7	-26.6 ±3	-31.3 ±3
C/S 1.2	22, 80	-15.8 ±6	31.1 ±3	-24.9 ±4	-26.8 ±4

Supplemental material

Supplemental Table S1: Kinetic models of sorption in two-phase systems used for the evaluation of ^{223}Ra sorption kinetics in systems with CSH.

Controlling process	**Model notation**	**Differential equation**
Mass transfer	DM	$\frac{dq}{dt} = K_{\mathrm{DM}}(q^* - q)$
Film diffusion	FD	$\frac{dq}{dt} = K_{\mathrm{FD}}(c - c^*);\ \ K_{\mathrm{FD}} = \frac{3D}{\delta R \rho}$
Diffusion in an inert layer	ID	$\frac{dq}{dt} = K_{\mathrm{ID}} \frac{c - c^*}{(1 - \frac{q}{q^*})^{-\frac{1}{3}} - 1};\ \ K_{\mathrm{ID}} = \frac{3D}{R^2 \rho}$
Chemical reaction (taking place in the reaction zone, here for the first order reversible reaction)	CR	$\frac{dq}{dt} = K_{\mathrm{CR}} \frac{(c - c^*)}{(1 - \frac{q}{q^*})^{-\frac{2}{3}}};\ \ K_{\mathrm{CR}} = \frac{3k_{\mathrm{CR}}}{R\rho};$ $r_{\mathrm{CR}} = k_{\mathrm{CR}}(c - c^*)$

Following equations hold:
$dq/dt = - r \cdot dc/dt$
if c is the integration variable: $q = r \cdot (c_0 - c) + q_0$
if q is the integration variable: $c = c_0 - (q - q_0)/r$

In Table S1, c is the concentration of the component in the aqueous phase at time t; q – concentration of the component in the sorbent at time t; c^* – equilibrium concentration of the component in the aqueous phase corresponding to the equilibrium concentration q^* of the component in the sorbent; q_0 – starting concentration of the component in the sorbent; t – time; r (L/S) – ratio of aqueous to solid phase; D – diffusion coefficient of the component, K_{DM}; K_{FD}, K_{ID}, K_{CR}, – over-all kinetic coefficients; k_{CR} – kinetic coefficient of the chemical reaction; r_{CR} – rate of the chemical reaction; R – mean radius of the solid phase particle; ρ – density of the solid sorbent; δ – thickness of the “liquid film” on the surface of the solid particle.

Supplemental Table S2: Selected equilibrium constants (log K^0) used in the thermodynamic calculations.

Reaction	**log *K*°**	**Reference**
$H_4(EDTA)(cr) \Leftrightarrow EDTA^{4-} + 4H^+$	-27.220 ±0.200	[S1]
$EDTA^{4-} + H^+ \Leftrightarrow H(EDTA)^{3-}$	11.240 ±0.030	[S1]
$EDTA^{4-} + 2H^+ \Leftrightarrow H_2(EDTA)^{2-}$	18.040 ±0.036	[S1]
$EDTA^{4-} + 3H^+ \Leftrightarrow H_3(EDTA)^-$	21.190 ±0.062	[S1]
$EDTA^{4-} + 4H^+ \Leftrightarrow H_4(EDTA)(aq)$	23.420 ±0.200	[S1]
$EDTA^{4-} + 5H^+ \Leftrightarrow H_5(EDTA)^+$	24.720 ±0.223	[S1]
$EDTA^{4-} + 6H^+ \Leftrightarrow H_6(EDTA)^{2+}$	24.220 ±0.300	[S1]
$Ca^{2+} + EDTA^{4-} \Leftrightarrow Ca(EDTA)^{2-}$	12.690 ±0.060	[S1]
$Ca^{2+} + EDTA^{4-} + H^+ \Leftrightarrow Ca(HEDTA)^-$	16.230 ±0.108	[S1]
$Ra^{2+} + EDTA^{4-} \Leftrightarrow Ra(EDTA)^{2-}$	9.13 ±0.07	[29]

[S1] Hummel, W., Anderegg, G., Puigdomènech, I., Rao, L., and Tochiyama, O., 2005, *Chemical Thermodynamics of Compounds and Complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with Selected Organic Ligands*, Elsevier, Amsterdam.

Supplemental Table S3: Ion interaction coefficients ($\varepsilon_{i,j}$) used in the thermodynamic calculations.

i	***J***	**$\varepsilon_{i,j}$**	**Reference**
H^+	Cl^-	0.12	[S2]
OH^-	Na^+	0.04	[S2]
Ca^{2+}	Cl^-	0.14	[S2]
$EDTA^{4-}$	Na^+	0.32	[S1]
$H(EDTA)^{3-}$	Na^+	-0.10	[S1]
$H_2(EDTA)^{2-}$	Na^+	-0.37	[S1]
$H_3(EDTA)^-$	Na^+	-0.33	[S1]
$H_5(EDTA)^+$	Cl^-	-0.23	[S1]
$H_6(EDTA)^{2+}$	Cl^-	-0.20	[S1]
$Ra(EDTA)^{2-}$	Na^+	-0.10	[29]

[S2] Lemire, R. J., Fuger, J., Spahiu, K., Sullivan, J. C., Nitsche, H., Ullman, W. J., Potter, P., Vitorge, P., Rand, M. H., Wanner, H., and Rydberg, J., 2001, *Chemical Thermodynamics of Neptunium and Plutonium*, Elsevier, Amsterdam.

Supplemental Fig. S1: Calculated speciation of EDTA in a solution containing $1\cdot10^{-3}$ mol/L Ca at two EDTA concentrations ($5\cdot10^{-5}$ and $5\cdot10^{-3}$ mol/L) as function of pH. F refers to fraction, n.b. two vertical axes in the left hand figure.