Applied Geochemistry 181 (2025) 106301

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Uptake of iodine by cement hydration phases: Implications for radioactive waste disposal

Steve Lange [a,1], Matthew Isaacs [a,b,2], Martina Klinkenberg [a,*], David Read [b], Dirk Bosbach [a], Guido Deissmann [a]

[a] Institute of Fusion Energy and Nuclear Waste Management – Nuclear Waste Management (IFN-2), Forschungszentrum Jülich GmbH, 52428, Jülich, Germany
[b] School of Chemistry and Chemical Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom

ARTICLE INFO

Editorial handling by: Dr Mavrik Zavarin

Keywords:
Cementitious materials
Iodine retention
Sorption
Uptake mechanisms

ABSTRACT

Iodine-129 (^{129}I) is an important radionuclide in the context of nuclear waste disposal owing to its long half-life and potentially high mobility in the environment. The uptake of iodide and iodate by cement hydration phases, including calcium silicate hydrates (CSH), AFm and ettringite, as well as hardened cement paste made from Ordinary Portland cement, has been studied in batch-type sorption experiments to enhance understanding of iodine retention mechanisms in engineered repositories. Uptake kinetics were generally fast, leading to steady state within 30 days. Strong uptake of iodine by AFm and ettringite was observed, the mechanism dependent on the iodine speciation. Iodide is retained in both AFm and ettringite by exchange for sulphate, whereas with iodate, iodate-substituted ettringite is formed by phase transformation or ion exchange in the case of AFm and ettringite, respectively. The contribution of CSH phases to iodine retention in cementitious systems depends on the Ca/Si-ratio of the CSH and the alkalinity of the solution, with stronger retention in young hyperalkaline cementitious materials. These findings have implications when selecting grouts for the immobilisation of radioactive waste streams containing ^{129}I or for choosing cementitious grouts and/or backfill materials in nuclear waste repositories.

1. Introduction

Cementitious materials are used extensively in the management of radioactive wastes, for example, for solidification and conditioning of low- and intermediate-level wastes, or for construction, backfilling and sealing of near surface and deep geological repositories (*e.g.* Atkins and Glasser, 1992; Glasser, 1997, 2001, 2002, 2011; Bel et al., 2006; Jantzen et al., 2010; Drace and Ojovan, 2013). Depending on the application, a large variety of cements are used (or are under consideration for future use), including Ordinary Portland cements (OPC) as well as formulations containing fly ash (PFA) or ground/granulated blast furnace slag (GGBS). The use of low alkalinity cements containing supplementary siliceous materials, such as silica fume, has been increasingly promoted to mitigate potentially deleterious interactions between highly alkaline cement pore waters and clay materials in the repository near-field (*e.g.* Cau Dit Coumes et al., 2006; Codina et al., 2008; Lothenbach et al., 2012; Bach et al., 2013). After hydration and curing, cementitious materials represent heterogeneous mixtures of various hydration phases, comprising nanocrystalline calcium silicate hydrates (CSH), portlandite ($Ca(OH)_2$), calcium aluminate/ferrate compounds (*e.g.* monosulphate (AFm), ettringite (AFt)) and other minor phases such as hydrotalcite (Taylor, 1997; Glasser, 2001). Phase assemblage, phase composition (*e.g.* Ca/Si ratio, Al content in CSH) and microstructural properties (*e.g.* porosity, diffusivity) of a cementitious material depend strongly on the cement types employed and the mixing and curing conditions (Taylor, 1997).

Retention of radionuclides in cement-based materials can occur by precipitation of sparingly soluble phases at high pH, surface (ad)sorption on hydration products, ion exchange, and/or by incorporation into existing or newly formed solids, either by entrapment or formation of solid solutions. Radionuclide uptake depends on the nature, valence state and speciation of the radionuclide, conditions in the pore water (*e.g.* pH, T, Eh, cation/anion concentrations), degradation state of the cementitious materials and the presence of additives such as

* Corresponding author.
E-mail address: m.klinkenberg@fz-juelich.de (M. Klinkenberg).
[1] present address: BGE Bundesgesellschaft für Endlagerung mbH, Schachtanlage Asse II, 38319 Remlingen, Germany.
[2] present address: Mott MacDonald, 10 Temple Back, Bristol BS1 6FL, United Kingdom.

https://doi.org/10.1016/j.apgeochem.2025.106301
Received 14 October 2024; Received in revised form 21 January 2025; Accepted 8 February 2025
Available online 8 February 2025
0883-2927/

superplasticisers or retarders (*e.g.* Ochs et al., 2016). The uptake and retention of various radionuclides by cementitious materials have been investigated extensively, often on a phenomenological basis (cf. reviews by Gougar et al., 1996; Glasser, 1997, 2011; Evans, 2008; Jantzen et al., 2010; Ochs et al., 2016) leading to the development of empirical 'sorption databases' (*e.g.* Heath et al., 2000; Wieland and Van Loon, 2002; Wang et al., 2013; Wieland, 2014; Ochs et al., 2016). Whereas the potential of the high pH cementitious environment to reduce the solubility and hence, mobility of certain cationic radionuclides is well established, the retention of anionic species has not been studied to the same extent. Thus, it is often assumed in safety assessments that anionic species of safety relevant radionuclides (*e.g.* ^{129}I, ^{99}Tc, ^{79}Se, ^{36}Cl) will be much more mobile (*e.g.* Posiva, 2012; SKB, 2015).

Several iodine isotopes are produced by thermal fission of ^{235}U in nuclear reactors; however, besides stable ^{127}I only ^{129}I, a β^--emitting radionuclide, possesses a sufficiently long half-life ((1.57 ± 0.04) x 10^7 years; Brown et al., 2018) to be relevant for the long-term safety of radioactive waste repositories. Iodide (I^-) is the predominant aqueous species under a wide range of conditions, whereas iodate (IO_3^-) is stable only in highly oxidising environments (Fig. 1). Elemental iodine ($I_{2(aq)}$) can also occur in oxidising, acidic solutions. Thus, it is generally assumed that the majority of iodine in a repository environment will be present in the form of iodide (Atkins and Glasser, 1990; Mattigod et al., 2001; Bonhoure et al., 2002; Toyohara et al., 2002; Shirai et al., 2011; Aimoz et al., 2012a), notwithstanding the fact that larger amounts of iodate (IO_3^-) are solidified in cement during treatment of waste streams from off-gas treatment at spent fuel reprocessing facilities (Tanabe et al., 2010). Recently, Kaplan et al. (2019) also pointed out the importance of organic iodine species in leachates of cementitious grouts, which were investigated for their potential for iodine immobilisation.

Iodine uptake and retention studies (*e.g.* Atkinson and Nickerson, 1987; Atkins and Glasser, 1992; Holland and Lee, 1992; Sarott et al., 1992; Rapin et al., 1999; Iwaida et al., 2001; Mattigod et al., 2001, 2004; Bonhoure et al., 2002; Toyohara et al., 2002; Chida and Sugiyama, 2009; Tanabe et al., 2010; Shirai et al., 2011; Niibori et al., 2012; Aimoz et al., 2012a,b; Idemitsu et al., 2013; Nedyalkova et al., 2021) demonstrated that the aqueous iodine species I^- and IO_3^- bind more strongly on cements than on most geological materials in soils or in the subsurface. The reviews by Evans (2008) and Ochs et al. (2016) concluded that I^- retention in cementitious systems can be either through surface adsorption, mainly by CSH, or by incorporation into crystalline phases, such as AFm and ettringite, due to substitution of SO_4^{2-} by $2I^-$ (Bonhoure et al., 2002; Shirai et al., 2011; Aimoz et al., 2012a, 2012b). Iodide uptake has been shown to increase with increasing Ca/Si ratios in CSH gels, suggesting I^- is adsorbed electrostatically (Glasser et al., 1989; Pointeau et al., 2008), although the processes controlling I^- interaction with hardened cement pastes (HCP) are still poorly understood (Wieland, 2014; Hummel, 2017). According to Bonhoure et al. (2002), the uptake of IO_3^- in cementitious materials is not controlled by CSH but by immobilisation into a solid similar to $Ca(IO_3)_2$ (Ochs et al., 2016; Kaplan et al., 2019); however, Idemitsu et al. (2013) pointed out that IO_3^- is also readily incorporated within the ettringite structure. The solidification of IO_3^--bearing wastes by cement has been shown to increase the final content of ettringite from 12 wt% to approximately 80 wt%, indicating a shift in the equilibrium of the sulphate phases (AFt/AFm) by iodate (Tanabe et al., 2010). Finally, Mattigod et al. (2001) observed a decrease of the leachability of iodine in cementitious material containing steel fibres, which they suggested was due to the reduction of IO_3^- to I^-.

