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1

2 Manuscript for Applied Geochemistry

3 **Retention and diffusion of radioactive and toxic species on cementitious**
4 **systems: main outcome of the CEBAMA project**

5

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22

23 **Highlights**

24

- understanding anion retention in cementitious materials

25

- reducing uncertainties with respect to radionuclide behaviour in hardened cement pastes

26

- justifying assumptions used when representing radionuclide migration in safety assessments

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- improving databases for assessing adsorption of radionuclides in fresh and degraded cement systems

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1 Abstract

2

3 Cement-based materials are key components in repository barrier systems. To improve the available knowledge
 4 base, the CEBAMA (Cement-based materials) project aimed to provide insight on general processes and
 5 phenomena than can be easily transferred to different applications. A bottom up approach was used to study
 6 radionuclide retention by cementitious materials in the European CEBAMA project, encompassing both individual
 7 cement mineral phases and hardened cement pastes. Solubility experiments were conducted with Be, Mo and Se
 8 under high pH conditions to provide realistic solubility limits and radionuclide speciation schemes as a
 9 prerequisite for meaningful adsorption studies. A number of retention mechanisms were addressed including
 10 adsorption, solid solution formation and precipitation of radionuclides within new solid phases formed during
 11 cement hydration and evolution. Sorption/desorption experiments were carried out on several anionic
 12 radionuclides and/or toxic elements which have received less attention than metals to date, namely: Be, Mo, Tc,
 13 I, Se, Cl, Ra and ^{14}C . Solid solution formation between radionuclides in a range of oxidation states (Se, I and Mo)
 14 and the main components (OH^- , SO_4^{2-} , Cl^-) of cementitious phases (AFm , $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\cdot\text{SO}_4\cdot 6\text{H}_2\text{O}$) were also
 15 investigated.

16

17 Keywords

18 Cement-based materials, radionuclide and toxic element retention, sorption, solubility, hydrolysis, diffusion,
 19 CEBAMA

20 Introduction

21 Cement-based materials are widely used as waste forms, backfill, seals, or as structural components in current
 22 and planned repositories for low, intermediate and high level radioactive waste (Glasser et al., 1989). Substantial
 23 data on these materials exists both in the nuclear and the civil engineering sectors but there are nevertheless,
 24 important gaps in our knowledge regarding their long-term performance. The European project CEBAMA was
 25 established to address key issues of relevance for long term safety and remaining scientific questions related to
 26 the use of cement-based materials as barrier in radioactive waste management. The research conducted was
 27 independent of specific disposal concepts and addressed the behaviour of cementitious materials in different
 28 host rocks considering where appropriate the likely presence of bentonite backfills. CEBAMA did not focus on one
 29 specific cement material, but rather aimed to provide insight into generic processes and phenomena that could
 30 then be transferred to different applications and repository projects.

31 Radionuclide retention in cementitious systems depends on the nature, charge and valence state of the
 32 radionuclide, on environmental conditions (cation and anion concentrations, Eh, pH, temperature), the type and
 33 degradation state of the cement pastes (see supplementary materials for definition) including carbonation, the
 34 presence of additives such as organic molecules (superplasticisers, retarders) and the water/cement ratio (Ochs
 35 et al., 2016). Cement pore water generates a high pH environment, which may reduce the solubility and hence
 36 migration of certain radionuclide species (Felipe-Sotelo et al., 2016, Felipe-Sotelo et al., 2017), but can increase
 37 mobility of anionic species. Anion retention has not been investigated to the same extent than that of cations.

38 The retention mechanism in any given situation depends on the total concentration of the investigated species,
 39 including radioactive and stable isotopes, and the solid to liquid ratio. For example, by using MoO_4^{2-} as a probe
 40 and supplementing adsorption isotherms with *in situ* time-resolved synchrotron-based X-ray diffraction, Ma et al.
 41 (2017) have identified three retention modes on AFm phases $(\text{Ca}_2(\text{Al},\text{Fe})(\text{OH})_6]\cdot\text{X}\cdot\text{xH}_2\text{O}$ where X equals an
 42 exchangeable singly charged or half of a doubly charged anion) depending on total Mo concentration: edge
 43 adsorption at low Mo concentrations, interfacial dissolution-precipitation as an AFm- MoO_4 phase (AFm phase
 44 where some of the sulphate anions forming the AFm structure are substituted by molybdate anions) at higher Mo
 45 concentrations and solubility constrained by precipitation of CaMoO_4 for the highest Mo concentrations
 46 investigated. In contrast, Marty et al. (2018), using a flow-through experimental system with an initial Mo

1 concentration around 5 mM, did not observe dissolution/ precipitation, but only interlayer adsorption. This was
 2 attributed to the fact that, in batch experiments, a fast AFm equilibration led to increase Ca and Al concentration
 3 that induced dissolution/precipitation phenomena. The present work covers several retention processes such as
 4 by adsorption, co-precipitation and precipitation of radionuclide-bearing solids.
 5 A bottom-up approach was used extending from radionuclide retention studies on synthesized individual
 6 hydrated cement phases to hardened cement pastes (HCP) covering a range of compositions (CEM I, CEM II, CEM
 7 V and a low pH cement formulation). Upon closure of a nuclear waste repository, influx of groundwater will alter
 8 the cement-based materials and could potentially compromise radionuclide containment. Therefore, the impact
 9 on retention of radionuclides of various geochemical alteration processes, such as carbonation and alteration of
 10 cement-based materials were also investigated. Since unsaturated conditions with relative humidity (RH) values
 11 as low as 50% may arise during repository development, some experiments were performed in humid air at
 12 corresponding RH values.

13 The individual hydrated cement phases were studied comprising the major phases of a CEM I cement, excluding
 14 portlandite ($\text{Ca}(\text{OH})_2$), as no significant interaction of the latter and the radionuclides of interest is expected (Ochs
 15 et al., 2016). Calcium silicate hydrate (C-S-H) and calcium aluminate as AFm or AFt, with general formula
 16 $\text{Ca}_6(\text{Al,Fe})_2\text{X}_3(\text{OH})_{12}\cdot x\text{H}_2\text{O}$, X being one divalent or two monovalent anions (Champenois et al., 2012, Goetz-
 17 Neunhoffer and Neubauer, 2006); these phases together constitute $\approx 60\%$ of bulk hydrated cement pastes and
 18 provide favourable sites for the adsorption of radionuclides (Evans, 2008 and Ochs et al., 2016). The properties of
 19 these phases are strongly dependent on their crystallographic structure, including crystal size and the nature of
 20 the layer charge (e.g., isomorphic substitutions, lattice vacancies). A good understanding of their interaction with
 21 radionuclides is vital for building a safety case for a geological disposal facility. As many data for radionuclide
 22 retention on cementitious materials have already been determined (e.g. Bradbury and Sarrot, 1995, Wieland,
 23 2014, Ochs et al., 2016), only those radionuclides regarded as being of high priority from the safety perspective
 24 and which have not yet received sufficient attention in the past, especially Be(stable), ^{14}C , ^{129}I , ^{36}Cl , ^{79}Se , ^{93}Mo ,
 25 ^{226}Ra and ^{99}Tc have been studied in this work. They are largely but not exclusively anionic species and are
 26 perceived as potentially more mobile under repository conditions. Depending on the redox state of the
 27 geochemical and engineered barrier environment, the key anionic species are Cl^- , I^- , IO_3^- , Se^{2-} , SeO_3^{2-} , SeO_4^{2-} ,
 28 MoO_4^{2-} , $^{14}\text{CO}_3^{2-}$ and TcO_4^- .

29 Important interactions of anions are expected to occur onto AFm phases, hydrotalcite-like phases
 30 ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{--}19\text{H}_2\text{O}$) and AFt phases. AFt phases have the general formula $\text{Ca}_6(\text{Al,Fe})_2\text{X}_3(\text{OH})_{12}\cdot n\text{H}_2\text{O}$, X being
 31 one divalent or two monovalent anions. They are characterized by a pillar structure consisting of positively
 32 charged $[\text{Ca}_3(\text{Al,Fe})(\text{OH})_6\cdot 12\text{H}_2\text{O}]^{+3}$ columns. The positive charge on the columns is compensated by exchangeable
 33 negatively charged $[3/2\text{X}\cdot n\text{H}_2\text{O}]^{-3}$ anions in channels. The most important AFt phase is ettringite ($\text{X}=\text{SO}_4$) which
 34 forms quite rapidly in the early stages of cement hydration (Taylor, 1997). AFm phases also formed during cement
 35 hydration, they have a lamellar structure composed of a positively charged main layer and a negatively charged
 36 interlayer, $[\text{X}\cdot n\text{H}_2\text{O}]^{-2}$, X : 2 singly charged or 1 doubly charged anion (Buttler et al., 1959). The general structural
 37 formula of an AFm is $[\text{Ca}^{+2}_4(\text{Al}^{+3}_x\text{Fe}^{+3}_{(1-x)})_2(\text{OH})_{12}]\cdot \text{X}\cdot n\text{H}_2\text{O}$, where the main layer species are put between brackets
 38 and $\text{X}\cdot n\text{H}_2\text{O}$ represents the hydrated exchangeable "interlayer anions" (n is the number of water
 39 molecules). These exchangeable interlayer anions compensate for the positive layer charge induced by the
 40 presence of trivalent cations in the layers, providing AFm with an anion-exchange capacity. Natural anionic
 41 species competing for exchange sites include OH^- , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_5^{2-}$ etc. There are two types of exchange
 42 sites identified for fixation of anions: surfaces ion exchange and interlayer anion exchange sites (Ma et al., 2017,
 43 Ma et al., 2018).

44 C-S-H phases precipitate during the hydration of Portland cement and blended cements. C-S-H are characterized
 45 by calcium to silica molar ratio (Ca/Si) between 0.7 and 1.7. They are nanocrystalline and disordered phases
 46 whose structure is thought to be close to tobermorite $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2\cdot n\text{H}_2\text{O}$ (although some authors also
 47 propose jennite $\text{Ca}_9\text{Si}_6\text{O}_{18}(\text{OH})_6\cdot 8\text{H}_2\text{O}$). The variability in the Ca/Si ratio is due to variable degree of
 48 polymerization of the Si chains, and subsequent charge compensation by interlayer Ca. At the highest Ca/Si ratios,

1 nanocrystalline $\text{Ca}(\text{OH})_2$ can be present. Surface charge of a solid phase may influence in a great extent the
2 interactions that occur between the solid surface and the species in solution. At low Ca/Si ratios, negative surface
3 charge is observed on C-S-H, while at higher Ca/Si ratios the sorption of Ca^{2+} results in an apparent positive
4 surface charge of C-S-H (Churakov et al., 2014). Hence, the variation on composition causes significant changes in
5 their properties as adsorbent. Due to the importance of C-S-H phases in cementitious materials, Ra^{2+} , I^- , MoO_4^{2-} ,
6 SeO_3^{2-} and SeO_4^{2-} retention was studied for different Ca/Si ratios (corresponding to different stages of alteration
7 of cements).

8 Mineral precipitation is a potentially significant retention process for both cationic and anionic radionuclide
9 species (Ma et al., 2019). In order to avoid misinterpretation of solubility derived data as 'sorption' processes,
10 adsorption studies were performed at sufficiently low concentrations to avoid precipitation. Specific solubility
11 studies in cementitious systems were conducted for CaMoO_4 (powellite), $\text{BeO}(\text{cr})$ and $\alpha\text{-Be}(\text{OH})_2(\text{cr})$. The
12 implications of calcite solubility on data interpretation for $^{14}\text{CO}_3^{2-}$ sorption is also addressed.

13 Pure hydrated cementitious phases and HCP were synthesized and characterized. Advanced micro-analytical and
14 spectroscopic techniques were used in order to derive detailed process understanding (see supplementary
15 information).

16

17 **Experimental**

18 The experimental techniques used include the fabrication of pure phases and solid solutions, solubility tests,
19 adsorption and diffusion studies. Different cement formulations are used. A large quantity of analytical
20 techniques have been used to characterise aqueous and solid phases before and after the experiments. Details
21 are given in the supplementary information.

22

23 **Results and Discussion**

24 **Solubility studies**

25 The low solubility of certain radionuclide phases in high pH solutions can provide an effective retention
26 mechanism. For example, precipitation of calcite at the high Ca concentrations present in cement pore water can
27 significantly reduce the mobility of $^{14}\text{CO}_3^{2-}$. In this work, the solubility of several potentially important
28 radionuclide-bearing solid phases has been determined.

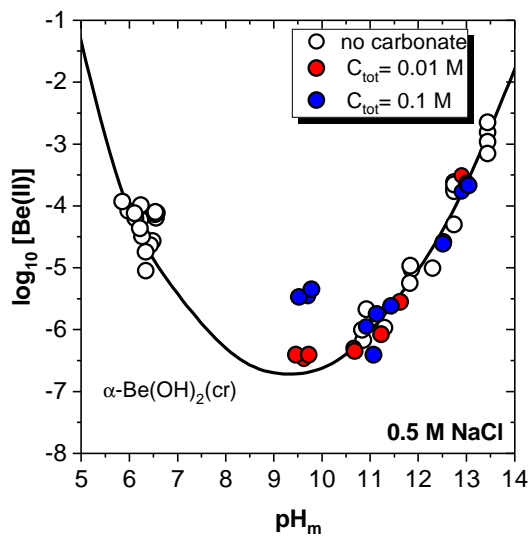
29 ***CaMoO₄***

30 Under cementitious conditions ($\text{pH} > 9$, $[\text{Ca}] = 1\text{-}20$ mM), powellite ($\text{CaMoO}_4(\text{s})$) is believed to be the solubility-
31 controlling phase under all stages of cement degradation (Kindness et al., 1994). In this case, molybdenum
32 solubility is very sensitive to differences in calcium concentrations. The conditions under which powellite might
33 precipitate cover a wide range of pH and Eh, suggesting the stability of this phase in cements-based materials.
34 Only at the more advanced stages of cement degradation and strongly reducing conditions would Mo solubility
35 be controlled by $\text{MoO}_2(\text{s})$ (Grive and Olmeda, 2016). Berner (2014) conducted solubility and speciation
36 calculations in cementitious pore waters using the Nagra/PSI Chemical Thermodynamic Data Base for Mo. He
37 established the total dissolved concentration of MoO_4^{2-} equal to $7.2 \cdot 10^{-6}$ M with $\text{CaMoO}_4(\text{s})$ as the stable solid;
38 $\text{MoO}_2(\text{s})$ was stable only below -750 mV/SHE.

39 Powellite solubility was evaluated using prepared Aft equilibrated waters. These solubility tests confirmed that
40 experimental data can be accurately described using the solubility constant reported in the bibliography
41 ($\log K_{\text{s}, 25^\circ\text{C}} = 7.90 \pm 0.33$ from Thermochemie Database vs 9.b.0; (Giffaut et al., 2014).

α -Be(OH)₂(cr) and BeO(cr)

1 Solubility data obtained in this work (see details in supplementary data, 4) confirm the amphoteric character of
 2 Be(II), with a solubility minimum at pH_m 9 (with pH_m = -log [H⁺]). At this pH_m, [Be(II)] in equilibrium with BeO(cr)
 3 and α -Be(OH)₂(cr) is $\approx 10^{-7.5}$ and $\approx 10^{-7}$ M, respectively. The hydrolysis constant previously reported for
 4 Be(OH)₂(aq) in potentiometric studies is substantially overestimate (Bruno, 1987, China et al., 1997, Kakihana
 5 and Sillen, 1956). The combination of solubility data determined in this work, slope analyses, solid phase
 6 characterization and ⁹Be NMR allow comprehensive chemical, thermodynamic and (SIT) activity models for the
 7 system Be⁺²-Na⁺-K⁺-H⁺-Cl⁻-OH⁻-H₂O(l) (see Cevirim-Papaioannou et al., 2019, this special issue). Additional
 8 experiments conducted in the presence of carbonate (see Figure 1) highlight that, within the boundary conditions
 9 expected in cementitious systems, carbonate cannot outcompete hydrolysis and that the aqueous speciation of
 10 Be(II) is dominated by the anionic species Be(OH)₃⁻ and Be(OH)₄⁻².
 11



12

13 **Figure 1.** Solubility of α -Be(OH)₂(cr) in 0.5 M NaCl-NaOH-NaHCO₃-Na₂CO₃ solutions at $9.5 \leq \text{pH}_m \leq 13$ and $C_{\text{tot}} = [\text{HCO}_3^-] +$
 14 $[\text{CO}_3^{2-}] = 0, 0.01$ and 0.1 M. Solid line corresponding to the solubility calculated with the thermodynamic model derived in
 15 (Cevirim-Papaioannou et al., 2019) (this special issue)

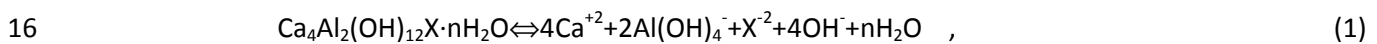
Characterization and solubility product of pure AFm phases

17 Pure AFm phases containing selenate, selenite, selenide and molybdate have been reported by to play a role in
 18 the retention of Se(IV) or Mo in cement systems (Felipe-Sotelo et al., 2016, Ma et al., 2017, Rojo et al., 2018).
 19 They appear to form at solution concentrations of Se or Mo lower than required for formation of pure CaSeO₃(s)
 20 or CaMoO₄(s), respectively. On the other hand side, pure Mo(VI)- and Se(VI)-AFm phases apparently are only able
 21 to form once surface sorption sites on the edges of the original S(VI)-AFm or Cl₂-AFm are saturated (Ma et al.,
 22 2017, Ma et al., 2018). In the present work pure S(VI)-AFm, S(IV)-AFm, S(II)-AFm, Se(IV), Se(VI) and the I-AFm
 23 were synthesised to allow comparison of the thermodynamic stabilities of Se- and I-containing AFm phases with
 24 the stabilities of AFm phases containing anions commonly present in cementitious environments under oxidizing
 25 and reducing conditions (L. Nedyalkova et al., 2019b). Most of the above-listed AFm phases were observed to
 26 crystallize in the rhombohedral $R\bar{3}$ space group with common position of the (110) reflection of the basal plane
 27 at $\sim 31^\circ 2\theta$. Only the Se(IV)-AFm sample and the Se(VI)-AFm sample exhibit diffraction patterns corresponding to
 28 a symmetry lower than rhombohedral.

29 The S(VI)-AFm sample after drying was found to be a mixture of two phases, one with 12 H₂O molecules and an
 30 interlayer distance of 8.93 Å, and the other one with 14 H₂O molecules and an interlayer distance of 9.50 Å, the
 31 latter being more relevant in H₂O-saturated conditions. The rhombohedral crystal structure of S(VI)-AFm was
 32 refined by (Allmann, 1977). Diffraction data of the S(IV)-AFm sample revealed a hexagonal lattice with a
 33 rhombohedral space group. The interlayer distance was found to be 8.51 Å. Structure analysis suggests that the
 34 SO₃²⁻ anions are positioned parallel to the main layer at the center of the interlayer region (L. Nedyalkova et al.,

1 2019b). Diffraction patterns of the S(II)-AFm sample suggest a symmetry lower than rhombohedral. The use of a
 2 monoclinic unit cell however cannot satisfactorily explain the diffraction data. An ab-initio structure
 3 determination from the powder diffraction data using FOX (Free objects for Cristallography, Favre-Nicolin and
 4 Černý, 2002) revealed on average a rhombohedral lattice for this AFm phase with an interlayer distance of
 5 10.33Å.

6 In the Se(IV)-sample the co-existence of two distinct Se(IV)-AFm hydrates was found (Latina Nedyalkova et al.,
 7 2019b) with rhombohedral and trigonal symmetries having interlayer distances of 11.05 Å and 9.65 Å,
 8 respectively, similar to the values of 11.03 Å and 9.93 Å reported by (Ma et al., 2018). The diffraction patterns
 9 found for Se(VI)-AFm phases suggest a symmetry lower than the previous AFm phases and correspond to an
 10 apparent monoclinic unit cell with an interlayer distance of 10.18 Å . The water content of the synthesized AFm
 11 phases was determined with thermogravimetry and dynamic vapor sorption (DVS). This information combined
 12 with the chemical composition of the solutions in equilibrium with the AFm phases allowed to determine
 13 solubility products (log K) using the thermodynamic modelling software GEMS (Kulik et al., 2013) and the
 14 NAGRA/PSI thermodynamic database (Hummel et al., 2002a, (Hummel et al., 2002b). Defining the solubility
 15 product of AFm phases, $\log_{-}K_{s0}$, described by the equation (1):



17 the following mean values were calculated: $\log_{-}K_{s0} = -26.9 \pm 0.9$ (S(IV)-AFm), -27.8 ± 0.5 (I-AFm), -28.4 ± 1.4
 18 (Se(IV)-AFm), 28.5 ± 1.4 (S(VI)-AFm), -29.2 ± 0.6 (Se(VI)-AFm) and -30.5 ± 0.8 (S(II)-AFm). These values are
 19 comparable with the solubility products for Se(VI)-AFm and Se(IV)-AFm obtained by Ma et al., (2018)
 20 reformulated to the above definition of $\log_{-}K_{s0}$.

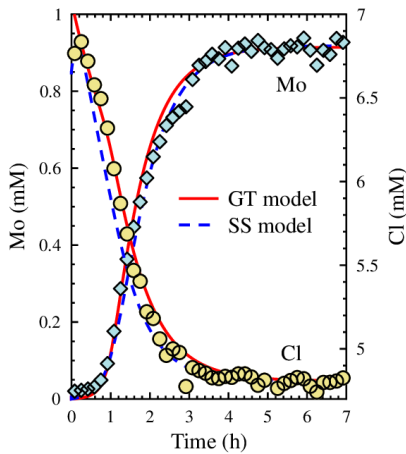
21 **Dissolution rates of AFm phases**

22 Dissolution rates for AFm-Cl phases have been determined in flow-through tests at pH values ranging from 9.2 to
 23 13 (Marty et al., 2017). For pH values from 10 to 13, congruent dissolution was observed (i.e. Ca/Al ratios close to
 24 2 both for solids and outlet concentrations). In contrast, precipitation of amorphous Al-phases and possibly
 25 amorphous mixed Al/Ca phases was suspected at pH 9.2 leading to Ca/Al ratios higher than those of the initial
 26 solid determined from the outlet solutions. The far-from-equilibrium dissolution rate at pH values ranging from
 27 9.2 to 13 and room temperature is given by $\log R = -9.23 \pm 0.18$, with R values provided in $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, indicating
 28 complete dissolution in few days (i.e. high reactivity). Hence, AFm phases are only stable in cementitious systems
 29 under close to equilibrium conditions.

30 **Exchange process of AFm phases with radionuclides of interest**

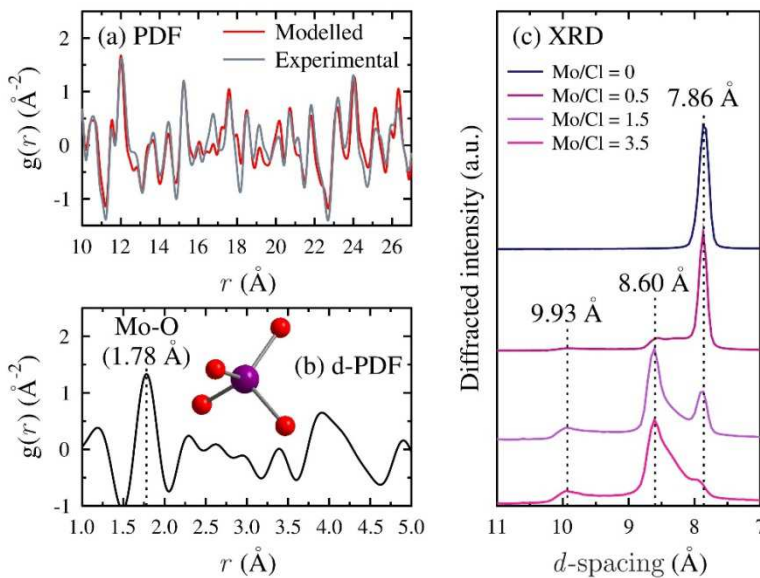
31 Using the $\text{Cl}^{-}/\text{MoO}_4^{-2}$ exchange on AFm-Cl as test case, flow-through experiments were conducted in alkaline
 32 conditions ((Marty et al., 2018; Grangeon and Marty, 2019). Experiments were performed using medium Mo
 33 concentrations (0.6–0.9 mM) under far-from-equilibrium conditions with respect to AFm (i.e. in conditions where
 34 precipitations of Cl-AFm and MoO_4 -AFm are unexpected). A MoO_4^{-2} -rich solution was flowed through an AFm-Cl
 35 suspension and chemical parameters (pH and concentrations) were monitored at the output of a reactor. The
 36 $\text{MoO}_4^{-2}/\text{Cl}^{-}$ and $\text{OH}^{-}/\text{Cl}^{-}$ selectivity coefficients were determined by modelling MoO_4^{-2} and Cl^{-} concentrations as a
 37 function of time (GT model in Fig 2); there were found to be $10^{1.3}$ and $10^{0.8}$, respectively. Nonetheless, it is also
 38 possible to model experimental data of Marty et al. (2018) using the solid solution approach described by Walker
 39 (2010) as show by the SS model in Fig 2. The SS model was an ideal solid solution with 3 end-members (Cl-AFm,
 40 OH^{-} -AFm and MoO_4 -AFm). Whatever the modelling approach (GT or SS models), one mole of MoO_4^{-2} replaced two
 41 moles of Cl^{-} , as expected from the ratio of charges. However, exchange reaction implies that MoO_4^{-2} sorption is
 42 fast and reversible, i.e. that no structural incorporation or coprecipitation occurred. To verify this hypothesis, a
 43 molecular-scale understanding of the sorption is mandatory. To this end Marty et al., (2018) collected the X-ray
 44 scattering signal of the AFm-Cl before and after reaction with MoO_4^{-2} , and processed the data in the reciprocal (q)
 45 and real (r) spaces to first check for AFm-Cl purity (Fig. 3a) and then decipher the local order around sorbed Mo
 46 and the modifications of the unit cell induced by Mo sorption. In the r space, authors determined that MoO_4^{-2}

1 replaces Cl⁻ in the interlayer and adopts a regular geometry, with the four Mo-O distances being equal to 1.78 Å
 2 (Fig 3b). In the q space, it could be shown that the incorporation of MoO₄²⁻ increases the layer-to-layer distance
 3 by 0.7-2.1 Å as compared to AFm-Cl (Fig. 3c). It is proposed that the heterogeneity in layer-to-layer distance
 4 results either from two different interlayer organizations of MoO₄²⁻ or from heterogeneous hydration state. At
 5 the crystal scale, it was observed that the Cl-/MoO₄²⁻ exchange involved interstratification of Mo- and Cl-rich
 6 interlayers. Authors found no evidence for sample recrystallization or secondary phase formation, possibly
 7 because the continuous solution renewing allowed keeping low Ca and Al concentration, thus preventing
 8 reaching supersaturation of any phase.



9

10 Fig. 2. Experimental (symbols) and modelled (lines) [Mo] (diamond) and [Cl] (circle) as a function of time of at the
 11 output of a reactor in which a solution containing Mo is flowed through an AFm-Cl suspension (modified from
 12 (Grangeon and Marty, 2019)).



13

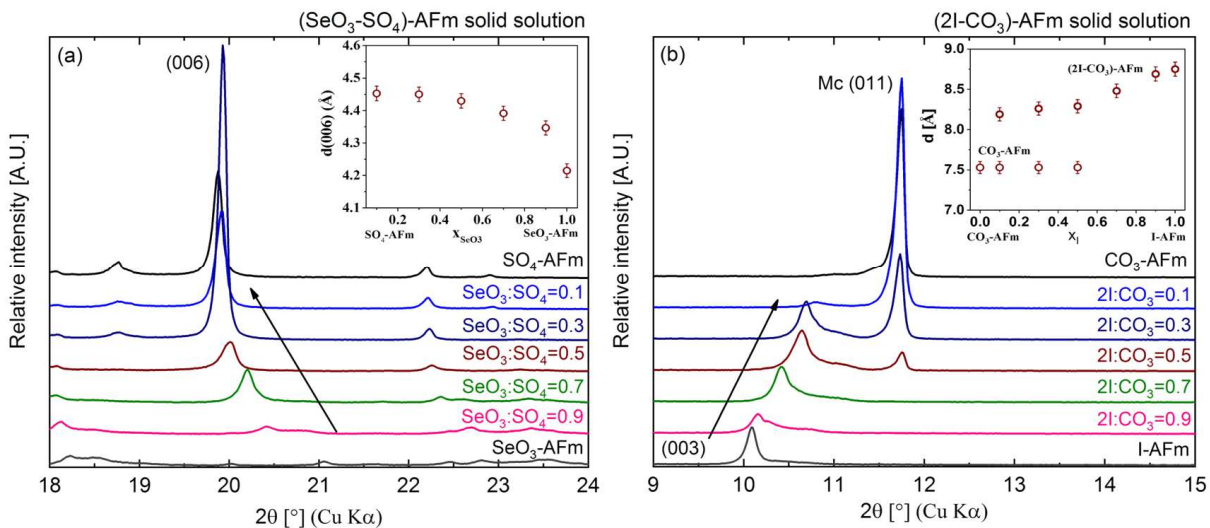
14 Fig. 3. (a): Experimental and modelled AFm-Cl PDF. (b): differential PDF (AFm-Cl minus a sample with Mo/Cl =
 15 3.5). The Mo-O peak at 1.78 Å is diagnostic for MoO₄²⁻ (schematized in the inset). The peak at ~4 Å is due to Mo-
 16 Ca and Mo-Al correlations, consistent with MoO₄²⁻ in the interlayer mid-plane. (c): X-ray diffraction pattern of
 17 samples having Mo/Cl ranging 0-3.5. Peak asymmetry is due to interstratification (extracted from (Grangeon and
 18 Marty, 2019)).