The aims of the present work are to further mechanistic understanding of the interaction of iodine species with cementitious materials and to explore the contributions of the different hydration phases present. A systematic bottom-up approach was pursued, investigating the uptake of I^- and IO_3^- on synthesised phases representative of those in hydrated cements, such as CSH, AFm and AFt, as well as with HCP itself. The effects of solution chemistry on iodine uptake were explored using solution compositions reflecting the porewater in HCP as leaching progresses in order to obtain insights into the mechanisms controlling iodine binding at various stages of cement degradation.

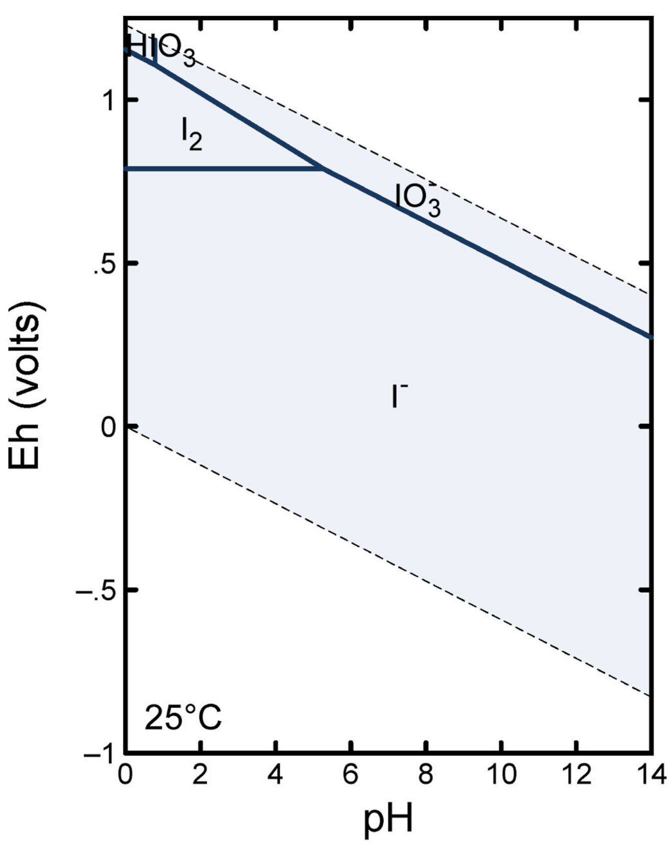

Fig. 1. Eh-pH diagram of iodine for a(I) = 10^{-6} M. (Thermodynamic Database: PSI Chemical Thermodynamic Database, 2020; Hummel and Thoenen, 2022).

2. Materials and methods

2.1. Cementitious materials

The synthesised cement hydration phases comprised CSH with Ca/Si ratios of 0.9 and 1.4 (termed CSH0.9 and CSH1.4, respectively), two AFm phases ($Ca_4Al_2(OH)_{12}(X^{2-})\cdot 6H_2O$), namely AFm-$SO_4$ and AFm-CO_3, ettringite (AFt, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$), hydrogarnet (C3AH6, $Ca_3Al_2(OH)_{12}$), portlandite ($Ca(OH)_2$), and calcite ($CaCO_3$). The synthesis routes followed established procedures from the literature (CSH: Atkins et al., 1992; AFm: Baur et al., 2004; Matschei et al., 2006; AFt: Atkins et al., 1991; Baur et al., 2004); the procedures are described in detail elsewhere (Lange et al., 2018; Lange, 2019). Synthesis of the individual phases as well as sample preparation and storage were carried out in a glove box under argon atmosphere (<10 ppm CO_2) to avoid carbonation.

The sorption behaviour of I^- and IO_3^- on crushed HCP prepared from a commercially available OPC (CEM I 32.5 R; Heidelberger Zement) at a water/cement ratio (w/c) of 0.4 was also investigated. The cement paste was prepared under argon atmosphere, cast into cylindrical moulds and cured for at least 28 days submerged in water under anoxic conditions; the demoulded monoliths were then stored under argon atmosphere. The HCP was mechanically crushed for use in the batch sorption experiments; the specific surface area of the crushed material was determined by BET to be 24.2 m^2 g^{-1}.

2.2. Materials characterisation

The structure and purity of the synthesised hydration phases were characterised by powder X-ray diffraction (XRD), using either a D4 Endeavor (Bruker AXS GmbH) with a θ-2θ geometry or a D8 Advance (Bruker AXS GmbH) with a θ-θ geometry, employing CuK_{α}–radiation. Microstructural investigations were performed by scanning electron microscopy (SEM) using a FEI Quanta 200F equipped with a field emission cathode; energy dispersive X-ray spectroscopy (EDS) was carried out using an Apollo X Silicon Drift Detector (SDD) from EDAX. All SEM-EDS analyses were performed in low vacuum mode (60 Pa) to avoid coating of the samples with gold or carbon. Detailed characterisation of the hydration phases is described in Lange et al. (2018) and Lange (2019). The synthesised hydration phases show similar features and no distinct differences to those observed in cementitious materials such as HCP (cf. Lange et al., 2018; Lange, 2019). The specific surface areas of the hydration phases are given in Table S1 in the Supplementary Material (Lange et al., 2024).

2.3. Batch sorption experiments

Sorption distribution ratios (R_d-values) for the halogen species and uptake kinetics on the model phases were determined in static batch experiments under anoxic conditions, employing a range of test solutions to address different cement degradation states. Sorption tests were generally performed in 20 mL LDPE bottles using solid to liquid (*S/L*) ratios between 0.005 kg L^{-1} and 0.1 kg L^{-1}, depending on the aim of the experiments. In a first set of sorption experiments, solutions equilibrated with the respective solids were used. These were prepared by equilibrating dried solids with deionized water (18.2 MΩ) for 14 days under anoxic conditions; subsequently, solid and liquid phases were separated by filtration. The pH of the equilibrium solutions is provided in Table S2 in the Supplementary Material (Lange et al., 2024). In addition, experiments with an artificial, alkali-rich 'young' cementitious water (ACW, pH > 13) and a saturated $Ca(OH)_2$ solution (CH, pH ~12.5) were performed to mimic conditions representative of cement degradation stages I and II, respectively (*e.g.* Glasser, 2011; Hoch et al., 2012; Ochs et al., 2016). The ACW solution was prepared following the method of Wieland et al. (1998) by filtration and dilution of highly concentrated NaOH and KOH solutions and subsequent saturation with $Ca(OH)_2$. The final ACW solution contained 0.114 mol L^{-1} Na and 0.18 mol L^{-1} K at pH 13.3; its Ca concentration was estimated by geochemical modelling at 0.0014 mol L^{-1}. The prepared saturated portlandite solution (CH) contained 0.19 mol L^{-1} Ca at pH = 12.3.

The respective model phases were added to the solutions and stored for 14 days, before the tracers were added in the form of KI and KIO_3, respectively, at concentrations in the range 10^{-6} to $10^{-2.5}$ mol L^{-1}. The tracer concentration and pH in solution were monitored for up to 60 days to ensure steady state had been reached; the bottles were shaken regularly by hand. The solution pH was found to be constant over the timescale of the experiments. A separate test batch was used for each time step in the kinetic experiments to avoid shifting the S/L-ratio by repeated sampling. For each system investigated, at least six separate batch experiments (at different times) were evaluated.

The iodine speciation in solution was not determined during the experiments; however, the experiments were performed in an inert gas glove box under Ar 6.0 containing less than 1 ppm of oxygen. Randomly measured redox potentials (*e.g.* in experiments with CSH and hydrogarnet) revealed redox potentials between −30 and −80 mV. Taking into account the slow kinetics of iodine oxidation/reduction (Atkins and Glasser, 1992) and the absence of redox active substances in the experiments with the single hydration phases prepared from high purity chemicals, it can be assumed that the iodine speciation is preserved during the experiments.