19

1 Formations of solid solutions between AFm phases and radionuclides of interest

2 The results of the exchange experiments above provide for a more systematic approach describing solid solution
 3 formation. The formation of solid solution of the type $\text{SeO}_3^{2-}\text{X}^{n-}$ and I^-X^{n-} (with $\text{X}^{n-} = \text{SO}_4^{2-}, \text{SO}_3^{2-}, \text{S}_2\text{O}_3^{2-}, \text{CO}_3^{2-}, \text{OH}^-$)
 4 as the intercalating anions was examined. Samples with total selenite/iodide mole fractions ($x_{\text{Se(IV)}} = \text{SeO}_3^{2-}/(\text{SeO}_3^{2-} + \text{X}^{n-})$) of 0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1 were synthesized. XRD analyses revealed solid solutions between the
 5 pairs: $\text{SeO}_3^{2-}\text{-SO}_4^{2-}$, $\text{I}^-\text{CO}_3^{2-}$, $\text{I}^-\text{OH}^-\text{CO}_3^{2-}$, and I^-OH^- . A continuous solid solution was found between the end
 6 members Se(IV)-AFm and S(VI)-AFm, favoured by the similar rhombohedral symmetry, where the larger ionic
 7 radius of the SO_4^{2-} anion (2.58 Å) compared to the SeO_3^{2-} anion (2.39 Å) (Jenkins and Thakur, 1979) results in a
 8 continuous peak shift towards higher basal spacing (d-spacing values) with increasing amount of SO_4^{2-} .
 9 Continuous solid solution formation was also observed between the $\text{I}^-\text{OH}^-\text{CO}_3^{2-}$ pair where the d value increases
 10 uninterrupted from 8.20 Å for the $\text{OH}^-\text{CO}_3^{2-}$ -AFm end member to 8.84 Å for the AFm end member.

12 Solid solution formation also takes place between the pairs I^-OH^- and $\text{I}^-\text{OH}^-\text{CO}_3^{2-}$, favoured by the rhombohedral
 13 structure of all three end-members I^- -AFm, OH^- -AFm and hemicarbonate ($\text{OH}^-\text{CO}_3^{2-}$ -AFm). The increasing
 14 substitution of the larger I^- anion (2.10 Å) by the smaller OH^- anion (1.33 Å) is reflected by a gradual decrease of
 15 the interlayer distance from 8.84 Å in the I^- -AFm phase down to 8.44 Å at a total iodide fraction of 0.1 ($x_1 = 0.1$). At
 16 this composition a miscibility gap at very low I^- contents is observed. The solid solution formation between the I^- -
 17 AFm and monocarbonate (CO_3^{2-} -AFm), is incomplete and a miscibility gap with the composition $0.5 \leq \text{CO}_3^{2-}/(2\text{I}^- + \text{CO}_3^{2-})$
 18 exists (Fig. 3 b). An initial peak shift up to a composition of $0.3 \leq \text{CO}_3^{2-}/(2\text{I}^- + \text{CO}_3^{2-})$ is observed, suggesting
 19 that small amounts of the CO_3^{2-} anion (ionic radius 1.78 Å, Jenkins and Thakur, 1979) can be readily incorporated
 20 into the I^- -AFm structure to form a mixed $(2\text{I}^-\text{CO}_3^{2-})$ -AFm phase. The solid solution is limited to compositions $0.5 \leq$
 21 $\text{CO}_3^{2-}/(2\text{I}^- + \text{CO}_3^{2-})$, where two coexisting phases - an $(2\text{I}^-\text{CO}_3^{2-})$ -AFm mixed phase and a CO_3^{2-} -AFm, indicate the
 22 presence of a miscibility gap. This miscibility gap could be related to the differences in the structure as
 23 monocarbonate has a triclinic structure, and to the planar arrangement of carbonate in the CO_3^{2-} -AFm interlayer
 24 which prevents the uptake of the larger I^- anion into the lattice. Comparable behaviour has been observed for
 25 chloride uptake by monocarbonate (Mesbah et al., 2011).



26
 27 Figure 4 a and b: Evolution of the position of the basal reflection in the $(\text{SeO}_3^{2-}\text{-SO}_4^{2-})$ -AFm (a) and the $(2\text{I}^-\text{CO}_3^{2-})$ -
 28 AFm (b) solid solution series. (b) modified from (L. Nedyalkova et al., 2019)

29 The solid solution behaviour observed in the XRD patterns was confirmed by FTIR analyses (L. Nedyalkova et al.,
 30 2019). In the $(\text{I}^-\text{OH}^-\text{CO}_3^{2-})$ -AFm solid solution series, the absorption band at 775 cm^{-1} caused by the Al-OH
 31 deformation vibration in the rhombohedral structure, gradually weakens and shifts towards 745 cm^{-1}
 32 corroborating the existence of a continuous solid solution.

33 Two coexisting phases can be distinguished clearly in the FTIR spectra of the I^-CO_3 solid solution series. For
 34 compositions where $x_1 \geq 0.7$, the behaviour of the Al-OH absorption band is similar as observed in the $(\text{I}^-\text{OH}^-\text{CO}_3^{2-})$

1 ²)-AFm solid solution series discussed previously, and only a single mixed phase is present. At the compositions
 2 below $x_1 = 0.5$ additional absorption bands at $\sim 948 \text{ cm}^{-1}$, $\sim 875 \text{ cm}^{-1}$ and $\sim 667 \text{ cm}^{-1}$ appear suggesting the presence
 3 of triclinic CO_3^{2-} -AFm in addition to the rhombohedral AFm phase.

4 **Sorption distribution ratios (R_d) on individual cementitious phases and HCP for the compilation of** 5 **sorption databases**

6 Adsorption is a retention process qualitatively different from solid solution formation or precipitation as it only
 7 involves retention processes on the surface of existing solids. Both adsorption and solid solution formation can be
 8 treated mathematically in a similar way, if bulk phase atoms become accessible for exchange, as shown above for
 9 the $2 \text{ Cl}^-/\text{MoO}_4^{2-}$ exchange in AFm- Cl^- planes. Consequently, as observed in the present work, both, a sorption and
 10 a solid solution model describe these exchange data equally well. Note however that these two phenomena
 11 should be distinguishable based on the aqueous concentration of AFm layer species (Al, Ca). Further work is
 12 required to test this hypothesis. The observations of (Ma et al., 2017, Ma et al., 2018) for fixation of MoO_4^{2-} or
 13 SeO_3^{2-} on AFm- Cl^- or AFm- SO_4^{2-} phases show that the adsorption process occurs at much lower radionuclide
 14 concentrations than the formation of pure AFm- SeO_3^{2-} or AFm- MoO_4^{2-} phases. If solid solution formation were to
 15 be the mechanism controlling molybdate ion uptake on AFm- Cl^- at low molybdate concentrations or selenite
 16 uptake on AFm- SO_4^{2-} at low selenite concentration in solution, one would expect a smooth transition in the
 17 corresponding solid solution controlled apparent sorption coefficients from the domain of solid solution
 18 formation at low radionuclide concentration to the domain of pure phase precipitation with increasing
 19 radionuclide concentrations. In contrast, the authors have observed a step increase of apparent R_d values, once
 20 AFm- MoO_4^{2-} is formed, indicating an adsorption/precipitation transition rather than a solid-solution/precipitation
 21 transition. . This step increase in R_d could however also be interpreted as being a consequence of using batch
 22 experiments. Indeed, since AFm has a very fast equilibration kinetics, equilibrium Al and Ca concentration are
 23 reached in batch experiments very fast (Marty et al., 2018). The combination of high Al and Ca concentration
 24 together with increasingly higher concentration of MoO_4^{2-} in solution could induce, once a given MoO_4^{2-}
 25 concentration exceeded, dissolution of pristine AFm and precipitation of the AFm- MoO_4^{2-} . However, this
 26 hypothesis requires further validation. This shows the very high degree of complexity that is inherent to the study
 27 of such cement phases.

28 Ma et al. (2018) have shown that is a relationship between surface edge area and sorption site density for MoO_4^{2-}
 29 sorption indicating edges as sorption sites. However, no such relation can be established in the case of SeO_3^{2-}
 30 sorption, suggesting that SeO_3^{2-} adsorption is not only taking place on surface edge sites. They observed outer
 31 sphere configuration of adsorbed Se(IV) for Se concentrations lower than those necessary for AFm- SeO_3^{2-}
 32 formation.

33 The retention of radionuclides by cementitious materials can also be quantified by a solid liquid distribution ratio,
 34 R_d , defined as

$$35 \quad R_d(\text{RN}) [\text{L}\cdot\text{kg}^{-1}] = \frac{\{\text{RN}\}}{[\text{RN}]} \quad (1)$$

36 with $\{\text{RN}\}$ the concentration of radionuclide sorbed on the solid (mol/kg) and $[\text{RN}]$ the radionuclide concentration
 37 in solution (M).

38 The R_d value only describes the distribution of a radionuclide between the solid phase and the liquid pore solution
 39 and does not imply any mechanistic process. Sorption constants were measured for a large suite of individual
 40 cementitious phases and various HCP. In some cases more than one laboratory has obtained R_d values for the
 41 same phase and radionuclide, allowing direct comparison.

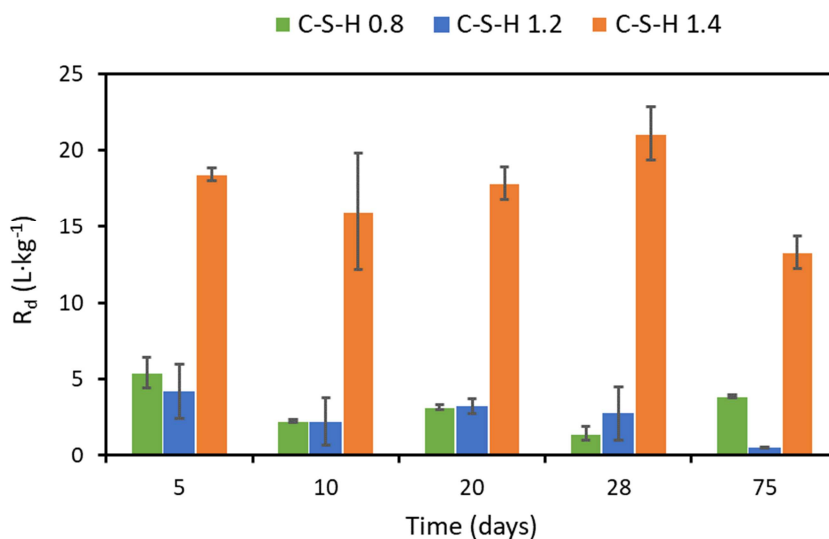
42 **MoO_4^{2-}**

43 The interaction of molybdenum with cementitious materials has received relatively little attention to date. In
 44 early studies at high Mo concentrations (Kindness et al., 1994), formation of CaMoO_4 generally prevented uptake

1 by cementitious phases. Those R_d values were obtained at initial Mo concentrations low enough to avoid
 2 powellite formation ranged between 30 and 100 L·kg⁻¹. Zhang and Reardon (2003) studied the incorporation of
 3 molybdate by hydrocalumite and ettringite using lower concentrations of molybdate. Ettringite showed an anion
 4 preference in the order $B(OH)_4^- > SeO_4^{2-} > CrO_4^{2-} > MoO_4^{2-}$.

5 In the present work, molybdate uptake on C-S-H phases and its dependency on the Ca/Si ratio were studied by
 6 two different laboratories. Both found a higher distribution ratio for high Ca/Si ratios (Figure 5). These findings
 7 are in agreement with the change in surface charge of C-S-H to positive values at Ca/Si ratios exceeding 1.2
 8 (Churakov et al., 2014), suggesting electrostatic sorption of the molybdate anion on C-S-H. In fact, R_d values for C-
 9 S-H1.4 ($R_d \sim 780$ vs. 20 L kg⁻¹) were much higher than for C-S-H0.9 or C-S-H 0.8 ($R_d \sim 430$ vs. 4 L·kg⁻¹), although,
 10 partly due to differences in specific surface area, significant differences in the R_d value occurred between the
 11 measurements of two different laboratories. These results show that C-S-H phases in cementitious materials can
 12 play an important role with respect to the retention of molybdenum, in particular in aged systems (stage II and
 13 III).

14 Much lower R_d values for molybdate sorption were observed in alkali-rich, young cementitious water (pH 13.5),
 15 probably due to competition with OH⁻ species for sorption sites on the C-S-H or to the negative zeta potential of
 16 CSH phases reported for pH 13.5 (Poiteau et al., 2006).



17

18 Figure 5: Dependency of MoO_4^{2-} retention on C-S-H phases as function of the Ca/Si ratio and time (Mo initial
 19 concentration 10^{-6} M) (for experimental conditions see supplementary materials 3.1 and 3.2).

20 Pronounced molybdate uptake ($R_d \sim 1500$ L·kg⁻¹) by **AFm-SO₄** and **AFm-CO₃** was observed by two independent
 21 laboratories suggesting no preferential uptake results from the nature of the interlayer anion (i.e. planar CO_3^{2-} or
 22 tetrahedral SO_4^{2-}). XRD studies on the AFm-SO₄²⁻ used in the batch sorption experiments showed an increase in
 23 the basal spacing compared to pure AFm-SO₄²⁻, indicating structural incorporation of MoO_4^{2-} -ions in the AFm-
 24 structure by anion exchange with the interlayer anion, since the size of the molybdate oxo-anions (Mo-O bond
 25 length ~ 1.77 Å) is larger than that of SO_4^{2-} -ions (S-O bond length ~ 1.47 Å).

26 Less definitive information was obtained for adsorption of MoO_4^{2-} on AFt. Uncertainties are between 122 L·kg⁻¹
 27 and 3 L·kg⁻¹, the latter value being similar to that given by Ochs et al. (2016) is considered too high (Table 2).

28 Molybdate sorption has also been studied in **AFm/AFt mixtures**. Low molybdate retention was observed in
 29 samples of S(VI)/Al equal to 2 and 2.5 where AFt is the major component. In contrast to the study of (Poiteau et
 30 al., 2006) of AFt suspensions in DDW or porewater from fresh HCP, in our study, the surface of AFt solids is
 31 expected at the observed pH of about 11.6 to have very low zeta potential, which turn negative in the presence of
 32 sulphate anions (Zingg et al., 2008) at sulphate concentrations such as those observed in our study (as high as 55

1 mM) and hence, may hinder the retention of anionic species as molybdate. In contrast, strong molybdate
 2 retention occurs in the samples of S(VI)/Al equal to 1 and 0.5 where AFm is the major component, with values
 3 ranging from $164 < R_d < 693 \text{ L}\cdot\text{kg}^{-1}$. The highest R_d was observed in samples without ettringite (S(VI)/Al = 0.5) with
 4 values ranging from 1200 to $46400 \text{ L}\cdot\text{kg}^{-1}$. This suggests that a revision of the literature, linking high retention of
 5 molybdate to presence of ettringite, is necessary (Ochs et al., 2016).

6 The high molybdate uptake by **hydrogarnet** ($R_d \sim 3000 \text{ L}\cdot\text{kg}^{-1}$) was found to be due to the neo-formation of a
 7 molybdenum bearing AFm-like phase, which can also become a pure AFm-MoO₄⁻² phase or a mixture of this
 8 phase with the Mo-analogue of the so called U-phase, depending on pH and alkali concentrations in solution.
 9 Hydrogarnet has also been identified (Hillier et al., 2007) as a major phase in chromium ore processing residue
 10 and has a capacity to host homologue CrO₄⁻².

11 ***I⁻, IO₃⁻***

12 Several publications in the literature provide indications that ettringite and AFm phases exhibit good I⁻ and IO₃⁻
 13 retention properties. Mattigod et al. (2001) observed a reduction of the leachability of iodine in a cement-based
 14 materials containing steel fibres due to the reduction of IO₃⁻ to I⁻. Iodide sorption onto cement has been shown to
 15 increase with increasing Ca/Si ratios in C-S-H gels in spite of an increased competition from OH⁻ at sorption sites,
 16 suggesting I⁻ is sorbed electrostatically (Glasser et al., 1989; Pointeau et al., 2008).

17 Aimoz et al. (2012) showed that I⁻ uptake strongly depends on the anion originally present in the AFm interlayer.
 18 No I⁻ uptake was observed in the case of AFm-CO₃ and AFm-Cl₂. Only AFm-SO₄ was found to take up considerable
 19 amounts of I⁻ in its interlayer. This observation is in excellent agreement with the solid solution studies described
 20 above and in (L. Nedyalkova et al., 2019) showing the existence of a miscibility gap in the composition range $0.5 \leq$
 21 $\text{CO}_3^{2-}/(2\text{I}^- + \text{CO}_3^{2-})$ indicating that small amounts of I⁻ cannot mix with the CO₃²⁻ anions present in the interlayer of
 22 AFm-CO₃.

23 The present work confirmed this dependence of the I⁻ uptake on the original interlayer occupancy. Structural
 24 incorporation of iodide (I⁻) by anion exchange in the interlayer was observed for **AFm-SO₄⁻²** ($R_d \sim 811 \pm 324 \text{ L}\cdot\text{kg}^{-1}$ at
 25 pH 12 and $R_d \sim 30 \pm 5 \text{ L}\cdot\text{kg}^{-1}$ at pH 13) and **AFm-CO₃⁻²** ($R_d \sim 81 \pm 32 \text{ L}\cdot\text{kg}^{-1}$). The observed decrease of R_d with
 26 increasing pH corresponds well to the data of Atkins and Glasser (1992). The uptake of iodate (IO₃⁻) by **Aft** as well
 27 as by **AFm-SO₄⁻²** was shown to lead to iodate-substituted ettringite, formed either by anion exchange or by phase
 28 transformation.

29 The increased uptake of iodide in **C-S-H** with increasing Ca/Si-ratio reflects increasing positive surface charge at
 30 high Ca/Si, as anticipated from the assumed electrostatic adsorption mechanism for iodide on C-S-H, although
 31 iodide uptake by C-S-H is generally lower ($R_d \sim 40 - 80 \text{ L}\cdot\text{kg}^{-1}$) than on AFm/t or hydrogarnet. In general, all model
 32 phases showed a higher uptake for iodide and iodate in artificial young cement water when compared to the
 33 equilibrium solutions. The results of experiments exploring iodide and iodate adsorption on crushed HCP based
 34 on **CEM I** revealed a fast uptake of both oxidation states, with slightly lower sorption of iodine ($R_d \sim 25 \text{ L}\cdot\text{kg}^{-1}$) than
 35 iodate ($R_d \sim 140 \text{ L}\cdot\text{kg}^{-1}$), in good agreement with existing literature data, (e.g. Bonhoure et al., 2002, Pointeau et
 36 al., 2008). Overall, the results obtained for the uptake of iodide and iodate by HCP systems are in qualitative
 37 agreement with results obtained for the single hydration phases under equilibrium conditions, indicating that at
 38 least for the low iodine concentrations expected under repository conditions, the major contribution to iodine
 39 uptake can be attributed to minor cement hydration phases such as AFm/Aft.

40 ***TcO₄⁻***

41 Allen, et al. (1997) demonstrated that the addition of blast furnace slag (BFS) to a cement formulation leads to
 42 partial reduction of any pertechnetate anions present, whereas the addition of Na₂S or FeS results in complete
 43 reduction to the less mobile Tc(IV). Berner (1999) suggested that binding and/or incorporation of TcO₄⁻ into the
 44 alumina ferric mono/tri-sulphate (AFm/Aft) phases of cement systems could also be expected, by analogy to
 45 other oxo-anions such as SO₄⁻² or MoO₄⁻², and possibly also SeO₃⁻². Moreover, several minerals are known to

1 incorporate technetium, for example fougérite (green rust), a layered double hydroxide ($[\text{Fe}^{2+}_4\text{Fe}^{3+}_2(\text{OH})_{12}][\text{CO}_3^{2-}] \cdot 3\text{H}_2\text{O}$) and potassium metal sulphides. A good overview of potential host phases is given by Luksic et al. (2015).

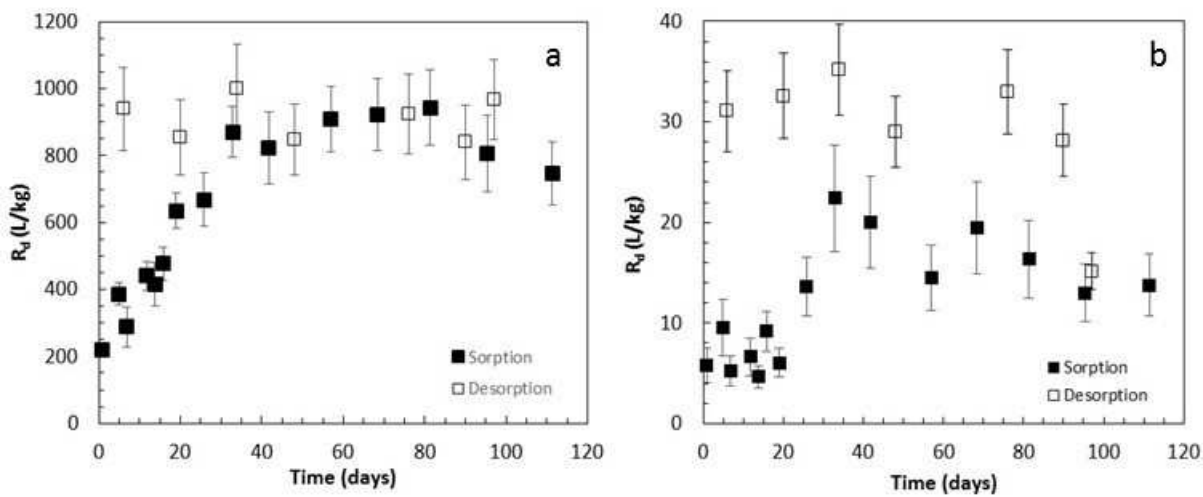
3 In the present work, the uptake of pertechnetate (TcO_4^-) by the individual cementitious phases investigated was
 4 found to be generally low (Table 2), suggesting that reductants such as Fe(II) and/or Fe(II)-containing phases,
 5 which were not studied here, may play a key role in technetium retention in certain cementitious system. These
 6 experiments elucidated the high mobility and low retention of TcO_4^- in cementitious environments in the absence
 7 of reductants. The possible uptake of TcO_4^- by AFm/Aft, which was suggested for example by Berner (1999), as a
 8 potential retention mechanism, was found to be weak; $R_d < 1 \text{ L} \cdot \text{kg}^{-1}$, indicating practically no uptake due to
 9 exchange for SO_4^{2-} -groups. Batch-uptake experiments on crushed HCP were performed in order to study the
 10 potential accumulation of reduced Tc on reductive sites such as Fe(II)-bearing phases originating from BFS. The
 11 uptake experiments conducted for more than 75 days, revealed only minor uptake of TcO_4^- by HCP. As expected
 12 considering the lower content of Fe(II) and/or sulphides, the distribution ratios of HCP based on CEM I tend to be
 13 lower ($R_d \sim 2 \text{ L} \cdot \text{kg}^{-1}$) than those obtained for CEBAMA low-pH paste ($R_d \sim 9 \text{ L} \cdot \text{kg}^{-1}$).

14 $^{14}\text{CO}_3^{2-}$

15 Inorganic carbon-14 sorption by cementitious materials can be considered in terms of two processes (Evans,
 16 2008): (i) electrostatic adsorption onto a positively charged site and (ii) precipitation. Adsorption for inorganic
 17 carbon ($^{14}\text{CO}_3^{2-}$) occurs only when carbonate levels are well below the threshold at which calcite precipitation
 18 starts (about $1\text{-}2 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$). Isotopic exchange with solid CaCO_3 present in HCP controls the $^{14}\text{CO}_3^{2-}$ retention in
 19 HCP (Bradbury and Sarrot, 1995) but the extent of removal of $^{14}\text{CO}_3^{2-}$ is very dependent on the particular cement
 20 system in question. Results obtained from batch sorption experiments and zeta potential measurements (Noshita
 21 et al., 1995) suggest that the adsorption mechanism for $^{14}\text{CO}_3^{2-}$ onto cationic surfaces of C-S-H phases at high
 22 Ca/Si ratio ($-\text{SiOCa}^+$) is electrostatic adsorption.

23 Adsorption experiments were conducted on both fresh and degraded cement pastes (experimental conditions
 24 and definition of degradation states: Supplementary material 1 and 2). The degradation stages III.a to IV describe
 25 the C-S-H evolution from C-S-H 1.3 (stage III.a) to C-S-H 0.7 (stage IV), all corresponding to the denotation of
 26 cement degradation I, II, III, IV given by Ochs et al. (2016). The kinetic tests carried out showed that equilibrium
 27 was achieved for all cement pastes based on CEM I and CEM V after ~ 40 days. At equilibrium, more than 80% of
 28 the initial ^{14}C present in the contacting solution was adsorbed onto non-degraded CEM I as well as onto the first
 29 two degraded pastes (stage III.a and stage III.b), but only $\sim 30\%$ was adsorbed on the most degraded cement
 30 paste (stage IV). Thus, the $^{14}\text{CO}_3^{2-}$ distribution ratio is greatly affected by the extent of cement degradation, with
 31 values ranging between $1600 \pm 268 \text{ L/kg}$ for stage I cement paste, to $120 \pm 36 \text{ L/kg}$ for stage IV. $^{14}\text{CO}_3^{2-}$ uptake on
 32 CEM V is significantly higher than on CEM I cement paste ($3500 \pm 275 \text{ L} \cdot \text{kg}^{-1}$). The experimental data indicate that
 33 ^{14}C adsorption is not attributable solely to isotopic exchange and that precipitation of ^{14}C containing calcite
 34 cannot be excluded. This could explain the results of desorption tests (carried out for non-degraded CEM I and on
 35 the most degraded paste, stage IV) which indicate that desorption equilibrium is attained after a slightly longer
 36 time than sorption equilibrium (~ 60 days) at which point around 80% of the ^{14}C originally adsorbed was released
 37 back to solution.

38 The effect of carbonation of CEM V samples on $^{14}\text{CO}_3^{2-}$ uptake and the degree of reversibility of the
 39 sorption/desorption process are shown in Figures 6 a and b.



1

2 Figure 6: Evolution of ^{14}C distribution ratios (R_d) vs time on non-carbonated (Fig. a) and carbonated CEM V (Fig. b).
 3 Initial ^{14}C concentration is $6 \cdot 10^{-8} \text{ mol}\cdot\text{L}^{-1}$

4 For non-carbonated CEM V (state I), the steady-state is reached after around 60 days. The corresponding R_d value
 5 is $800 \pm 100 \text{ L}\cdot\text{kg}^{-1}$ for a pH of 13.5, much lower than the value of $3200 \text{ L}\cdot\text{kg}^{-1}$ obtained at pH 12.5 (Fig. 6 a). The
 6 magnitude of the R_d values measured and their dependency on pH are in close agreement with the data obtained
 7 by Poiteau et al. (2008) for CEM I HCP at pH=12.5 ($5000 \text{ L}\cdot\text{kg}^{-1}$) and pH=13.2 ($500 \text{ L}\cdot\text{kg}^{-1}$).

8 The desorption experiments show that the uptake process at trace level seems to be reversible. In contrast, for
 9 ^{14}C concentrations above the solubility limit of calcite ($5 \cdot 10^{-6}$ - $5 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$), ^{14}C uptake was found to be
 10 irreversible ($R_{d,\text{desorption}} > R_{d,\text{sorption}}$ by one order of magnitude). For non-carbonated HCP, ^{14}C can be either adsorbed
 11 on C-S-H or exchanged on the "residual" calcite (always present as dispersed particles in cement paste at $\sim 5\%$ in
 12 mass).

13 For carbonated CEM V HCP (state IV), steady-state is reached after 40-50 days and the corresponding R_d value is
 14 $20 \pm 5 \text{ L}\cdot\text{kg}^{-1}$. Due to the predominance of calcium carbonates in these samples, this R_d value can directly be
 15 compared to Poiteau et al's value (cited in Henocq et al., 2018) obtained on calcite in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NaOH}$ solution
 16 ($R_d = 10\text{-}20 \text{ L}\cdot\text{kg}^{-1}$). As noted above, $R_{d,\text{desorption}}$ values of $30 \pm 5 \text{ L}\cdot\text{kg}^{-1}$ are slightly higher than $R_{d,\text{sorption}}$ values. In this
 17 case, the partial irreversibility could be consistent with the uptake of ^{14}C on calcite by a two-step mechanism
 18 (isotopic exchange and subsequent incorporation by diffusion in calcite).

19 ***SeO₄²⁻ and SeO₃²⁻***

20 Under the alkaline reducing conditions expected in a cementitious near-field, Se(IV), Se(0) and Se(-II) are
 21 expected to be the predominant redox states and aqueous Se speciation dominated by the anionic species SeO_3^{2-} ,
 22 HSe^- and a series of polyselenides (Se_x^{2-}), mainly Se_2^{2-} , Se_3^{2-} and Se_4^{2-} . Relatively few studies have focused on the
 23 solubility of selenium under high pH conditions. Baur and Johnson (2003) and Ma et al. (2018) found
 24 experimental evidence for the formation of $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ as solubility controlling Se(IV) phase in their Se(IV)
 25 sorption studies onto AFm phases. These authors could reproduce their Se(IV) sorption data onto AFm phases
 26 only assuming $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ precipitation at high loadings applying apparent $\log K_{s0}$ values of -7.29 to -7.27. These
 27 values are more than half an order of magnitude lower than the $\log K_{s0}$ value for $\text{CaSeO}_3 \cdot \text{H}_2\text{O}(\text{s})$ reported in most
 28 selenium thermodynamic databases (e.g. Hummel et al., 2002b).