At the end of the experiments, liquid and solid phases were separated by filtration using USY-1 ultrafilters (10,000 Da, Advantec) prior to analysis. The iodine concentrations in solution were determined by ICP-MS using an Elan 6100 DRC instrument (PerkinElmer) or by ICP-OES (Thermo Scientific iCAP7600). When measuring the aqueous iodine concentrations, blank samples were added to account for iodine trailing within the measurement equipment (*e.g.* within tubes). The iodine concentrations in the blanks were subtracted from the concentrations measured within the uptake experiments. Prior to the uptake experiments, blank samples comprising 'liquid + spike' were analysed with respect to loss of iodine due to sorption of the iodine species to reaction vessels and filters. Loss of iodine was found to be negligible among the five replicates per iodine species.

The sorption experiments with crushed HCP were performed in an analogous manner to those with the single phases at a S/L-ratio of 0.005 kg L^{-1}, using test solutions which had been pre-equilibrated for at least 14 days with crushed HCP.

Uptake of the iodine species by the solid phases is described here in terms of a distribution ratio (R_d) between the amount of iodine taken up by the solids (I_{sorbed}; mol kg^{-1}) and the concentration remaining in solution ($I_{solution}$; mol L^{-1}) as

$$R_d = \frac{I_{sorbed}}{I_{solution}} \qquad \text{(eq. 1)}$$

and calculated according to

$$R_d = \frac{C_i - C_t}{C_t} \frac{V}{m} \qquad \text{(eq. 2)}$$

where C_i is the initial tracer concentration in solution and C_t the concentration at time t, respectively, *V* is the volume of the liquid phase and *m* the mass of solid phase used in the experiment. Uncertainties in the R_d values were estimated from those associated with the experimental design and procedures (*e.g.* weighing and pipetting) and those resulting from (at least) triplicate solution analysis by ICP-MS using Gaussian error propagation. Since the model phases were synthesised using high purity reagents, the impact of potential background iodine concentrations in the solids was assumed to be negligible. In contrast, the presence of natural stable iodine (*i.e.* ^{127}I) in the HCP cannot be ruled out, which might lead to an underestimation of the R_d values in that case.

3. Results and discussion

3.1. Uptake of I^- and IO_3^- by individual cement hydration phases

The uptake kinetics of each iodine species by the model hydration phases in the various solutions were determined at a *S/L*-ratio of 0.005 kg L^{-1}; the results of these tests as a function of time are depicted in Fig. 2. For the majority of the model phases, fast uptake of both iodine species was observed, leading to equilibrium within 30 days. Exceptions were found for the sorption of IO_3^- by AFm-SO_4 and ettringite, where steady state conditions were not reached within the experimental timeframe of 60 days.

The equilibrium R_d values are shown in Fig. 3 and summarised in Table S3 in the Supplementary Material (Lange et al., 2024). In general, the data show that i) several hydration phases contribute to the retention of inorganic iodine species in cementitious materials, and ii) while statistically not conclusive in several cases, the extent of iodine uptake appears to depend on the aqueous iodine species and background electrolyte, the latter reflecting the degradation state of the cementitious material.

3.1.1. Iodide

The uptake of I^- by CSH was found to increase with increasing Ca/Si-ratio from R_d = 48 L kg^{-1} for CSH0.9 to R_d = 83 L kg^{-1} for CSH1.4 in equilibrium solutions, in agreement with the observations of Aggarwal et al. (2000), though there is some overlap in the error bars. This trend, in line with the increasingly positive surface charge of CSH at

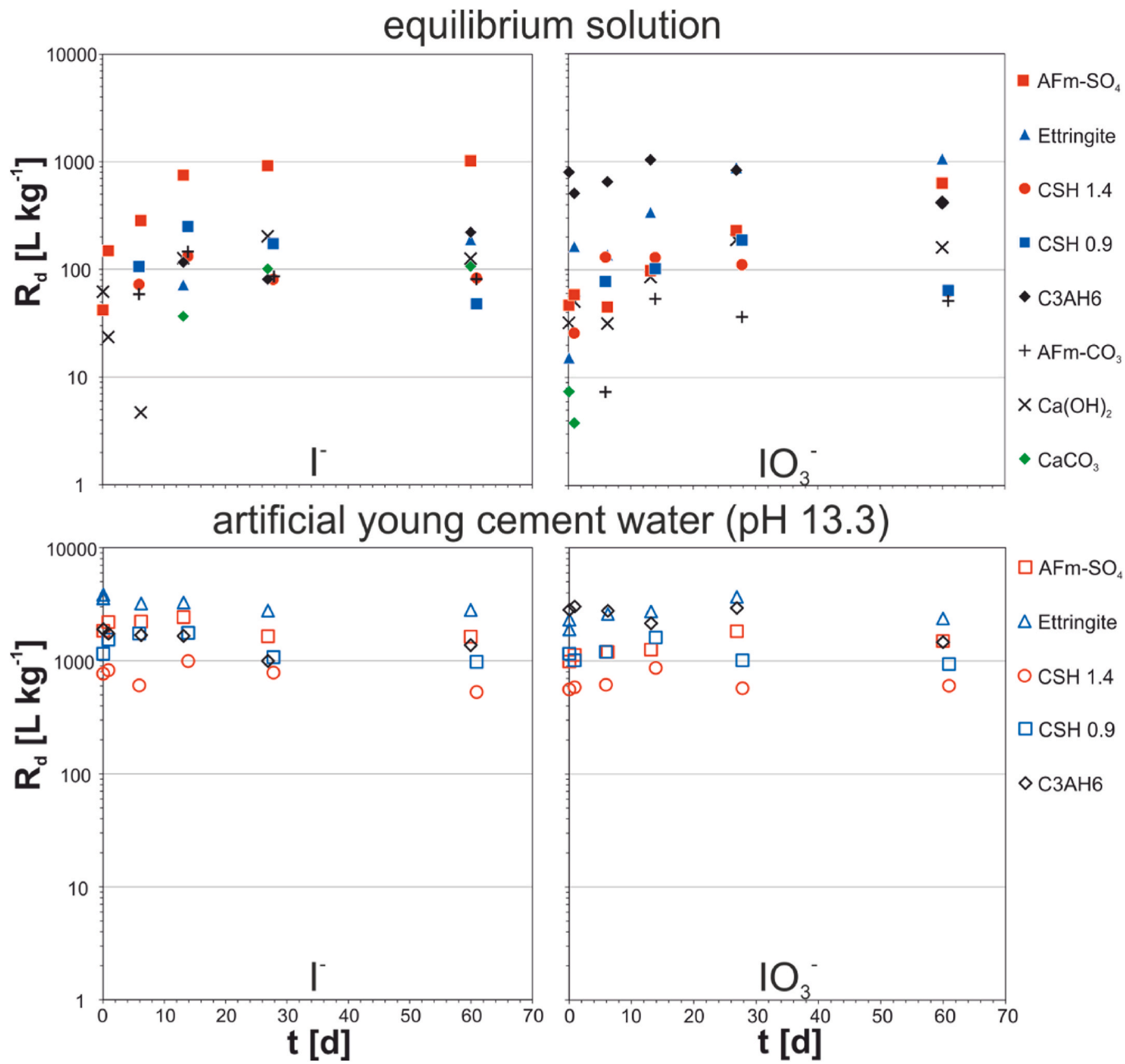

Fig. 2. Uptake kinetics of I^- and IO_3^- by selected cement hydration phases in equilibrium solution (top) and artificial young cement water (pH 13.3, bottom); (C3AH6: hydrogarnet); error bars are omitted for clarity.

Ca/Si-ratios >1.2, supports the presumed uptake mechanism of I^- on CSH due to electrostatic adsorption (*cf.* Bonhoure et al., 2002; Ochs et al., 2016). A distinctly stronger sorption of I^- onto the CSH phases was observed in young cementitious water at pH > 13. Here, there is apparently an inverse trend with respect to the Ca/Si-ratio; however, there is a significant overlap of the error bars. Generally, there seems to be a tendency for the R_d for I^- to decrease as the cement system degrades and pH falls (Ochs et al., 2016).