29 Felipe-Sotelo et al. (2016) observed on the other hand the formation of $\text{Ca}_2\text{SeO}_3(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ as the solubility
 30 limiting phase in 95%-saturated $\text{Ca}(\text{OH})_2$ and NRVB (Nirex Reference Vault Backfill)-equilibrated solutions whereas
 31 Solem-Tishmack et al. (1995) indicating that selenite could be retained as 'selenite-ettringite' in sulphate-rich
 32 cement admixtures. Mace et al. (2007) suggest that ettringite could play an important role in the retention of
 33 Se(IV) at higher temperatures (70°C). Calcite may also contribute to the retention of selenite and other oxyanions
 34 in alkaline conditions (Cornelis et al., 2008). Johnson et al. (2000) investigated the adsorption of SeO_3^{2-} onto 27
 35 cement formulations. They found that the water to cement ratio during curing and the clay content of the cement

1 mix had no influence on the selenite uptake. Increasing silica fume contents, however, decreased the selenite
 2 uptake probably caused by decreasing Ca/Si ratios of the C-S-H phases resulting in a negative surface charge and
 3 thus in lower anion sorption.

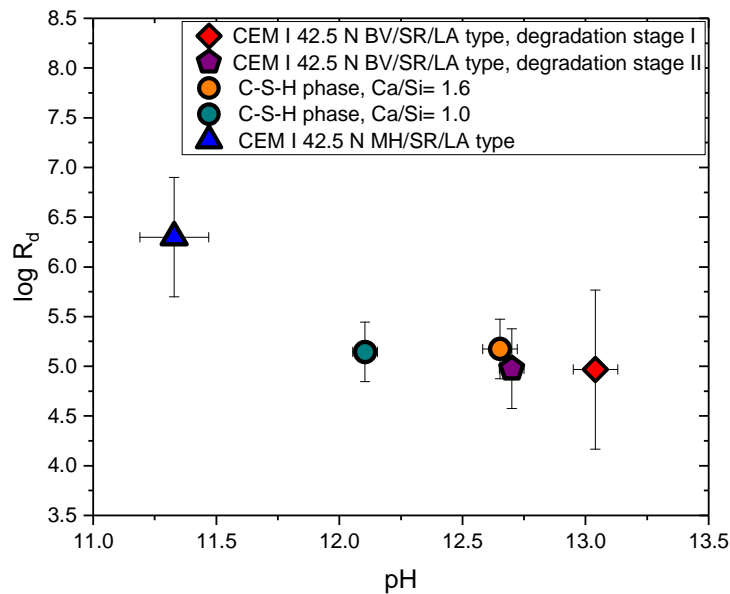
4 Baur and Johnson (2003) carried out batch studies on the uptake of SeO_3^{-2} by individual cement phases, namely
 5 ettringite, monosulphate and C-S-H; they postulated that binding of SeO_3^{-2} occurs mainly on mineral surfaces
 6 owing to surface complexation and surface precipitation with calcium. This hypothesis is supported by extended
 7 X-ray absorption fine structure (EXAFS) experiments carried out by Bonhoure et al. (2006) where SeO_3^{-2} bound to
 8 the cement appears to show non-specific interaction with the cement minerals, whether C-S-H, portlandite,
 9 ettringite or monosulphate. Moderately strong uptake of Se(IV) was observed in these studies on main cement
 10 phases with R_d values of $180 \text{ L}\cdot\text{kg}^{-1}$, $380 \text{ L}\cdot\text{kg}^{-1}$ and $210 \text{ L}\cdot\text{kg}^{-1}$ on ettringite, C-S-H phases and AFm phases,
 11 respectively. Some association between calcium and selenium is a common observation in the majority of the
 12 investigations.

13 In the present work, the retention of selenium species ($\text{Se}^{\text{IV}}\text{O}_3^{-2}/\text{Se}^{\text{VI}}\text{O}_4^{-2}$) was shown to be due to uptake by AFm
 14 phases and to a lesser degree, AFt, which all showed a tendency for higher uptake of the more oxidised selenium
 15 species. Moreover, a distinctively stronger retention of both Se-species by AFm- SO_4 compared to AFm- CO_3^{-2} was
 16 observed, indicating a dependency on the interlayer anion. In comparison to the aluminate phases, the uptake of
 17 selenium on C-S-H was found to be comparatively low ($R_d \text{ Se}^{\text{IV}}\text{O}_3^{-2}$: $\sim 100 \text{ L kg}^{-1}$; $R_d \text{ Se}^{\text{VI}}\text{O}_4^{-2}$: $\sim 10 \text{ L kg}^{-1}$). Due to the
 18 higher proportion of aluminate phases in HCP based on CEM I, the retention capacity for selenite and selenate is
 19 higher than on the low-pH CEBAMA reference paste; remarkably, in all cases, the HCP showed higher R_d values
 20 for $\text{Se}^{\text{IV}}\text{O}_3^{-2}$ than for $\text{Se}^{\text{VI}}\text{O}_4^{-2}$. Retention values for all systems studied are given in Table 2.

21 ***Be(OH)₃⁻ and Be(OH)₄⁻²***

22 No experimental investigations of Be(II) uptake by cement and cementitious minerals are available in the
 23 literature. Due to the lack of experimental data and the predominance of negatively charged hydrolysis species
 24 Be(OH)_3^- and Be(OH)_4^{-2} in the pore water conditions expected in cement systems, some review studies
 25 conservatively proposed a $R_d = 0$ for this system (Wieland and Van Loon, 2003, Ochs et al., 2016).

26 Figure 7 shows the main results obtained in the present study (experimental data: see supplementary data, 4) for
 27 the uptake of Be(II) by standard and low pH cement (CEM I 42,5 N BV/SR/LA and CEM I 42,5 MH/SR/LA,
 28 respectively) and C-S-H phases with Ca/Si = 1.0 and 1.6. The data points shown in the figure represent average log
 29 R_d values for systems with Be concentration below the solubility limit for the corresponding pH. A very strong
 30 uptake of beryllium by cement and C-S-H phases is observed in all investigated systems. The figure shows a trend
 31 to decrease $\log_{10} R_d$ with increasing pH, with the highest $\log_{10} R_d$ values observed for low pH cement with pH \approx
 32 11.4, and the lowest for CEM I in degradation stage I (pH \approx 13). A good agreement is obtained between $\log_{10} R_d$
 33 values obtained for C-S-H with Ca/Si = 1.6 and CEM I in degradation stage II. This is in line with the predominance
 34 of C-S-H phases with Ca/Si = 1.6 in degradation stage II of standard Portland cement (pH \approx 12.5).



1

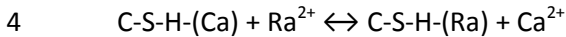
2 Figure 7: Uptake of Be(II) by cement (CEM I 42,5 N BV/SR/LA type, degradation stages I and II) and C-S-H phases
3 with Ca/Si = 0.6, 1.0 and 1.6. R_d values provided in $L \cdot kg^{-1}$.

4 Ra^{+2}

5 Experimental data on radium sorption on cementitious materials are scarce. (Tits et al., 2006a) investigated the
6 interaction of Ra with C-S-H and hydrated cement pastes. For fresh HCP a two-step process could explain the
7 Ra(II) uptake: fast sorption within one day (R_d value of $260 L \cdot kg^{-1}$), followed by a slowly increase of Ra (II) uptake
8 towards equilibrium over a period of 60 days (to an R_d value of $400 L \cdot kg^{-1}$). This may be compared to the very fast
9 uptake of degraded HCP, which reaches equilibrium within one day at a R_d of $140 L \cdot kg^{-1}$. There is good evidence
10 that Ra^{+2} sorption increases as the Ca/Si ratio decreases on C-S-H. It is assumed that Ra(II) only sorbs on the C-S-H
11 fraction in HCP and that the aqueous Ra(II) speciation is dominated by the Ra^{+2} species. The maximum
12 distribution ratio was reported by (Tits et al., 2006a) for C-S-H with Ca/Si = 0.96, approx. $4 \times 10^3 L \cdot kg^{-1}$, and
13 decreased to approx. $1.5 \times 10^2 L \cdot kg^{-1}$ for C-S-H with Ca/Si = 1.6. Tits et al. (2006a) also investigated the desorption
14 of radium from the above mentioned phases and observed that radium sorption onto C-S-H phases is linear and
15 reversible.

16 In the frame of CEBAMA, the uptake of Ra^{2+} by both, HCP and various hydrated cement phases, including C-S-H,
17 AFm/Aft, hydrogarnet and portlandite, was studied. The results revealed a fast Ra uptake by the various
18 hydration phases leading to sorption equilibrium within 10 to 28 days. **C-S-H** was the only investigated phase
19 showing a significant uptake of ^{226}Ra , whereas the uptake of ^{226}Ra in systems with Aft and AFm phases was found
20 to be significantly lower (Lange et al., 2018). A distinct dependence of the ^{226}Ra uptake by C-S-H on the Ca/Si ratio
21 and solution composition was confirmed, decreasing from about $22000 L \cdot kg^{-1}$ (C-S-H0.9) to $1800 L \cdot kg^{-1}$ (C-S-H1.4)
22 in alkali-free systems. This effect is probably due to the negative surface charge at Ca/Si <1.2, facilitating cation
23 uptake, as well as to the higher competition with Ca ions in solution for sorption sites at high Ca/Si ratios. The
24 measured R_d values are however higher than those reported by Tits et al. (2006a) but consistent to recent
25 observations of Olmeda et al. (2019). R_d values were about a factor of 2 lower in systems with artificial young
26 cementitious water (pH 13.5) due to competition with alkalis for sorption sites, as well as changes in C-S-H surface
27 charge and speciation at higher pH. The results suggest a stronger retention and lower mobility of ^{226}Ra in alkali-
28 poor, aged cementitious systems at stage II (portlandite stage) compared to young cementitious materials in
29 stage I. Moreover, the lower Ca/Si ratios of C-S-H in cementitious materials prepared from low pH cements – as
30 well as partly decalcified C-S-H during stage III – should provide for a higher retention capacity for ^{226}Ra than C-S-
31 H in young OPC based systems.

1 The uptake of ^{226}Ra by C-S-H is generally explained in terms of cation exchange with calcium and sorption to two
 2 silanol-like sites at the C-S-H surface. Assuming Ra exchange for Ca as the main uptake mechanism (cf. Tits et al.,
 3 2006a), selectivity coefficients for the exchange reaction



5 where C-S-H-(Ca) refers to the exchangeable Ca in the C-S-H structure, were calculated from the R_d -values and Ca-
 6 concentrations obtained in the sorption experiments. The selectivity coefficient, K_c , for this reaction is defined as:

$$7 \quad K_c = \frac{N_{\text{Ra}} \cdot a(\text{Ca}^{2+})}{N_{\text{Ca}} \cdot a(\text{Ra}^{2+})}$$

8 where $a(\text{Ca}^{2+})$ and $a(\text{Ra}^{2+})$ are the ion activities in the aqueous phase and N_{Ra} and N_{Ca} refer to the equivalent
 9 fractional occupancies:

$$10 \quad N_M = \frac{2 \cdot \{M_s^{2+}\}}{CEC}$$

11 with $\{M_s^{2+}\}$ as the amount of the respective divalent cation sorbed (mol kg^{-1}), and CEC the cation exchange
 12 capacity of the C-S-H phase in eq kg^{-1} . For homovalent cation exchange, the activity coefficients for both cations
 13 are identical; thus the activities can be substituted by concentrations, leading to:

$$14 \quad K_c = \frac{N_{\text{Ra}} \cdot [\text{Ca}^{2+}]}{N_{\text{Ca}} \cdot [\text{Ra}^{2+}]}$$

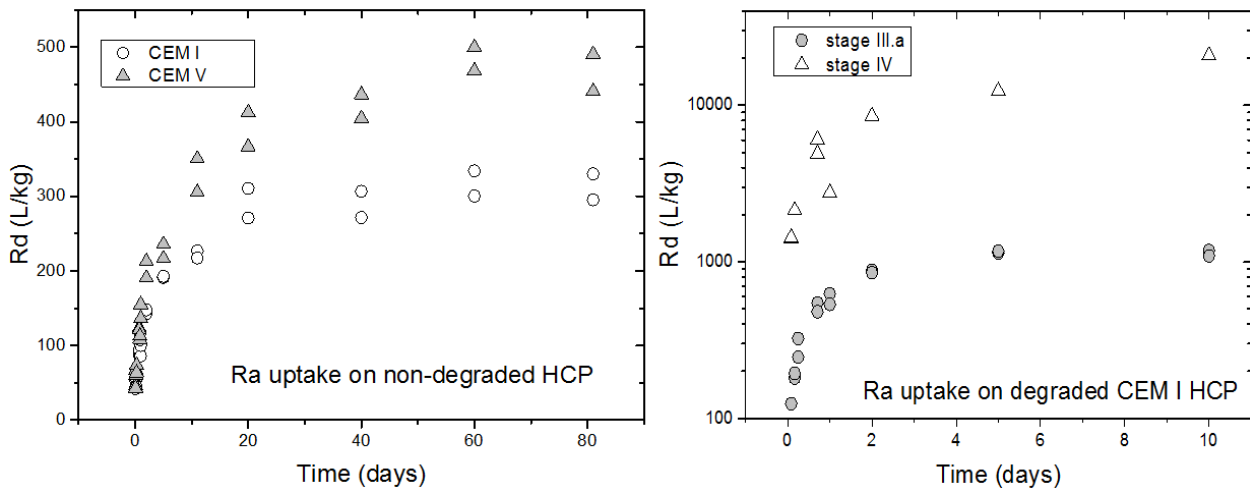
15 Attributing the Ra uptake only to cation exchange, the relation between the selectivity coefficient for the Ra-Ca
 16 exchange and the distribution coefficient R_d of Ra can be calculated as:

$$17 \quad R_d = \frac{0.5 \cdot CEC \cdot K_c}{[\text{Ca}^{2+}]}$$

18 Based on this, we obtained selectivity coefficients for the Ra/Ca exchange in the alkali free systems of $\log K_c = 2.2$
 19 for C-S-H0.9 and $\log K_c = 1.8$ for C-S-H1.4 (Lange et al., 2018). These values are much higher than the values given
 20 by Tits et al. (2006a) $\log K_c(\text{Ra-Ca}) = 0.77$, independent of the Ca/Si ratio. No explanation is yet available for this
 21 inconsistency. The comparison with data for other alkaline-earth elements reveals a decreasing affinity for uptake
 22 by C-S-H in the order $\text{Ra}^{+2} > \text{Ba}^{+2} > \text{Sr}^{+2}$ (Ba^{+2} : $\log K_c=1.05$, (Missana et al., 2017); Sr^{+2} : $\log K_c=0.08$, (Tits et al.,
 23 2006b)). Sr^{+2} is not a meaningful analogue for the uptake of ^{226}Ra in cementitious systems due to the significantly
 24 lower selectivity coefficient.

25 The uptake of $^{226}\text{Ra}^{+2}$ by HCP prepared from CEM I reached a steady state after about 10 days with an R_d value of
 26 $\sim 60 \text{ L kg}^{-1}$. In contrast, in the sorption experiments using the low pH (Cebama reference blend) HCP, equilibrium
 27 conditions were not attained in 100 days, which, in combination with the changes in solution pH, suggested an
 28 ongoing hydration process in this material and the formation of C-S-H with low Ca/Si-ratios from remaining
 29 unreacted clinker phases, silica fume and blast furnace slag. The final R_d value of $12,300 \text{ L kg}^{-1}$ is attributed to
 30 both, the lower system pH and the lower Ca/Si ratio of the C-S-H compared to CEM I based systems.

31 The results from the kinetic sorption tests (supplementary data, 1.1) on degraded and non-degraded CEM I and
 32 CEM V HCP indicate that most of the $^{226}\text{Ra}^{+2}$ was sorbed mostly in the first 2 days of contact (sorption percentage
 33 $\sim 33\%$ for CEM I and 35% for CEM V). After two days, radium uptake slowly increase up to 20 days for both
 34 cement pastes, up to an distribution ratio of $\sim 300 \text{ L} \cdot \text{kg}^{-1}$ for CEM I and $\sim 400 \text{ L} \cdot \text{kg}^{-1}$ for CEM V (Figure 8). No
 35 significant increase was observed in radium uptake between 20 and 80 days of contact, indicating that 20 days of
 36 contact are enough to attain the sorption equilibrium.



1

2 Figure 8: Comparison of Ra uptake on non-degraded CEM I and CEM V (left Fig.) and
 3 uptake on CEM I (right Fig.).

4 For degraded HCP (stage III.a and stageIV) the Ra uptake is faster than for non-degraded pastes. The radium
 5 uptake on these two degraded pastes is significantly higher than on the non-degraded one ($\sim 1000 \text{ L}\cdot\text{kg}^{-1}$ for stage
 6 III.a and $\sim 20000 \text{ L}\cdot\text{kg}^{-1}$ for stage IV of degradation, Figure 8 right). Sorption isotherms were linear between 45
 7 $\text{Bq}\cdot\text{ml}^{-1}$ and $136 \text{ Bq}\cdot\text{ml}^{-1}$ ($5.4\cdot 10^{-9}$ to $1.6\cdot 10^{-8}$ mol/L) for non-degraded and degraded ones samples.

8 The reversibility of radium sorption on non-degraded cement pastes was assessed by desorption tests. Radium
 9 desorption is much slower than sorption. After 20 days, only about 40% of sorbed Ra was desorbed from CEM I
 10 and $\sim 20\%$ from CEM V and even after 80 days less than 50% is desorbed from both cement pastes.

11 The temperature dependency was studied for Ra uptake on CEM II/A-S 42.5 R both in saturated $\text{Ca}(\text{OH})_2$ and
 12 synthetic cement water CPW (Table 1) and in Concrete Richard (containing cement of CEM III B/32.5 type) and
 13 Concrete UJV (with cement of CEM I 42.5 type).

14

15 Table 1: Distribution coefficients R_d [$\text{L}\cdot\text{kg}^{-1}$] for Ra sorption on cement based materials as a function of
 16 temperature. R_d values are averages obtained for liquid to solid ratio of 10, 60 and $100 \text{ L}\cdot\text{kg}^{-1}$

| | HCP CEM II/A-S 42.5 R, $\text{Ca}(\text{OH})_2$ | | | | CEM II / B-M (S-LL) 32.5R | Concrete UJV/ $\text{Ca}(\text{OH})_2$ | Concrete Richard/ $\text{Ca}(\text{OH})_2$ |
|---|---|--------|--------|---------|------------------------------|---|--|
| | 22 °C | 50 °C | 65 °C | 80 °C | 22 °C | 22 °C | 22 °C |
| R_d [$\text{L}\cdot\text{kg}^{-1}$] | 93±21 | 121±11 | 213±72 | 275±169 | 352±154 | 179±47 | 166±65 |

17

18 At room temperature, the R_d increased in the order: hydrated cement paste CEM II/A-S 42.5 R < concrete Richard
 19 <concrete UJV in saturated $\text{Ca}(\text{OH})_2$ solution, despite the lower content of cement and hence of C-S-H in concrete.
 20 Interesting were the resulting R_d for CEM II - B-M (S-LL) 32.5 R. However, both CEM II materials differ in the value
 21 of specific surface area (2.4 times higher for CEM II-B-M (S-LL)32.5 R)) and also different liquid phases were used
 22 for the sorption experiments.

23 In order to assess some general tendencies, a comparison for sorption constants is given in Table 2. The sorption
 24 constants in this Table show same variability depending on the measurement conditions used in the different
 25 laboratories including S/L ratio, specific surface area and total concentration of the element whose sorption is
 26 tested. In general, the anions MoO_4^{2-} , SeO_3^{2-} , SeO_4^{2-} , TCO_4^- , I^- , IO_3^- , and Cl^- were bound preferentially on AFm and
 27 AFt phases while the uptake on C-S-H was weaker, but still relevant. AFm and AFt phases sorb preferentially the

1 divalent anions (MoO_4^{2-} , SeO_3^{2-} and SeO_4^{2-}) over monovalent anions such as TcO_4^- , I^- , IO_3^- , and Cl^- . The cation Ra^{2+}
 2 is preferentially bound on C-S-H; its uptake on AFm phases is much weaker. The sorption measured on cement
 3 pastes shows a large variability due to the complexity of cementitious systems and due to the presence of high
 4 concentrations of competing anions such as sulfate in the solution. The table show clearly higher Rd values for
 5 the uptake of Be(II) than Ra(II). Although both elements belong to the alkali-earth series, they are characterized
 6 by very different ionic radii ($r_{\text{Be}^{2+}} = 0.27 \text{ \AA}$ for coordination number (CN) = 4; $r_{\text{Ra}^{2+}} = 1.48 \text{ \AA}$ for CN = 8). This
 7 results also in a very different hydrolysis behaviour (strong hydrolysis for Be(II) against weak hydrolysis for Ra(II)),
 8 which is expectedly the main reason for the observed differences in the uptake by C-S-H phases.”

9 Table 2: Comparison of sorption constants Rd [$\text{L}\cdot\text{kg}^{-1}$] obtained by the various laboratories in the CEBAMA project
 10 (P=PSI/EMPA, J=Jülich, B=BRGM, A=Amphos21, R=RATEN, K=KIT, S=SUBATECH, C=CTU). Data for Be are: $10^{-6} \text{ M} \leq$
 11 $[\text{Be(II)}] \leq 10^{-2.5} \text{ M}$ (depending upon Ca:Si of C-S-H and Be(II) solubility limit at the investigated pH) and $[\text{S/L}] = 2$
 12 $\text{g}\cdot\text{L}^{-1}$. For Ra: initial concentrations are $5.5\cdot 10^{-9} \text{ M}$ (pH 12.5) and S/L is $2.5 \text{ g}\cdot\text{L}^{-1}$ for CEM I and V for RATEN. For C14
 13 sorption initial concentrations are 10^{-7} M (CEMI) and $3\cdot 10^{-8}$ (CEMV) S/L = $2.5 \text{ g}\cdot\text{L}^{-1}$ and pH 12.5 for RATEN.

| | I | IO3 | Se(VI) | Se(IV) | C-14 | Ra | Be | TcO4- | MoO4 |
|-------------------------|---------------------------------------|----------------------|--|---------------------------------------|---|---------------------------|---------------|------------|--------------------------------|
| AFm-SO4 | 30±5 (P) pH13 811±324 (J) pH 12 | 634±253 (J) pH 12 | 92±18 (P) pH13 9836±1680 (J) pH12 | 718 ±144 (P) pH13 4430±538(J) pH12 | | 7±4.3(J) | | 4.0±1.9(J) | 1500 (B) 1571±115(J) pH12 |
| AFm-CO3 | 81±32 (J) pH 11.3 | 51±20 (J) | 5±1 (P) pH13 120±36(J) pH 11.3 | 47±10(J) pH11.3 | | 4±3.9(J) | | 2.3±1.7(J) | 1500 (B) 1564±90(J) pH 11.3 |
| Afm-CO3-OH | 55±10 (P) | | 935 ±187 (P) | | | | | | |
| Afm/Aft S(VI)/Al=0.5 | | | | | | | | | 1200-46000 (A) |
| Afm/Aft S(VI)/Al=1 | | | | | | | | | 160-170 (A) |
| Aft | 190±76 (J) | 1068±427 (J) | 728±90 (J) | 97±4 (J) | | 139±28 (J) (precipit?) | | 0.6±0.9(J) | <<3 (A) 122±4(J) pH 11.2 |
| Hydrogarnet | | | | | | | | | 3000 (J) |
| CSH 1.4±0.2 | 83±33 (J) | 62±24 (J) | | | | 1805±772 (J) | 150000 (K) | 2.3±2.4(J) | 20±5(A) pH 12.3 781±41 (J) |
| CSH 0.8±0.2 | 48±19 (J) | 64±25 (J) | 13±1 (J) | 124±20(J) | | 22530 ±3980 (J) | 150000 (K) | 4.5±2.7(J) | 4±2 (A) pH 10.3 432±26 (J) |
| CEM I | 25 (J) | 140 (J) | | | 1300 (R) | 300 (R) 60 (J) | | | |
| CEM II | | | | | | 130 (C) S/L>0.01 | | | |
| CEM V | | | | | 3200 (R) pH 12.4 800 (S) pH 13.5 | 500 (R) | | | |
| CEBAMA mix | | | | | | 12600 (J) | | | |

14 15 16 Diffusion of Cl^- , I^- , TcO_4^- , HTO , $^{14}\text{CO}_3^{2-}$, Sr^{+2} and Ra^{+2} in HCP 17

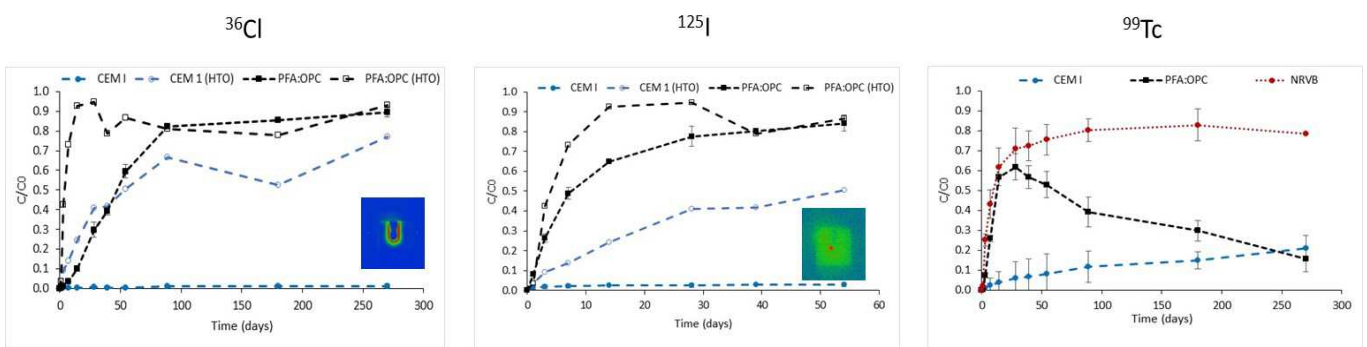
18 Diffusion of $^{36}\text{Cl}^-$ through Nirex Reference Vault Backfill (a candidate cementitious backfill material) has been
 19 investigated by van Es et al. (2015), who reported significant retardation of ^{36}Cl in NRVB. Moreover, the data
 20 displayed a pronounced dependence on the background chloride concentration, whereby trace ^{36}Cl retention was
 21 substantially reduced in saline solutions. Autoradiographic and elemental mapping by energy-dispersive X-ray
 22 spectroscopy (EDX) suggested that ^{36}Cl is bound to partially hydrated, glassy, sulphate-bearing, residual clinker
 23 particles. In this work, the PFA blend showed the lowest retention for $^{36}\text{Cl}^-$ with recovery reaching 90% of the
 24 input concentration after 270 days (Fig. 9). . On the basis of this result, the diffusion of chloride through PFA:OPC

1 could be assumed conservatively, to correspond to that of HTO. In contrast, no breakthrough was observed for
 2 ^{36}Cl with CEM I. Whether binding to clinker can account for the retardation, as suggested for NRVB (van Es et al.,
 3 2015), is by no means certain since there has clearly been some diffusion from the central well and this appears
 4 to be homogeneous, as shown by the accompanying autoradiograph (Fig 9).

5 A number of studies have been carried out investigating the through-diffusion (Atkinson and Nickerson, 1984,
 6 Sarott et al., 1992, Felipe-Sotelo et al., 2014) and out-diffusion (Mattigod et al., 2001) of Γ^- . The rate of Γ^- diffusion
 7 has been shown to correlate strongly with the water to cement ratio of the paste where an increase from 0.2 to
 8 0.7 can increase the diffusion rate by three orders of magnitude (Atkinson and Nickerson, 1984). This work would
 9 seem to corroborate these findings as markedly different diffusion behaviour was observed for the respective
 10 cement formulations (Fig. 9). The breakthrough curves for iodide and tritiated water in PFA:OPC are similar in
 11 terms of both earliest appearance of the tracer at the first sampling point (1 day) and overall recovery ($C/C_0 >$
 12 80%). Thus, as a first and conservative approximation, the diffusion coefficient for iodide through this particular
 13 cement could be assumed to be the same as for HTO. Conversely, Γ^- is effectively retarded by CEM I with no
 14 breakthrough observed on the timescale of the experiment and therefore, no reliable diffusion rate can be
 15 inferred. The remaining cements studied all displayed a greater capacity for retarding iodide migration than
 16 chloride but detailed discussion is beyond the scope of this paper.

17 No comparable data for ^{99}Tc are available in the literature but analogous experiments to those described above
 18 (Felipe-Sotelo et al., 2014; van Es et al., 2015) were carried out for various HCP samples, including NRVB. Selected
 19 breakthrough curves highlight the differential transport of $^{99}\text{TcO}_4^-$ in NRVB, PFA and CEM I (Fig. 9c). $^{99}\text{TcO}_4^-$ was
 20 observed to migrate through each of the cements, albeit at different rates. For PFA:OPC, the trend of Tc
 21 migration reverses after 30 days suggesting that a fraction of the initially released ^{99}Tc is taken up in a later stage
 22 by the cement matrix. The likely cause is reduction of Tc(VII) to Tc(IV). The results of batch tests described above
 23 indicate that Tc(VII) is only weakly adsorbed onto any hydrated cement phase, including AFt. Therefore, the likely
 24 cause of Tc retardation is reduction of Tc(VII) to Tc(IV), and consequently, both the rate and extent of migration
 25 will depend upon the presence of reductants in the blend. Such behavior does not lend itself to a simple
 26 modelling description based on equilibrium partitioning of a tracer between solution and the solid phase.