AFm is thought to be the strongest scavenger for I^- in cementitious systems (Brown and Grutzeck, 1985; Atkins and Glasser, 1990, 1992; Ochs et al., 2016) and, as expected, strong uptake of I^- was observed for AFm-SO_4 ($R_d = 811$ L kg^{-1} in equilibrium solution). Anion exchange of SO_4^{2-} by I^- in the interlayer of this layered double hydroxide (LDH) phase is considered to be the predominant process (Atkins and Glasser, 1990, 1992; Aimoz et al. 2012a, 2012b). The comparatively lower uptake of I^- by AFm-CO_3 indicates preferential anion exchange of I^- with tetrahedral sulphate in the interlayer over the planar carbonate ion. In comparison to AFm-SO_4, ettringite (AFt), which can similarly incorporate I^- by exchange for sulphate groups (*e.g.* Atkins and Glasser, 1990, 1992; Ochs et al., 2016), revealed only moderate I^- sorption ($R_d = 190$ L kg^{-1} in equilibrium solution) though very strong retention in young cementious water ($R_d = 2810$ L kg^{-1}); the latter in a similar range as AFm-SO_4 ($R_d = 1633$ L kg^{-1}), when taking into account the overlapping error bars. Some I^- retention by other minor hydration phases, such as hydrogarnet, portlandite, and calcite was noted (Table S3 in the Supplementary Material, Lange et al., 2024).

Systematic evaluation of the various hydration phases shows that the aluminates, AFm and AFt, are more effective substrates for I^- retention in cementitious systems; thus, the results do not support lower R_d values for AFm and AFt in comparison to CSH, as suggested by Noshita et al.

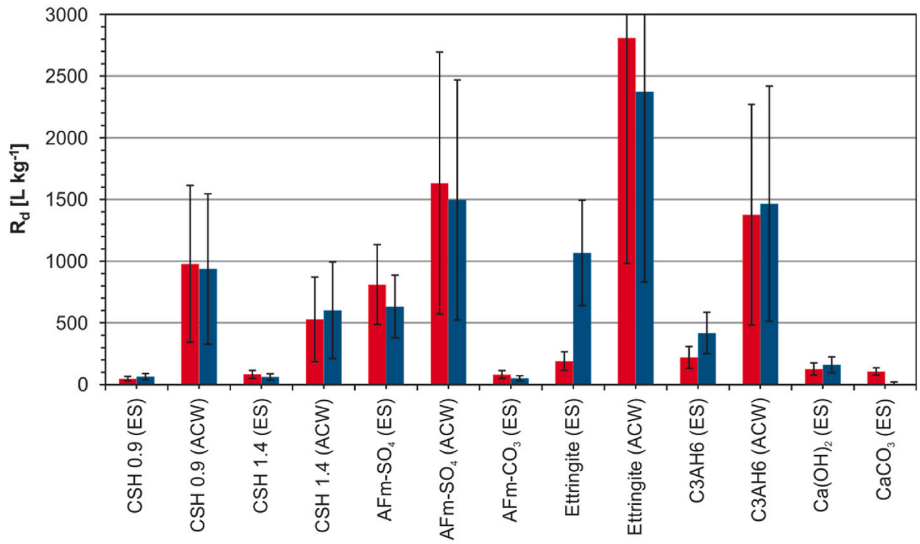

Fig. 3. Distribution ratios R_d for the uptake of I^- (red) and IO_3^- (blue) by selected cement hydration phases in different background electrolytes (ES: equilibrium solution; ACW: artificial young cement water (pH 13.3); C3AH6: hydrogarnet). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(2001). In general, all model phases show higher uptake of I^- in ACW when compared to the equilibrium solutions. This indicates higher retention potential for I^- in young cement waters and supports the observed tendency for decreasing retention with progressive degradation of the cementitious materials (Ochs et al., 2016).

3.1.2. Iodate

Distribution ratios for the uptake of IO_3^- by CSH in equilibrium solutions (CSH0.9, $R_d = 64$ L kg^{-1}; CSH1.4, $R_d = 62$ L kg^{-1}) were, within experimental error, independent of the Ca/Si-ratio. This could indicate that electrostatic sorption is not the main retention mechanism, as suggested by Bonhoure et al. (2002), who proposed that the uptake of IO_3^- in cementitious materials is controlled by formation of a $Ca(IO_3)_2$ phase rather than CSH. The measured R_d values for IO_3^- are also within the range of those values determined for the uptake of I^- by CSH0.9 and CSH1.4 under similar conditions.

As expected, pronounced IO_3^- sorption by AFm-SO_4 (R_d = 634 L kg^{-1}) and, in particular, by ettringite was observed ($R_d = 1068$ L kg^{-1}), probably due to anion exchange for sulphate. Idemitsu et al. (2013) synthesised AFt-IO_3 and showed that two IO_3^- anions can be incorporated into the ettringite structure by substituting for one sulphate group. Microstructural SEM/EDS investigations on needle-like ettringite crystals present in CEM I HCP revealed incorporation of iodate (up to about 11 wt%) during ettringite crystal growth (Fig. 4).

As with I^-, the interlayer anion in AFm seems to play an important role in the retention of IO_3^-; uptake by AFm-CO_3 was about one order of magnitude lower than with AFm-SO_4. In addition, the postulated uptake mechanism for iodate by AFm-SO_4 is thought to depend strongly on the initial concentration. At low iodate concentrations (10^{-6} mol L^{-1}), no changes in the AFm phase were observed in post-mortem analyses by XRD and SEM, suggesting simple exchange of sulphate by iodate in the interlayer. In contrast, at initial iodate concentrations of 10^{-3} mol L^{-1}, the neo-formation of a needle-shaped iodate-bearing phase, probably ettringite, at the expense of the AFm-SO_4 was observed (Fig. 5). These results indicate that elevated iodate levels in solution have a similar effect to increasing sulphate concentrations, favouring the formation and stability of iodate-bearing ettringite over AFm-SO_4. However, it has to be noted that iodate concentrations will probably be much lower than those of sulphate in 'real' systems.

AFm-SO_4 was reacted with solutions containing between 10^{-4} and 10^{-1} mol L^{-1} IO_3^- for 30 days in order to investigate the dependence of the AFm-SO_4 to iodate-bearing ettringite phase transition on iodate concentration. The XRD patterns of the solids at the end of the experiments are shown in Fig. 6, revealing incipient formation of an iodate-containing ettringite at c(IO_3^-) = 10^{-2} mol L^{-1}. At higher iodate concentrations, ettringite is the dominant phase.

In addition to iodate uptake by CSH, AFt and AFm, as described above, some retention of IO_3^- by hydrogarnet and portlandite was also observed, whereas the uptake of IO_3^- by calcite was found to be negligible. This suggests that the incorporation of IO_3^- into calcite and its polymorphs due to substitution for a carbonate group, as proposed by Feng and Redfern (2018) from first principles computational simulations using density functional theory (DFT), does not play an important role in iodate retention, with implications for carbonated concrete.

As observed with I^-, all model phases show higher uptake of IO_3^- in ACW when compared to the equilibrium solutions and portlandite saturated solution, indicating higher retention of iodine in young cementitious systems and decreasing R_d values with advancing degradation. Comparing the behaviour of the two iodine species, the most significant difference is the substantially higher uptake of IO_3^- by ettringite (Idemitsu et al., 2013).

3.2. Uptake of I^- and IO_3^- by HCP

Uptake of I^- and IO_3^- on crushed HCP CEM I is shown in Fig. 7. For both iodine species, uptake was fast, leading to steady state conditions after about 1 day. The uptake of IO_3^- (R_d ~270 L kg^{-1}) by HCP CEM I was more pronounced than I^- (R_d ~140 L kg^{-1}) after 60 days. The results obtained are in qualitative agreement with the results for the single hydration phases, indicating that the dominant contribution to iodine uptake can be attributed to the minor cement hydration phases such as AFm/AFt; which in some cases exhibited slightly higher R_d values for IO_3^- than for I^-. The distribution ratios for I^- sorption are in good agreement with published data on I^- uptake by HCP based on CEM I, as provided, for example, by Holland and Lee (1992), (R_d ~70 L kg^{-1}), Bayliss et al. (1996), (R_d 10–100 L kg^{-1}), Aggarwal et al. (2000), (R_d ~150 L kg^{-1}), Bonhoure et al. (2002), (R_d 20–200 L kg^{-1}), or Pointeau et al. (2008), (R_d ~150 L kg^{-1}). No specific data for IO_3^- adsorption on HCP are available.

In contrast to the experiments with the model phases, in this system changes of the redox speciation of iodine, *i.e.* reduction of iodate, cannot completely be ruled out, due to the potential presence of redox active

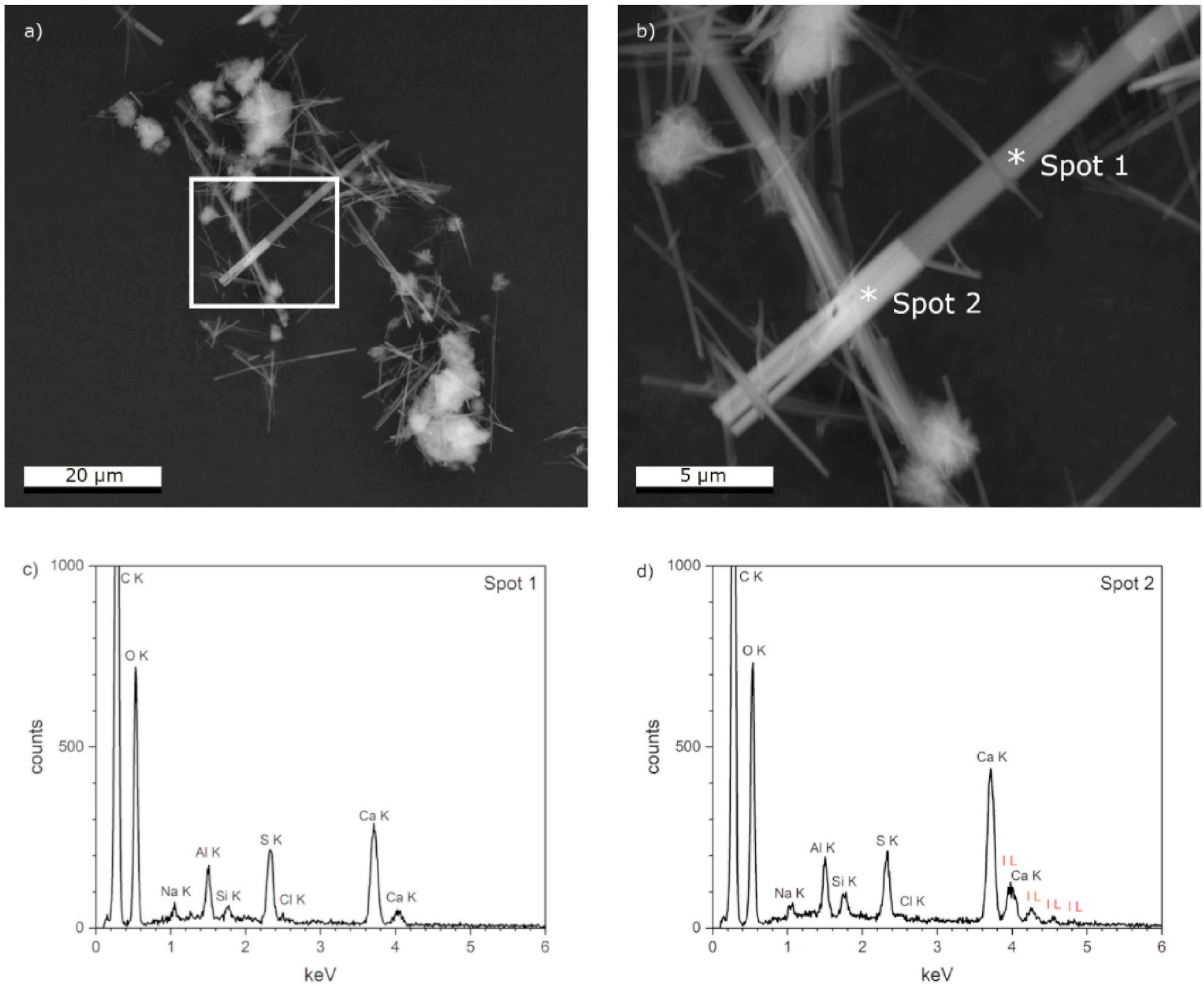

Fig. 4. a) SEM image (back scattered electron mode) of a needle-shaped ettringite crystal after 30 days reaction with a solution initially containing 10^{-3} mol L^{-1} IO_3^-. Brighter regions correspond to higher iodate concentrations; b) detail from Fig. 4a indicating EDS measurement spots; c) EDS spectrum at spot 1 (<1 wt% I) and d) EDS spectrum at spot 2 (11.1 wt% I; I_L energies labelled in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

species (*e.g.*, Fe(II)) in the HCP, which could contribute to similar observations for both iodine species. According to Atkins and Glasser (1992), this is one of the reasons why iodine is expected to be present mainly as I^- in cementitious systems.

The solution pH remained constant throughout the course of the sorption experiments using crushed HCP CEM I (pH ~12.6). Owing to the low *S*/*L*-ratio (0.005 kg L^{-1}) and the presumed leaching of alkalis, inferredby the solution pH probably controlled by portlandite dissolution, the experiments correspond to a slightly degraded (stage II) cementitious material (Lange et al., 2018). In this degradation state, iodine uptake was found to be greater (up to 1 order of magnitude) than in degradation stages I and III (Pointeau et al., 2008; Ochs et al., 2016). In contrast, the single phases show stronger iodine retention in young artificial cement water (ACW), compared to a portlandite saturated solution. Moreover, in degradation stage II, the Ca/Si ratio of CSH decreases, suggesting lower anion uptake due to the decreasing positive surface charge. The contrasting behaviour of the composite HCP materials with age/degradation might be explained by changes in the proportions of hydration phases due to ongoing pozzolanic reactions (Nedyalkova et al., 2021).

4. Conclusions

In this study, the uptake of iodine by several cement hydration phases and HCP was investigated in a bottom-up approach. Batch experiments on individual phases present in hydrated OPC and blended cements confirm the important role of AFm and AFt with respect to iodine retention in cementitious systems. The uptake mechanism for inorganic iodine by these phases depends on aqueous redox speciation. Structural incorporation of iodide (I^-) by simple anion exchange in the interlayer was observed for both AFm-SO_4 and AFm-CO_3. On the other hand, uptake of iodate (IO_3^-) by AFt as well as by AFm-SO_4, led to the formation of an iodate-substituted ettringite. Moreover, we observed that the uptake of I^- by AFm-phases is dependent on the nature of the anion complex, with stronger I^- uptake by AFm-SO_4 than AFm-CO_3. The indicated increasing uptake of I^- by CSH with increasing Ca/Si-ratio and thus, increasing positive surface charge, is in agreement with an assumed electrostatic adsorption mechanism, however, statistically not