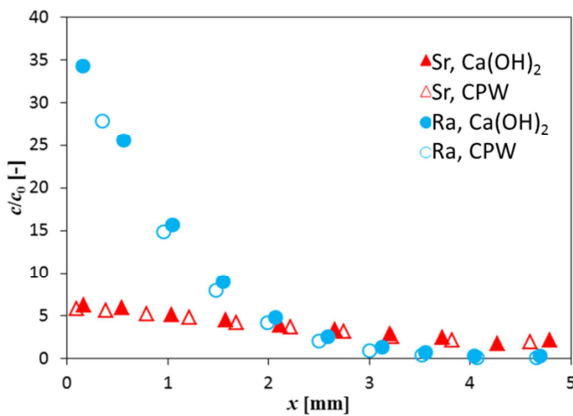
27



28

29 Figure 9: Break through curves of selected anionic species in HCP samples. Inserts are autoradiographic images
 30 for ^{36}Cl in CEM I and for ^{125}I in PFA HCP.

31 A set of diffusion experiments for ^{223}Ra and ^{85}Sr with a carrier ($c_0 = 0.35 \text{ mmol}\cdot\text{L}^{-1}$) was carried out for 3 weeks in
 32 Portlandite water or CPW through the CEM II/A-S 42.5 R layer (with a diffusion length of 0.5 cm) that was
 33 prepared unconventionally by pressing a crushed hydrated cement paste and saturated with the selected solution
 34 prior to the addition of the migrating element (Figure 10). The volume of the inlet and outlet reservoirs was 50
 35 ml. The initial concentrations of both radionuclides were the same as for sorption experiments. The experimental
 36 time was limited because of the short half-life of the ^{223}Ra isotope. Consequently, the breakthrough of Ra did not
 37 occur.



1

2 Figure 10: Concentration profiles (volumetric activity or concentration in both phases) of the sorbed elements in
 3 the CEM II/A-S 42.5 R HCP in contact with portlandite water (saturated Ca(OH)₂ solution) or synthetic cement
 4 water (CPW).

5 The determined R_d values, obtained by an original evaluation of through-diffusion experiments in the transient
 6 state were (Vopalka et al., 2019) around 9 L·kg⁻¹ for Sr for both liquid phase used, 150 L·kg⁻¹ for Ra in the
 7 portlandite water (slightly higher than in batch sorption studies, see table 2), and 100 L·kg for Ra in CPW. Based
 8 on the comparison of the dry sample weight with the sum of the weights of the cut slices generated at the end of
 9 the diffusion experiment it can be stated that $V \cdot m^{-1}$ phase ratio was equal to 0.3 L·kg⁻¹. The results are in good
 10 agreement with the R_d values originating from sorption experiments.

11 Using tritiated water (HTO), diffusion properties for fully water-saturated CEM V samples were compared to
 12 those for unsaturated samples ($S_w=0.85$) and samples exposed to drying (55-80% RH) and rewetting cycles (for
 13 experimental conditions see supplementary material, 5). An effective diffusion coefficient $D_e^{ref}(HTO)$ was
 14 obtained for a fully water saturated reference sample of CEM V of $3.94 \pm 0.4 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$, in agreement with
 15 literature data (Savoye et al., 2018). For up to 70% RH, wet/drying cycles seems to have no influence on $D_e(HTO)$,
 16 whereas for up to 55% RH, $D_e(HTO)$ values increased slightly ($D_e(HTO)=5.1 \pm 0.5 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$). These data are
 17 interpreted as resulting from a mesoporosity which locally favours the transport of HTO in the pore network
 18 without modifying the total water accessible porosity. For unsaturated conditions ($S_w=0.85$), $D_e(HTO)=11 \pm 1 \cdot 10^{-13}$
 19 $\text{m}^2 \cdot \text{s}^{-1}$, which is four times higher than the reference value ($S_w=1$), the opposite trend of what is expected. This
 20 may be explained by changes in HCP microstructure caused by osmosis; eg. microcracks forming due to locally
 21 heterogeneous desaturation but this has not yet been confirmed.

22 For carbonated HCP samples, the drying/rewetting cycle results in an increase of $D_e(HTO)$ by a factor of three with
 23 respect to the reference sample. The result is consistent with the impact of carbonation on CEM V HCP as
 24 recently described by Auroy et al. (2015). Unlike Portland HCP, for which carbonation and precipitation of CaCO₃
 25 leads to porosity clogging, for composite HCP, such as CEM V, the carbonation process induces the formation of
 26 microcracks (due to C-S-H decalcification, subsequent polymerization which generates shrinkage and eventually
 27 cracking). Globally, microcracks then act as a connected porosity network, accelerating HTO diffusion.
 28 Nevertheless, during through-diffusion experiments with fully saturated samples, conditions are favorable for a
 29 self-sealing process to occur in the microcrack network, thus reducing $D_e(HTO)$ values.

30 The transport properties of ¹⁴CO₃²⁻ in saturated and unsaturated carbonated CEM V samples was studied by
 31 digital autoradiography (Beaver system, AI4R, France) in order to estimate diffusion coefficients for ¹⁴C. The
 32 experiments were run for approximately 1 year. For the non-carbonated HCP sample, ¹⁴C is located in a single
 33 zone at 200-300 μm depth below the surface (on the upstream side) giving an estimated diffusion depth for ¹⁴C of
 34 240 μm. For the carbonated HCP sample, ¹⁴C penetrates more deeply into the sample; concentrated in a zone of
 35 500 μm below the surface, again on the upstream side, followed by a more diffuse zone up to about 1.2 mm. The
 36 upper limit for a diffusion coefficient of ¹⁴C is therefore, $10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$.

1

2 **Conclusions**

3 A large part of this work was focused on the role of AFm phases in anion retention. The thermodynamic
 4 properties of each of the pure AFm-Se and AFm-I phases were determined as well as AFm phases containing
 5 binary mixtures of Se and I with a common anions present in cement. Strong evidence was observed for the
 6 intercalation of sulfur, selenium and iodine anions in the AFm interlayers. Literature data from Ma et al. (2018)
 7 were confirmed showing that differences in basal spacing and crystal symmetry are due to the size and position
 8 of the interlayer anion as well as the hydration number of the anions.

9 Experimental data can sometimes be described in terms of both adsorption constant and by solid solution
 10 formation. The presence of Se in AFm systems leads in most cases to the formation of a new discrete Se-AFm
 11 phase. There could be miscibility gap between I-AFm and monocarbonate (AFm-CO₃). Limiting factors for solid
 12 solution formation are crystal symmetry, size of the interlayer anion and the hydration state of the phase. The
 13 uptake of iodate (IO₃) by AFt as well as by AFm-SO₄ led to iodate-substituted ettringite, formed either by anion
 14 exchange or phase transformation. New thermodynamic models have been derived, allowing a quantitative
 15 description of the sorption competition between the uptake of Se(VI), Se(IV) and I(-I) on AFm phases. The
 16 retention capacity for selenite and selenate is higher HCP based on CEM I than in the low-pH CEBAMA reference
 17 paste due to the higher proportion of aluminate phases in the former.

18 Exchange processes on AFm phases are fast; accurate rate laws have been determined which are readily
 19 implementable in reactive transport modelling. Diffusion experiments were performed with various anionic
 20 species (³⁶Cl⁻, ⁹⁹TcO₄⁻, ¹²⁵I⁻, ¹⁴C) or sorbing radionuclides (Ra, Sr) through saturated hardened cement pastes
 21 considering as well partially water saturated conditions.

22 The work has shown that the uptake of molybdenum by cements is not associated with ettringite, as often
 23 assumed. However, the data obtained and models derived still need to be tested with real concrete and
 24 integrated in reactive transport models.

25 The present work has provided a first set of sorption parameters for beryllium onto cementitious phases. In
 26 contrast to the traditional hypothesis of very weak Be sorption, assumed on the basis of the negative charge of
 27 the Be(II) species at high pH values, strong uptake has been confirmed for all systems investigated.

28 The results obtained provided an improved understanding of the behaviour of several safety relevant
 29 radionuclides within cementitious barriers in repository environment, thus decreasing uncertainties with respect
 30 to relevant radionuclide retention processes. The results can be used to substantiate and justify assumptions
 31 made with respect to radionuclide migration behavior in safety assessments.

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38 **References**

39

40 Aimoz, L., Wieland, E., Taviot-Guého, C., Dähn, R., Vespa, M., Churakov, S.V., 2012. Structural insight into iodide
 41 uptake by AFm phases. *Environ Sci Technol* 46, 3874–3881. <https://doi.org/10.1021/es204470e>
 42 Allen, P.G., Siemering, G.S., Shuh, D.K., Bucher, J.J., Edelstein, N.M., Langton, C.A., Clark, S., Reich, T., Denecke,

- 1 M., 1997. Technetium speciation in cement waste forms determined by X-ray absorption fine structure
2 spectroscopy. *Radiochim. Acta.* 76, 77–86.
- 3 Allmann, R., 1977. Refinement of the hybrid layer structure $[\text{Ca}_2\text{Al}(\text{OH})_6]^+[\frac{1}{2}\text{SO}_4\cdot 3\text{H}_2\text{O}]^-$. *Neues Jahrb. Mineral.*
4 *Monatsh.* 3, 136–144.
- 5 Atkins, M., Glasser, F.P., 1992. Application of portland cement-based materials to radioactive waste
6 immobilization. *Waste Management* 12, 105–131. [https://doi.org/10.1016/0956-053X\(92\)90044-J](https://doi.org/10.1016/0956-053X(92)90044-J)
- 7 Atkinson, A., Nickerson, A.K., 1984. The diffusion of ions through water-saturated cement. *J Mater Sci* 19, 3068–
8 3078. <https://doi.org/10.1007/BF01026986>
- 9 Auroy, M., Poyet, S., Le Bescop, P., Torrenti, J.-M., Charpentier, T., Moskura, M., Bourbon, X., 2015. Impact of
10 carbonation on unsaturated water transport properties of cement-based materials. *Cement and Concrete*
11 *Research* 74, 44–58. <https://doi.org/10.1016/j.cemconres.2015.04.002>
- 12 Baur, I., Johnson, C.A., 2003. Sorption of Selenite and Selenate to Cement Minerals. *Environ. Sci. Technol.* 37,
13 3442–3447. <https://doi.org/10.1021/es020148d>
- 14 Berner, U., 2014. Solubility of Radionuclides in a Concrete Environment for Provisional Safety Analyses for SGT-E2
15 (No. 14–07). NAGRA, CH-5430 Wettingen Switzerland.
- 16 Berner, U., 1999. Concentration Limits in the Cement Based Swiss Repository for Long-lived, Intermediate-level
17 Radioactive Wastes (LMA) (PSI Bericht No. 99–10). Paul Scherrer Institut CH - 5232 Villigen PSI.
- 18 Bonhoure, I., Baur, I., Wieland, E., Johnson, C.A., Scheidegger, A.M., 2006. Uptake of Se(IV/VI) oxyanions by
19 hardened cement paste and cement minerals: An X-ray absorption spectroscopy study. *Cement and*
20 *Concrete Research* 36, 91–98.
- 21 Bonhoure, I., Scheidegger, A.M., Wieland, E., Dähn, R., 2002. Iodine species uptake by cement and CSH studied by
22 I K-edge X-ray absorption spectroscopy. *Radiochimica Acta* 90. [https://doi.org/10.1524/ract.2002.90.9-](https://doi.org/10.1524/ract.2002.90.9-11_2002.647)
23 [11_2002.647](https://doi.org/10.1524/ract.2002.90.9-11_2002.647)
- 24 Bradbury, M, Sarrot, F.A., 1995. Sorption Databases for the Cementitious Near-Field of a L/ILW Repository for
25 Performance Assessment (PSI Bericht No. 95–06). Paul Scherrer Institut.
- 26 Bruno, J., 1987. Beryllium(II) hydrolysis in 3.0 mol dm⁻³ perchlorate. *J. Chem. Soc., Dalton Trans.* 2431–2437.
27 <https://doi.org/10.1039/DT9870002431>
- 28 Buttler, F.G., Dent Glasser, L.S., Taylor, H.F.W., 1959. Studies on $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ and the Related Natural
29 Mineral Hydrocalumite. *J American Ceramic Society* 42, 121–126. [https://doi.org/10.1111/j.1151-](https://doi.org/10.1111/j.1151-2916.1959.tb14078.x)
30 [2916.1959.tb14078.x](https://doi.org/10.1111/j.1151-2916.1959.tb14078.x)
- 31 Cevirim-Papaioannou, N., Gaona, X., Altmaier, M., 2019. Thermodynamic description of Be(II) solubility and
32 hydrolysis in acidic to hyperalkaline NaCl and KCl solutions,. *Applied Geochemistry* this issue.
- 33 Champenois, J.-B., Mesbah, A., Cau Dit Coumes, C., Renaudin, G., Leroux, F., Mercier, C., Revel, B., Damidot, D.,
34 2012. Crystal structures of Boro-AFm and sBoro-AFt phases. *Cement and Concrete Research* 42, 1362–
35 1370. <https://doi.org/10.1016/j.cemconres.2012.06.003>
- 36 Chinae, E., Dominguez, S., Mederos, A., Brito, F., Sanchez, A., Ienco, A., Vaca, A., 1997. Hydrolysis of beryllium(II)
37 in DMSO:H₂O. *Main Group Metal Chemistry* 20, 11–17.
- 38 Churakov, S.V., Labbez, C., Pegado, L., Sulpizi, M., 2014. Intrinsic Acidity of Surface Sites in Calcium Silicate
39 Hydrates and Its Implication to Their Electrokinetic Properties. *J. Phys. Chem. C* 118, 11752–11762.
40 <https://doi.org/10.1021/jp502514a>
- 41 Cornelis, G., Johnson, C.A., Gerven, T.V., Vandecasteele, C., 2008. Leaching mechanisms of oxyanionic metalloid
42 and metal species in alkaline solid wastes: A review. *Applied Geochemistry* 23, 955–976.
43 <https://doi.org/10.1016/j.apgeochem.2008.02.001>
- 44 Es, E. van, Hinchliff, J., Felipe-Sotelo, M., Milodowski, A.E., Field, L.P., Evans, N.D.M., Read, D., 2015. Retention of
45 chlorine-36 by a cementitious backfill. *Mineralogical Magazine* 79, 1297–1305.
46 <https://doi.org/10.1180/minmag.2015.079.6.05>
- 47 Evans, N.D.M., 2008. Binding mechanisms of radionuclides to cement. *Cement and Concrete Research*, 38, 543–
48 553.
- 49 Favre-Nicolin, V., Černý, R., 2002. FOX, 'free objects for crystallography': a modular approach to ab initio
50 structure determination from powder diffraction. *J Appl Cryst* 35, 734–743.
51 <https://doi.org/10.1107/S0021889802015236>
- 52 Felipe-Sotelo, M., Hinchliff, J., Drury, D., Evans, N.D.M., Williams, S., Read, D., 2014. Radial diffusion of
53 radiocaesium and radioiodide through cementitious backfill. *Physics and Chemistry of the Earth*
54 *Complete*, 60–70. <https://doi.org/10.1016/j.pce.2014.04.001>
- 55 Felipe-Sotelo, M., Hinchliff, J., Evans, N.D.M., Read, D., 2016. Solubility constraints affecting the migration of
56 selenium through the cementitious backfill of a geological disposal facility. *Journal of Hazardous Materials*
57 305, 21–29. <https://doi.org/10.1016/j.jhazmat.2015.11.024>