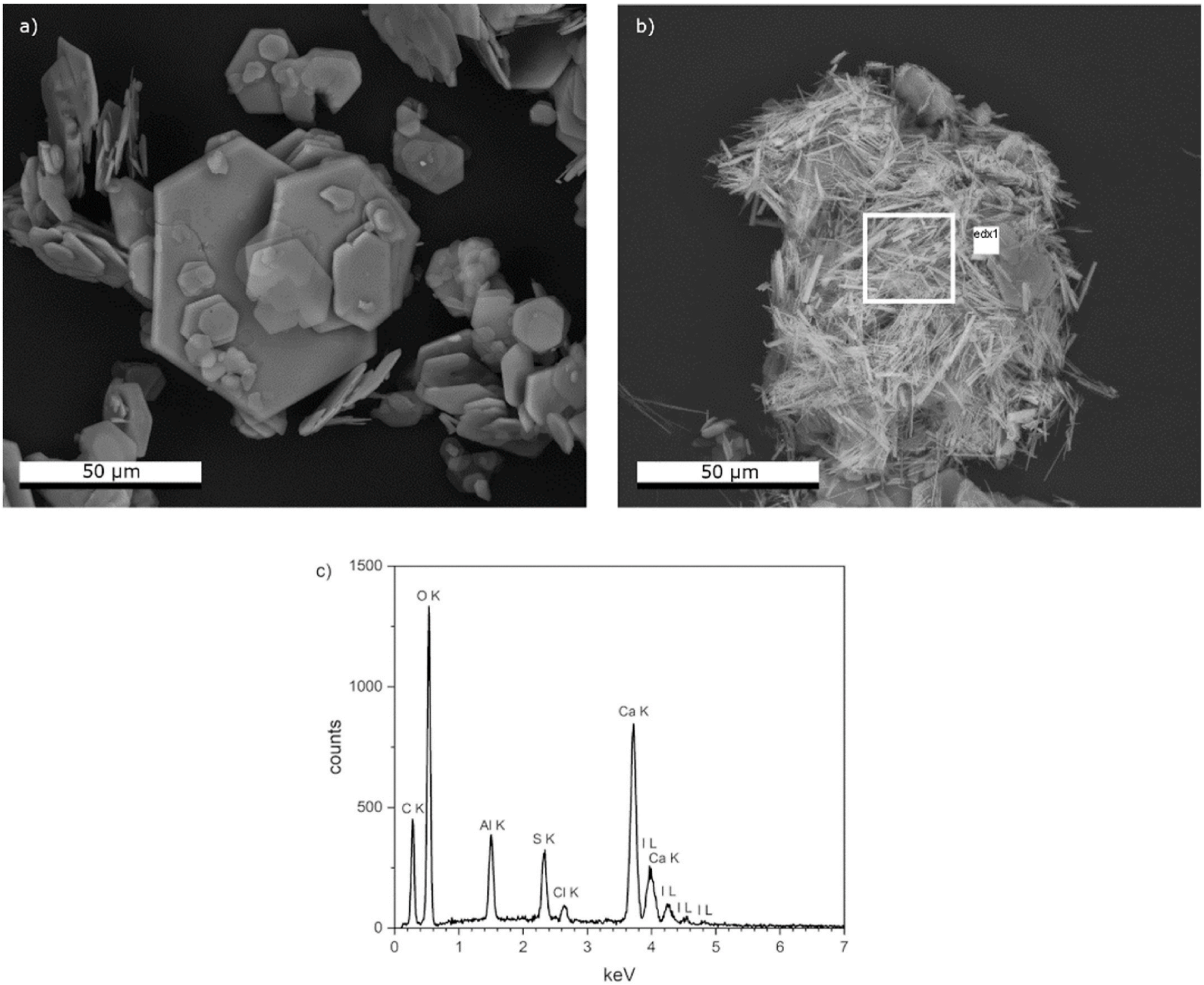

Fig. 5. SEM images (back scattered electron mode) of a) unreacted AFm-SO_4, b) AFm-SO_4 after 30 days reaction with a solution initially containing 10^{-3} mol L^{-1} IO_3^-, showing the neo-formation of an acicular iodate-bearing phase and c) EDS spectrum of the area marked in Fig. 5b.

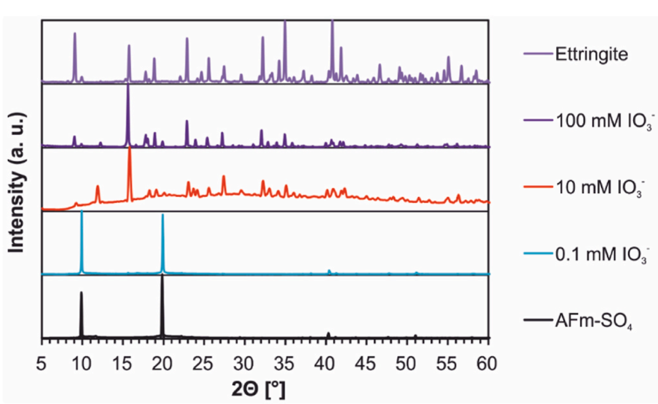

Fig. 6. XRD patterns of AFm-SO_4 contacted with solutions containing initial IO_3^- concentrations ranging from 10^{-4} to 10^{-1} mol L^{-1} for 30 days compared to the diffraction patterns of AFm-SO_4 and ettringite.

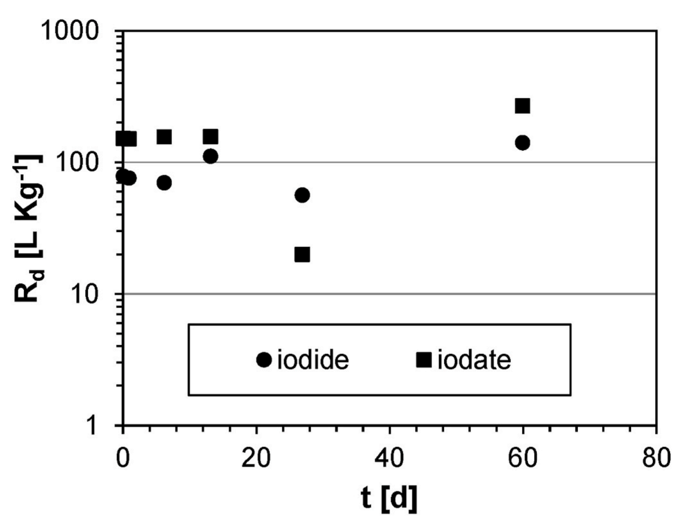

Fig. 7. Uptake kinetics for I^- and IO_3^- on HCP prepared from CEM I.

completely conclusive. Iodine uptake by CSH is generally weaker than by AFm/AFt or hydrogarnet. All model phases show higher uptake of I^- and IO_3^- in alkali-rich, young cement water, indicating higher potential iodine retention in younger cementitious systems. Conversely, based on literature data, iodine uptake by HCP seems to be more pronounced in slightly degraded materials (stage II, pH 12.5), which might be due to changes in the phase assemblage due to ongoing pozzolanic reactions.

The bottom-up approach pursued in this study has helped to improve our understanding of the contributions made by individual hydration phases to the overall retention of iodine in cementitious materials and the respective uptake mechanisms. The R_d values obtained under pore water conditions representing different stages of cement degradation could be used as the basis for an component additive approach, thereby providing an envelope for the likely iodine retention properties of more complex cement-based materials, such as backfill mortars or structural concretes in disposal facilities. The results suggest that cementitious materials with high AFm/AFt content and CSH with high Ca/Si ratios would be beneficial for the solidification of iodine-containing waste streams with enhanced retention properties for both I^- and IO_3^-. In addition to safety assessments for disposal of radioactive wastes, these data can also be utilised in models for the evaluation of clearance or disposal options for contaminated and/or activated rubble arising during the dismantling of nuclear facilities (Bath et al., 2003; Deissmann et al., 2006).

CRediT authorship contribution statement

Steve Lange: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Matthew Isaacs:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Martina Klinkenberg:** Writing – review & editing, Methodology, Investigation. **David Read:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization. **Dirk Bosbach:** Writing – review & editing, Resources, Funding acquisition, Conceptualization. **Guido Deissmann:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

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.

Acknowledgement

This research has received funding from the European Union's Horizon 2020 Research and Training Programme of the European Atomic Energy Community (EURATOM) (H2020-NFRP-2014/2015) under grant agreement n° 662147 (CEBAMA).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2025.106301.

Data availability

Data will be made available on request.

References

Aggarwal, S., Angus, M.J., Ketchen, J., 2000. Sorption of radionuclides onto specific mineral phases present in repository cements. In: AEA Technology Report NSS/R312, AEA-D&R-0395. AEA Technology PLC, Windscale, Cumbria, United Kingdom.

Aimoz, L., Kulik, D.A., Wieland, E., Curti, E., Lothenbach, B., Mäder, U., 2012a. Thermodynamics of AFm-(I_2, SO_4) solid solution and of its end-members in aqueous media. Appl. Geochem. 27, 2117–2129. https://doi.org/10.1016/j.apgeochem.2012.06.006.

Aimoz, L., Wieland, E., Taviot-Gueho, C., Dahn, R., Vespa, M., Churakov, S.V., 2012b. Structural insight into iodide uptake by AFm phases. Environ. Sci. Technol. 46, 3874–3881. https://doi.org/10.1021/es204470e.

Atkins, M., Glasser, F.P., 1990. Encapsulation of radioiodine in cementitious waste forms. Mater. Res. Soc. Symp. Proc. 176, 15–22. https://doi.org/10.1557/PROC-176-15.

Atkins, M., Glasser, F.P., 1992. Application of Portland cement-based materials to radioactive waste immobilization. Waste Manag. 12, 105–131. https://doi.org/10.1016/0956-053X(92)90044-J.

Atkins, M., Macphee, D., Kindness, A., Glasser, F.P., 1991. Solubility properties of ternary and quaternary compounds in the CaO-Al_2O_3-SO_3-H_2O system. Cement Concr. Res. 21, 991–998. https://doi.org/10.1016/0008-8846(91)90058-.

Atkins, M., Glasser, F.P., Kindness, A., 1992. Cement hydrate phases: solubility at 25°C. Cement Concr. Res. 22, 241–246. https://doi.org/10.1016/0008-8846(92)90062-Z.

Atkinson, A., Nickerson, A.K., 1987. Diffusion and sorption of caesium, strontium, and iodine in water-saturated cements. Nucl. Technol. 81, 100–113. https://doi.org/10.13182/NT88-A34082.

Bach, T., Pochard, I., Cau-dit-Coumes, C., Mercier, C., Nonat, A., 2013. Prediction of long-term chemical evolution of a low-pH cement designed for underground radioactive waste repositories. In: Bart, F., Cau-dit-Coumes, C., Frizon, F., Lorente, S. (Eds.), Cement-based Materials for Nuclear Waste Storage. Springer, pp. 239–250.

Bath, A., Deissmann, G., Jefferis, S., 2003. Radioactive contamination of concrete: uptake and release of radionuclides. In: ASME 2003: the 9th International Conference on Radioactive Waste Management and Environmental Remediation. https://doi.org/10.1115/ICEM2003-4814. September 21–25, 2003, Oxford, United Kingdom.

Baur, I., Keller, P., Mavrocordatos, D., Wehrli, B., Johnson, C.A., 2004. Dissolution-precipitation behaviour of ettringite, monosulfate, and calcium silicate hydrate. Cement Concr. Res. 34, 341–348. https://doi.org/10.1016/j.cemconres.2003.08.016.

Bayliss, S., McCrohon, R., Oliver, P., Pilkington, N.J., Thomason, H.P., 1996. Near-field Sorption Studies: January 1989–June 1991. UK NIREX report NSS/R277, AEA-ESD-0353, Harwell, United Kingdom.

Bel, J.P., Wickham, S.M., Gens, R.M.F., 2006. Development of the supercontainer design for deep geological disposal of high-level heat emitting radioactive waste in Belgium. Mater. Res. Soc. Symp. Proc. 932 (1). https://doi.org/10.1557/PROC-932-122.

Bonhoure, I., Scheidegger, A.M., Wieland, E., Dähn, R., 2002. Iodine species uptake by cement and C-S-H studied by I K-edge X-ray absorption spectroscopy. Radiochim. Acta 90, 647–651. https://doi.org/10.1524/ract.2002.90.9-11_2002.647.

Brown, D.R., Grutzeck, M.W., 1985. Iodine waste forms: calcium aluminate hydrate analogues. Mater. Res. Soc. Symp. Proc. 44, 911–918. https://doi.org/10.1557/PROC-44-911.

Brown, D.A., Chadwick, M.B., Capote, R., Kahler, A.C., Trkov, A., Herman, M.W., Sonzogni, A.A., Danon, Y., Carlson, A.D., Dunn, M., Smith, D.L., Hale, G.M., Arbanas, G., Arcilla, R., Bates, C.R., Beck, B., Becker, B., Brown, F., Casperson, R.J., Conlin, J., Cullen, D.E., Descalle, M.-A., Firestone, R., Gaines, T., Guber, K.H., Hawari, A.I., Holmes, J., Johnson, T.D., Kawano, T., Kiedrowski, B.C., Koning, A.J., Kopecky, S., Leal, L., Lestone, J.P., Lubitz, C., Marquez Damian, J.I., Mattoon, C.M., McCutchan, E.A., Mughabghab, S., Navratil, P., Neudecker, D., Nobre, G.P.A., Noguere, G., Paris, M., Pigni, M.T., Plompen, A.J., Pritychenko, B., Pronyaev, V.G., Roubtsov, D., Rochman, D., Romano, P., Schillebeeckx, P., Simakov, S., Sin, M., Sirakov, I., Sleaford, B., Sobes, V., Soukhovitskii, E.S., Stetcu, I., Talou, P., Thompson, I., van der Marck, S., Welser-Sherrill, L., Wiarda, D., White, M., Wormald, J.L., Wright, R.Q., Zerkle, M., Zerovnik, G., Zhu, Y., 2018. ENDF/B-VIII.0: the 8th major release of the Nuclear Reaction Data Library with CIELO-project cross sections, new standards and thermal scattering data. Nucl. Data Sheets 148, 1–142. https://doi.org/10.1016/j.nds.2018.02.001.

Cau Dit Coumes, C., Courtois, S., Nectoux, D., Leclercq, S., Bourbon, X., 2006. Formulating a low-alkalinity, high-resistance and low-heat concrete for radioactive waste repositories. Cement Concr. Res. 36, 2152–2163. https://doi.org/10.1016/j.cemconres.2006.10.005.

Chida, T., Sugiyama, D., 2009. Diffusion behaviour of organic carbon and iodine in low-heat Portland cement containing fly ash. Mater. Res. Soc. Symp. Proc. 1124, 379–384. https://doi.org/10.1557/PROC-1124-Q10-15.

Codina, M., Cau-dit-Coumes, C., Le Bescop, P., Verdier, J., Ollivier, J.P., 2008. Design and characterization of low-heat and low-alkalinity cements. Cement Concr. Res. 38, 437–448. https://doi.org/10.1016/j.cemconres.2007.12.002.

Deissmann, G., Bath, A., Jefferis, S., Thierfeldt, S., Wörlen, S., 2006. Development and application of knowledge-based source-term models for radionuclide mobilisation from contaminated concrete. Mater. Res. Soc. Symp. Proc. 932, 259–266. https://doi.org/10.1557/PROC-932-99.1.

Drace, Z., Ojovan, M.I., 2013. A summary of IAEA coordinated research project on cementitious materials for radioactive waste management. In: Bart, F., Cau-dit-Coumes, C., Frizon, F., Lorente, S. (Eds.), Cement-based Materials for Nuclear Waste Storage. Springer, pp. 3–11.

Evans, N.D.M., 2008. Binding mechanisms of radionuclides to cement. Cement Concr. Res. 38, 543–553. https://doi.org/10.1016/j.cemconres.2007.11.004.

Feng, S., Redfern, S.A.T., 2018. Iodate in calcite, aragonite and vaterite $CaCO_3$: insights from first-principles calculations and implications for the I/Ca geochemical proxy. Geochem. Cosmochim. Acta 236, 351–360. https://doi.org/10.1016/j.gca.2018.02.017.

Glasser, F.P., Macphee, D., Atkins, M., Pointer, C., Cowie, J., Wilding, C.R., Mattingley, N.J., Evans, P.A., 1989. Immobilisation of Radwaste in Cement Based Matrices. Department of the Environment, London, United Kingdom. Report DOE/RW/89/058.

Glasser, F.P., 1997. Fundamental aspects of cement solidification and stabilization. J. Hazard Mater. 52, 151–170. https://doi.org/10.1016/S0304-3894(96)01805-5.

Glasser, F.P., 2001. Mineralogical aspects of cement in radioactive waste disposal. Mineral. Mag. 65, 621–633. https://doi.org/10.1180/002646101317018442.

Glasser, F.P., 2002. Characterisation of the barrier performance of cements. Mater. Res. Soc. Symp. Proc. 713, 91. https://doi.org/10.1557/PROC-713-JJ9.1.

Glasser, F.P., 2011. Application of inorganic cements to the conditioning and immobilisation of radioactive wastes. In: Ojovan, M.I. (Ed.), Handbook of Advanced Radioactive Waste Conditioning Technologies. Woodhead, pp. 67–135.

Gougar, M.L.D., Scheetz, B.E., Roy, D.M., 1996. Ettringite and C-S-H Portland cement phases for waste ion immobilization: a review. Waste Manag. 16, 295–303. https://doi.org/10.1016/S0956-053X(96)00072-4.

Heath, T.G., Illet, D.J., Tweed, C.J., 2000. Development of a near-field sorption model for a cementitious repository. UK NIREX Report AEAT/R/ENV/0229. AEA Technology, Harwell, United Kingdom.

Hoch, A.R., Baston, G.M.N., Glasser, F.P., Hunter, F.M.I., Smith, V., 2012. Modelling evolution in the near field of a cementitious repository. Mineral. Mag. 76, 3055–3069. https://doi.org/10.1180/minmag.2012.076.8.21.

Holland, T.R., Lee, D.J., 1992. Radionuclide getters in cement. Cement Concr. Res. 22, 247–258. https://doi.org/10.1016/0008-8846(92)90063-2.

Hummel, W., 2017. Chemistry of selected dose-relevant radionuclides. Nagra Technical Report NTB 17-05. Nagra, Wettingen, Switzerland.

Hummel, W., Thoenen, T., 2022. The PSI chemical thermodynamic database 2020. Nagra Technical Report NTB 21-03. Nagra, Wettingen, Switzerland.

Idemitsu, K., Matsuki, Y., Kishimoto, M., Inagaki, Y., Arima, T., Haruguchi, Y., Yamashita, Y., Sasoh, M., 2013. Migration of iodine solidified in ettringite into compacted bentonite. Ceram. Trans. 241, 23–34. https://doi.org/10.1002/9781118751176.ch3.

Iwaida, T., Yano, K., Tanaka, S., Nagasaki, S., 2001. Synthesis and characterization of sulfate-iodate ettringite; and their potential role in immobilization of ^{129}I. J. Nucl. Fuel. Cycle Env. 7, 57–63. https://doi.org/10.3327/jnuce.7.57.

Jantzen, C., Johnson, A., Read, D., Stegemann, J., 2010. Cements in waste management. Adv. Cement Res. 22, 225–231. https://doi.org/10.1680/adcr.2010.22.4.225.

Kaplan, D.I., Xu, C., Li, D., Lin, P., Xing, W., Nichols, R., Schwehr, K., Santschi, P.H., 2019. Iodine speciation in cementitious environments. Appl. Geochem. 103, 15–22. https://doi.org/10.1016/j.apgeochem.2019.02.007.

Lange, S., 2019. Structural Uptake and Retention of Safety Relevant Radionuclides by Cementitious Materials. PhD Thesis. RWTH Aachen University, Aachen, Germany.

Lange, S., Kowalski, P., Pšenička, M., Klinkenberg, M., Rohmen, S., Bosbach, D., Deissmann, G., 2018. Uptake of ^{226}Ra in cementitious systems: a complementary solution chemistry and atomistic simulation study. Appl. Geochem. 96, 204–216. https://doi.org/10.1016/j.apgeochem.2018.06.015.

Lange, S., Isaacs, M., Klinkenberg, M., Read, D., Bosbach, D., Deissmann, G., 2024. Experimental data for: uptake of iodine by cement hydration phases: implications for radioactive waste disposal. https://doi.org/10.26165/JUELICH-DATA/FXSAYY. Jülich DATA, V1.

Lothenbach, B., Le Saout, G., Ben Haha, M., Figi, R., Wieland, E., 2012. Hydration of a low-alkali CEM III/B–SiO_2 cement (LAC). Cement Concr. Res. 42, 410–423. https://doi.org/10.1016/j.cemconres.2011.11.008.

Matschei, T., Lothenbach, B., Glasser, F.P., 2006. The AFm phase in Portland cement. Cement Concr. Res. 37, 118–130. https://doi.org/10.1016/j.cemconres.2006.10.010.

Mattigod, S.V., Whyatt, G.A., Serne, R.J., Martin, P.F., Schwab, K.B., Wood, M.I., 2001. Diffusion and leaching of selected radionuclides (Iodine-129, Technetium-99, and Uranium) through category 3 waste encasement concrete and soil fill material. Report PNNL-13639, Pacific Northwest National Laboratory (PNNL), Richland, WA, United States. https://doi.org/10.2172/965706.

Mattigod, S.V., Whyatt, G.A., Serne, J.R., Wood, M.I., 2004. Diffusion of iodine and technetium-99 through waste encasement concrete and unsaturated soil fill material. Mater. Res. Soc. Symp. Proc. 824, 391–398. https://doi.org/10.1557/PROC-824-CC7.6.

Nedyalkova, L., Tits, J., Bernard, E., Wieland, E., Mäder, U., 2021. Sorption experiments with HTO, 36-Cl, 125-I and 14-C labeled formate on aged cement matrices retrieved from long-term in-situ rock laboratory experiments. J. Adv. Concr. Technol. 19, 811–829. https://doi.org/10.3151/jact.19.811.

Niibori, Y., Funabashi, T., Mimura, H., 2012. Some experiments on sorption behavior of iodide ions into C-S-H gel under the condition saturated with saline groundwater. Mater. Res. Soc. Symp. Proc. 1518, 225–230. https://doi.org/10.1557/opl.2012.1715.

Noshita, K., Nishi, T., Yoshida, T., Fujihara, H., Saito, N., Tanaka, S., 2001. Categorization of cement hydrates by radionuclide sorption mechanism. Mater. Res. Soc. Symp. Proc. 663, 115–121. https://doi.org/10.1557/PROC-663-115.

Ochs, M., Mallants, D., Wang, L., 2016. Radionuclide and Metal Sorption on Cement and Concrete. Springer, p. 301.

Pointeau, I., Coreau, N., Reiller, P.E., 2008. Uptake of anionic radionuclides onto degraded cement pastes and competing effect of organic ligands. Radiochim. Acta 96, 367–374. https://doi.org/10.1524/ract.2008.1503.

Posiva, 2012. Safety Case for the Disposal of Spent Nuclear Fuel at Olkiluoto. Posiva Oy, Eurajoki, Finland. Posiva Report 2012-12.

Rapin, J.-P., Walcarius, A., Lefevre, G., Francois, M., 1999. A double-layered hydroxide, $3CaO{\cdot}Al_2O_3{\cdot}CaI_2{\cdot}10H_2O$. Acta Crystallogr. C55, 1957–1959. https://doi.org/10.1107/S0108270199008665.

Sarott, F.A., Bradbury, M.H., Pandolfo, P., Spieler, P., 1992. Diffusion and adsorption studies on hardened cement paste and the effect of carbonation on diffusion rates. Cement Concr. Res. 22, 439–444. https://doi.org/10.1016/0008-8846(92)90086-B.

Shirai, K., Niibori, Y., Kirishima, A., Mimura, H., 2011. Sorption behavior of iodine on calcium silicate hydrates formed as a secondary mineral. ASME 2010 ^{13}th International Conference on Environmental Remediation and Radioactive Waste Management. https://doi.org/10.1115/ICEM2010-40089. October 3–7, 2010, Tsukuba, Japan.

SKB, 2015. Safety Analysis for SFR Long-Term Safety: Main Report for the Safety Assessment SR-PSU. SKB Technical Report 14-01. Svensk Kärnbränslehantering AB, Stockholm, Sweden.

Tanabe, H., Sakuragi, T., Yamaguchi, K., Sato, T., Owada, H., 2010. Development of new waste forms to immobilize iodine-129 released from a spent fuel reprocessing plant. Adv. Sci. Technol. 73, 158–170. https://doi.org/10.4028/www.scientific.net/AST.73.158.

Taylor, H.F.W., 1997. Cement Chemistry. Thomas Telford, p. 459.

Toyohara, M., Kaneko, M., Mitsutsuka, N., Fujihara, H., Saito, N., Murase, T., 2002. Contribution to understanding iodine sorption mechanism onto mixed solid alumina cement and calcium compounds. J. Nucl. Sci. Technol. 39, 950–956. https://doi.org/10.1080/18811248.2002.9715281.

Wang, L., Ochs, M., Mallants, D., Vielle-Petit, L., Martens, E., Jacques, D., de Cannière, P., Berry, J.A., Leterme, B., 2013. A new radionuclide sorption data base for benchmark cement accounting for geochemical evolution of cement. In: Bart, F., Cau-dit-Coumes, C., Frizon, F., Lorente, S. (Eds.), Cement-based Materials for Nuclear Waste Storage. Springer, pp. 103–112.

Wieland, E., 2014. Sorption Data Base for the Cementitious Near Field of L/ILW and ILW Repositories for Provisional Safety Analyses for SGT-E2. Nagra Technical Report NTB 14-08. Nagra, Wettingen, Switzerland.

Wieland, E., Van Loon, L.R., 2002. Cementitious near-field sorption data base for performance assessment of an ILW repository in Opalinus Clay. Nagra Technical Report NTB 02-20. Nagra, Wettingen, Switzerland.

Wieland, E., Tits, J., Spieler, P., Dobler, J.P., 1998. Interaction of Eu(III) and Th(IV) with sulfate-resisting portland cement. Mater. Res. Soc. Symp. Proc. 506, 573–578. https://doi.org/10.1557/PROC-506-573.