- 1 Felipe-Sotelo, M., Hinchliff, J., Field, L.P., Milodowski, A.E., Preedy, O., Read, D., 2017. Retardation of uranium and
2 thorium by a cementitious backfill developed for radioactive waste disposal. *Chemosphere* 179, 127–138.
3 <https://doi.org/10.1016/j.chemosphere.2017.03.109>
- 4 Giffaut, E., Grivé, M., Blanc, P., Vieillard, P., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N., Madé, B., Duro, L.,
5 2014. Andra thermodynamic database for performance assessment: ThermoChimie. *Applied*
6 *Geochemistry*, *Geochemistry for Risk Assessment: Hazardous waste in the Geosphere* 49, 225–236.
7 <https://doi.org/10.1016/j.apgeochem.2014.05.007>
- 8 Glasser, F.P., Macphee, D., Atkins, M., Pointer, C., Cowie, J., Wilding, C.R., Mattingley, N.J., Evans, P.A., 1989.
9 Immobilisation of radwaste in cement based matrices (No. DOE-RW--89.058). Department of the
10 Environment.
- 11 Goetz-Neunhoeffler, F., Neubauer, J., 2006. Refined ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) structure for
12 quantitative X-ray diffraction analysis. *Powder Diffr.* 21, 4–11. <https://doi.org/10.1154/1.2146207>
- 13 Grangeon, S., Marty, N., 2019. in press.
- 14 Grive, M., Olmeda, J., 2016. Molybdenum behaviour in cementitious materials. CEBAMA state of the art report.
- 15 Henocq, P., Robinet, J.C., Perraud, D., Munier, I., et al., 2018. CARbon-14 Source Term CAST, – Integration of CAST
16 results to safety assessment (Deliverable of EU project CAST No. D 6.3).
- 17 Hillier, S., Lumsdon, D.G., Brydson, R., Paterson, E., 2007. Hydrogarnet: A Host Phase for Cr(VI) in Chromite Ore
18 Processing Residue (COPR) and Other High pH Wastes. *Environ. Sci. Technol.* 41, 1921–1927.
19 <https://doi.org/10.1021/es0621997>
- 20 Hummel, W., Berner, U., Curti, E., Pearson, F.J., Thoenen, T., 2002a. Nagra/PSI Chemical Thermodynamic Data
21 Base 01/01. *Radiochimica Acta* 90. https://doi.org/10.1524/ract.2002.90.9-11_2002.805
- 22 Hummel, W., Berner, U., Curti, E., Pearson, F.J., Thoenen, T., 2002b. Nagra/PSI Chemical Thermodynamic Data
23 Base 01/01. Universal Publisher/uPublish.com, Parkland, Florida.
- 24 Jenkins, Thakur, 1979. Reappraisal of thermochemical radii for complex ions. *J. Chem. Educ.* 56, 576.
- 25 Johnson, E.A., Rudin, M.J., Steinberg, S.M., Johnson, W.H., 2000. The sorption of selenite on various cement
26 formulations. *Waste Management* 20, 509–516. [https://doi.org/10.1016/S0956-053X\(00\)00024-6](https://doi.org/10.1016/S0956-053X(00)00024-6)
- 27 Kakahana, H., Sillen, G., 1956. Studies on the Hydrolysis of Metal Ions. XVI. The Hydrolysis of the Beryllium Ion,
28 Be^{2+} . *Acta Chemica Scandinavica* 10, 985–1005.
- 29 Kindness, A., Lachowski, E.E., Minocha, A.K., Glasser, F.P., 1994. Immobilisation and fixation of molybdenum (VI)
30 by Portland cement. *Waste Management* 14, 97–102. [https://doi.org/10.1016/0956-053X\(94\)90002-7](https://doi.org/10.1016/0956-053X(94)90002-7)
- 31 Kulik, D.A., Wagner, T., Dmytrieva, S.V., Kosakowski, G., Hingerl, F.F., Chudnenko, K.V., Berner, U., 2013. GEM-
32 Selektor geochemical modeling package: Revised algorithm and GEMS3K numerical kernel for coupled
33 simulation codes. *Computational Geosciences* 17, 1–24. <https://doi.org/10.1007/s10596-012-9310-6>
- 34 Lange, S., Kowalski, P.M., Pšenička, M., Klinkenberg, M., Rohmen, S., Bosbach, D., Deissmann, G., 2018. Uptake of
35 ^{226}Ra in cementitious systems: A complementary solution chemistry and atomistic simulation study.
36 *Applied Geochemistry* 96, 204–216. <https://doi.org/10.1016/j.apgeochem.2018.06.015>
- 37 Luksic, S.A., Riley, B.J., Schweiger, M., Hrma, P., 2015. Incorporating technetium in minerals and other solids: A
38 review. *Journal of Nuclear Materials* 466, 526–538. <https://doi.org/10.1016/j.jnucmat.2015.08.052>
- 39 Ma, B., Charlet, L., Fernandez-Martinez, A., Kang, M., Madé, B., 2019. A review of the retention mechanisms of
40 redox-sensitive radionuclides in multi-barrier systems. *Applied Geochemistry* 100, 414–431.
41 <https://doi.org/10.1016/j.apgeochem.2018.12.001>
- 42 Ma, B., Fernandez-Martinez, A., Grangeon, S., Tournassat, C., Findling, N., Carrero, S., Tisserand, D., Bureau, S.,
43 Elkāim, E., Marini, C., Aquilanti, G., Koishi, A., Marty, N.C.M., Charlet, L., 2018. Selenite Uptake by Ca–Al
44 LDH: A Description of Intercalated Anion Coordination Geometries. *Environ. Sci. Technol.* 52, 1624–1632.
45 <https://doi.org/10.1021/acs.est.7b04644>
- 46 Ma, B., Fernandez-Martinez, A., Grangeon, S., Tournassat, C., Findling, N., Claret, F., Koishi, A., Marty, N.C.M.,
47 Tisserand, D., Bureau, S., Salas-Colera, E., Elkāim, E., Marini, C., Charlet, L., 2017. Evidence of Multiple
48 Sorption Modes in Layered Double Hydroxides Using Mo As Structural Probe. *Environ. Sci. Technol.* 51,
49 5531–5540. <https://doi.org/10.1021/acs.est.7b00946>
- 50 Mace, N., Landesman, C., Pointeau, I., Grambow, B., Giffaut, E., 2007. Characterisation of thermally altered
51 cement pastes. Influence on selenite sorption. *Advances in Cement Research*.
52 <https://doi.org/10.1680/adcr.2007.19.4.157>
- 53 Marty, N.C.M., Grangeon, S., Elkāim, E., Tournassat, C., Fauchet, C., Claret, F., 2018. Thermodynamic and
54 crystallographic model for anion uptake by hydrated calcium aluminate (AFm): an example of
55 molybdenum. *Scientific Reports* 8, 7943. <https://doi.org/10.1038/s41598-018-26211-z>
- 56 Marty, N.C.M., Grangeon, S., Lerouge, C., Warmont, F., Rozenbaum, O., Conte, T., Claret, F., 2017. Dissolution
57 kinetics of hydrated calcium aluminates (AFm-Cl) as a function of pH and at room temperature. *Mineral.*

- 1 mag. 81, 1245–1259. <https://doi.org/10.1180/minmag.2016.080.161>
- 2 Mattigod, S.V., Whyatt, G.A., Serne, R.J., Martin, P.F., Schwab, K.E., Wood, M.I., 2001. Diffusion and Leaching of
3 Selected Radionuclides (Iodine-129, Technetium-99, and Uranium) Through Category 3 Waste
4 Encasement Concrete and Soil Fill Material (No. PNNL-13639). Pacific Northwest National Laboratory,
5 Richland, Wa 99352, USA.
- 6 Mesbah, A., Cau-dit-Coumes, C., Frizon, F., Leroux, F., Ravaux, J., Renaudin, G., 2011. A New Investigation of the
7 Cl—CO₂— Substitution in AFm Phases. *Journal of the American Ceramic Society* 94, 1901–1910.
8 <https://doi.org/10.1111/j.1551-2916.2010.04305.x>
- 9 Missana, T., García-Gutiérrez, M., Mingarro, M., Alonso, U., 2017. Analysis of barium retention mechanisms on
10 calcium silicate hydrate phases. *Cement and Concrete Research* 93, 8–16.
11 <https://doi.org/10.1016/j.cemconres.2016.12.004>
- 12 Nedyalkova, L., Lothebach, B., Geng, G., Mäder, U., Tits, J., 2019. Uptake of iodide by carbonate-bearing calcium
13 aluminate phases (AFm phases). *Applied Geochemistry* submitted.
- 14 Nedyalkova, Latina, Lothenbach, B., Renaudin, G., Mäder, U., Tits, J., 2019. Effect of redox conditions on the
15 structure and solubility of sulfur- and selenium-AFm phases. *Cement and Concrete Research* 123, 105803.
16 <https://doi.org/10.1016/j.cemconres.2019.105803>
- 17 Noshita, K., Nishi, T., Matsuda, M., Izumida, T., 1995. Sorption Mechanism of Carbon-14 by Hardened Cement
18 Paste. *MRS Online Proceedings Library Archive* 412. <https://doi.org/10.1557/PROC-412-435>
- 19 Ochs, M., Mailants, D., Wang, L., 2016. *Radionuclide and Metal Sorption on Cement and Concrete*. Springer,
20 Cham.
- 21 Olmeda, J., Missana, T., Grandia, F., Grivé, M., García-Gutiérrez, M., Mingarro, M., Alonso, U., Colàs, E., Henocq,
22 P., Munier, I., Robinet, J.C., 2019. Radium retention by blended cement pastes and pure phases (C-S-H
23 and C-A-S-H gels): Experimental assessment and modelling exercises. *Applied Geochemistry* 105, 45–54.
24 <https://doi.org/10.1016/j.apgeochem.2019.04.004>
- 25 Pointeau, I., Coreau, N., Reiller, P.E., 2008. Uptake of anionic radionuclides onto degraded cement pastes and
26 competing effect of organic ligands. *Radiochimica Acta* 96, 367–374.
- 27 Pointeau, I., Reiller, P., Macé, N., Landesman, C., Coreau, N., 2006. Measurement and modeling of the surface
28 potential evolution of hydrated cement pastes as a function of degradation. *Journal of Colloid and
29 Interface Science* 300, 33–44. <https://doi.org/10.1016/j.jcis.2006.03.018>
- 30 Rojo, H., Scheinost, A.C., Lothenbach, B., Laube, A., Wieland, E., Tits, J., 2018. Retention of selenium by calcium
31 aluminate hydrate (AFm) phases under strongly-reducing radioactive waste repository conditions. *Dalton
32 Trans.* 47, 4209–4218. <https://doi.org/10.1039/C7DT04824F>
- 33 Sarott, F.-A., Bradbury, M.H., Pandolfo, P., Spieler, P., 1992. Diffusion and adsorption studies on hardened cement
34 paste and the effect of carbonation on diffusion rates. *Cement and Concrete Research, Special Double
35 Issue Proceedings of Symposium D of the E-MRS Fall Meeting 1991* 22, 439–444.
36 [https://doi.org/10.1016/0008-8846\(92\)90086-B](https://doi.org/10.1016/0008-8846(92)90086-B)
- 37 Savoye, S., Rajyaguru, A., Macé, N., Lefèvre, S., Spir, G., Robinet, J.C., 2018. How mobile is tritiated water through
38 unsaturated cement-based materials? New insights from two complementary approaches. *Appl Radiat
39 Isot* 139, 98–106. <https://doi.org/10.1016/j.apradiso.2018.04.019>
- 40 Solem-Tishmack, J.K., McCarthy, G.J., Dockett, B., Eylands, K.E., Thompson, J.S., Hassett, D.J., 1995. High-calcium
41 coal combustion by-products: Engineering properties, ettringite formation, and potential application in
42 solidification and stabilization of selenium and boron. *Cement and Concrete Research* 25, 658–670.
43 [https://doi.org/10.1016/0008-8846\(95\)00054-G](https://doi.org/10.1016/0008-8846(95)00054-G)
- 44 Taylor, T., 1997. *Cement-Chemistry - 2nd Edition*.
- 45 Tits, J., Iijima, K., Kamei, G., Wieland, E., 2006a. The uptake of radium by calcium silicate hydrates and hardened
46 cement paste. *Radiochimica Acta* 94, 637–643.
- 47 Tits, J., Wieland, E., Müller, C.J., Landesman, C., Bradbury, M.H., 2006b. Strontium binding by calcium silicate
48 hydrates. *Journal of Colloid and Interface Science* 300, 78–87. <https://doi.org/10.1016/j.jcis.2006.03.043>
- 49 Vopalka, D., Rosendorf, T., Barborova, L., Kitternova, J., 2019. Modelling and interpretation of diffusion
50 experiments of selected radionuclides through cementitious samples. Final results and interpretation of
51 the modelling of experiments within CEBAMA (No.
52 <https://www.cebama.eu/Content/PublicArea/WP3/D3.06.pdf>)).
- 53 Walker, C., 2010. C-S-H gel models (in PHREEQC), 3rd GEMS workshop, Thermodynamic modeling in cementitious
54 systems, Dubendorf, Switzerland.
- 55 Wieland, E., 2014. Sorption Data Base for the Cementitious Near Field of L/ILW and ILW Repositories for
56 Provisional Safety Analyses for SGT-E2 (No. 14– 08), Nagra Technical Report. CH-5430 Wettingen
57 Switzerland.

- 1 Wieland, E., Van Loon, L., 2003. Cementitious Near-Field Sorption Data Base for Performance Assessment of an
2 ILW Repository in Opalinus Clay (No. PSI Bericht Nr . 03-06). Paul Scherrer Institut, CH-5232 Villigen PSI.
- 3 Zhang, M., Reardon, E.J., 2003. Removal of B, Cr, Mo, and Se from wastewater by incorporation into
4 hydrocalumite and ettringite. *Environ. Sci. Technol.* 37, 2947–2952.
- 5 Zingg, A., Winnefeld, F., Holzer, L., Pakusch, J., Becker, S., Gauckler, L., 2008. Adsorption of polyelectrolytes and its
6 influence on the rheology, zeta potential, and microstructure of various cement and hydrate phases.
7 *Journal of Colloid and Interface Science* 323, 301–312. <https://doi.org/10.1016/j.jcis.2008.04.052>
8

Highlights

- understanding of retention processes of anions on cementitious materials
- decreasing uncertainties with respect to radionuclide on cementitious materials
- justifying assumptions for radionuclide migration in safety assessments
- improving sorption databases for fresh and degraded cement systems

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: