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

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Abstract
The long-term performance of a cement-based barrier system, envisaged worldwide in many concepts for deep geological storage of radioactive waste, depends on its material properties and how they evolve with time. Chemical interactions with the service environment may lead to mineralogical alterations and related physico-chemical changes at material interfaces, influencing radionuclide migration. Predictive (reactive) transport modelling therefore requires information on transport properties (e.g. sorption properties, porosity) of aged cement matrices.

Radionuclide binding by fresh and aged cement matrices (> 10 years) has been investigated using two different aged cementitious materials retrieved from long-term in-situ rock laboratory (at the Mont Terri and Grimsel test sites, Switzerland) experiments to provide sorption data for use in predictive modelling and interpretation of the field diffusion experiments. For this purpose, the uptake of 36Cl, 125I, 3H (HTO) and 14C has been investigated in a series of batch sorption experiments. Fresh cement paste shows the strongest sorption for 36Cl and 125I due to the largest proportion of radionuclide sorbing cement phases (ettringite, C-S-H, AFm). Measured sorption values for 36Cl and 125I on the aged cement matrices are about an order of magnitude lower. Sorption values for HTO and 14C-formate on cementitious materials are generally very low, suggesting only weak interaction with the surfaces of the cement minerals.

1. Introduction
Cementitious binder materials serve as waste matrix, structural elements and backfill in most concepts for deep geological storage of radioactive waste. The long-term performance of a cement-based barrier may be affected by interactions with its service environment (e.g. claystone or granitic host rock, or bentonite), driven by chemical gradients in the pore water composition at the interfaces. Hyper-alkaline cement pore water is initially at disequilibrium with its surrounding materials, leading to mineralogical alterations at contact areas and thus to changes in the material properties, including transport properties (sorption properties, pore geometry and connectivity). The cementitious matrix continuously undergoes also internal physico-chemical changes as cement hydration may continue to evolve over decades. Predictive (reactive) transport modelling or interpretation of long-term field and laboratory experiments therefore require information on transport properties of aged cement matrices that are expected to be different from properties of freshly mixed materials for which published data are more abundant. We address this aspect of radionuclide binding to aged cement matrices (> 10 years) with new laboratory experiments using two different cementitious materials recovered from long-term in-situ experiments installed at the Mont Terri Rock Laboratory and the Grimsel Test Site (both in Switzerland).

1.1 Field experiments
The CI-D project [Mont Terri Rock Laboratory, St. Ursanne, Switzerland. Further information can be found at the website (https://www.mont-terri.ch/)] is a companion of the long-term Cement-Opalinus clay Interaction (CI) experiment (Mäder et al. 2017). The aim is to provide a better understanding of the processes related to cement-clay interfaces by studying the mineralogical changes over a long time period (at least 20 years) and under realistic boundary conditions. The experiment was installed in 2007 and consists of two vertical boreholes (368 mm diameter, up to 9 m deep) in the Opalinus clay (OPA), the selected host rock for deep geological storage in Switzerland (Nagra 2016). Each borehole is filled with sections of three different concretes and a section of compacted bentonite (e.g. borehole BCI-6 in Fig. 1). The
Concrete formulations are based on three different cement types: a Portland cement (OPC), a mix based on Portland cement and fumed silica shotcrete cement (ESDRED) and low-alkali cement (LAC) (Jenni et al. 2014). Since the installation of the CI experiment, five sampling campaigns have been carried out (in 2009, 2012, 2015, 2017 and 2018), recovering undisturbed interface samples between clay materials (Opalinus clay, bentonite) in contact with the three types of cement, after different contact times. Simultaneously with the last sampling campaign in 2018, a monopole diffusion test was installed in a section of aged OPC. This CI-D project (Diffusion across 10-year-old Concrete/claystone Interface) is an in-situ diffusion experiment, installed close to the aged concrete/claystone interface of the BCI-6 borehole (Fig. 1) (Mäder 2018). The CI-D experiment is expected to last for 3 to 4 years and aims to assess the impact of the alteration processes occurring at such interfaces on solute transport. For this purpose, a radionuclide tracer cocktail containing $^{36}$Cl and $^3$H (tritiated water, HTO) is circulated since May 2019 in the aged OPC, and the tracer concentrations in circulation are monitored and will be measured along selected profiles across the claystone/concrete interface after excavation. Our study aims at providing necessary data ($^{36}$Cl, HTO but also $^{129}$I) for numerical simulations of tracer transport, both in currently ongoing predictive modelling and in the interpretation after post-mortem analysis of the CI-D experiment.

The CIM (Carbon-14 and Iodine-129 Migration in Cement) project is a field diffusion experiment installed in 2019 in an old mortar section emplaced in the granodiorite of the Grimsel Test Site [GTS, Guttannen/Gerstenegg, Switzerland. Further information can be found at the website (https://www.grimsel.com/)]. The aim of the experiment is to examine the transport of HTO, $^{14}$C-labeled formate, $^{129}$I, $^{36}$Cl, $^{134}$Cs, and $^{133}$Ba through aged cementitious backfill of a low- and intermediate-level (L/ILW) or transuranic (TRU) waste repository (and possibly into the host rock) in order to improve process understanding of the radionuclide behavior under expected in-situ hyper-alkaline conditions. For the CIM experiment, a large diameter borehole (388 mm, 14 m deep) backfilled with OPC mortar in 2004 is being used (Fig. 1). This borehole was part of the HPF (Hyper-alkaline Plume in Fractured Rock) experiment, with details given in Mäder et al. (2006). In the center of the mortar backfill, a small diameter (56 mm) borehole was drilled and equipped with a double-packer system for a mono-pole circulation test with a hyper-alkaline radionuclide cocktail. The non-active circulation was started in November 2019, and the start of the active circulation is scheduled for early 2021, lasting for 2 to 3 years. Analyses of radionuclide diffusion profiles in the mortar and/or in the host rock are planned after excavation. Our study focuses on the dose-relevant more mobile species $^{14}$C (formate) and $^{129}$I, but also HTO and $^{36}$Cl for comparison. The data underpin predictive and post-mortem reactive transport modeling simulations of the field test that are ongoing or in planning.

Fig. 1 Left: Setup of the CI-D experiment (boreholes in white), consisting of an approach borehole (BCI-D1) and an experimental borehole (BCI-D2). The vertical borehole BCI-6 was filled in 2007 with three different types of concrete (OPC, LAC and ESDRED) and compacted bentonite (MX-80). Monitoring boreholes are shown in red and sampling boreholes for different campaigns are color-coded (Jenni et al. 2014). Right: Schematic of the CIM mono-pole diffusion test set-up, with a central double-packer system within an aged mortar section, hosted by granodiorite. The insert shows the location of the CIM experiment (red ellipse) in back-filled borehole relative to one of the galleries (figure courtesy of Nagra, Grimsel Test Site).
1.2 $^{36}\text{Cl}$, $^{125}\text{I}$, HTO and $^{14}\text{C}$ uptake by cement paste

Cementitious materials are not at equilibrium with the conditions encountered in the geological formations of a deep geological repository, or with the environment in the case of surface disposal facilities, and are exposed to degradation processes. Therefore, different stages of cement degradation are considered in state-of-the-art safety assessments for a cement-based repository for radioactive waste as reported, for example, in (Nagra 2002). Models of cement degradation currently in use and reported in literature (for example, Atkinson et al. (1988, 1989) and Faucon et al. (1996)], have been developed in accordance with experimental observations and focus on the temporal evolution of the cement matrix and pore water composition by leaching due to groundwater ingress from the host rock as reported, for example, by Atkinson et al. (1989), Berner (1992), Hoch et al. (2012), Kosakowski and Berner (2013) and Kosakowski et al. (2014), or due to ingress of rain and soil-type water (Jacques et al. 2010). Most recent models further account for internal degradation of cementitious materials by interaction with the waste (e.g. degradation of organic materials, dissolution of siliceous aggregates) (Kosakowski et al. 2020; Huang et al. 2021). As a result of the degradation process, cementitious materials are subjected to changes in their mineral composition with time, which may strongly influence sorption properties for radionuclides. To the authors’ knowledge, no work reported to date has looked into the sorption properties of cement pastes that have been aged by in-situ interaction with formation water. Thus, this study afforded a unique opportunity to quantify the uptake of selected radionuclides on cement paste aged in contact with potential host rocks (clay and crystalline formations) over more than ten years.

The uptake of $^{36}\text{Cl}$ and $^{125}\text{I}$ by hardened cement paste (HCP) has been the subject of numerous studies as seen in the reviews by Evans (2008), Wieland (2014) and Ochs et al. (2016). The binding capacity of HCP for Cl is primarily determined by the amount of ettringite (AFT), AFm phases and C-S-H phases with Ca/Si (C/S) ratios $\geq$ 1.2 (Wieland 2014). AFm phases react with the Cl to form Friedel’s salt [or solid solutions between other AFm phases such as monocarbonate, monosulfate and Friedel’s salt (Balonis et al. 2010)], whereas C-S-H phases can sorb Cl by electrostatic attraction on their positively charged surfaces at higher C/S ratios [Ca$^{2+}$ binds on the negatively charged silanol sites on the C-S-H surfaces provoking a charge reversal (Labbez et al. 2007)]. Cl$^-$ may also substitute for OH$^-$ and SO$_4^{2-}$ in the interlayers of hydrotalcite (Ochs et al. 2016), however, due to the small portion of hydrotalcite usually present in HCP, its sorption capacity is limited (Wieland 2014). Furthermore, increasing concentrations of stable Cl$^-$ in solution were found to reduce $^{36}\text{Cl}$ uptake by HCP (Pointeau et al. 2008). Note that infiltrating formation water may contain high salt concentrations resulting in increasing stable Cl$^-$ concentrations with progressing degradation. Similar mechanisms are expected to govern the uptake of I$^-$ by HCP, such as adsorption via surface processes (e.g. on C-S-H phases) and/or incorporation into the structures of some of the cement minerals, such as AFm phases (Evans 2008). The sorption potential of the cement minerals for I$^-$ uptake was found to decrease in the order AFm > C-S-H with high C/S ratio $\approx$ AFT > C-S-H with low C/S ratio > hydrotalcite (Ochs et al. 2016). Hemicarbonate (AFm-OH/CO$_3^-$) and monosulfate (AFm-SO$_4^-$) are the AFm phases with the highest sorption potentials for I$^-$ (Aimoz et al. 2012; Nedyalkova 2019). Therefore, their presence or absence in the HCP has a major impact on the $^{125}\text{I}$ interaction with HCP.

Limited information, however, is available on the interaction of HTO and low molecular weight (LMW) organics (e.g. $^{14}\text{C}$-bearing formate) with HCP as reported, for example, in the reviews by Wieland and Van Loon (2002), Wieland (2014) and Ochs et al. (2016). HTO may be retained by HCP along with physically and chemically adsorbed water and through isotope exchange with water molecules accommodated in the structure of some cement minerals (Tits et al. 2003; Takata et al. 2005). Note that considerable amounts of water are bound in the structure of AFT, AFm, C-S-H phase and hydrotalcite, while the question remains as to what extent the structural water is accessible for exchange with HTO (Ochs et al. 2016). In general, very weak interaction of HTO with HCP was reported with sorption values typically $<$ 1 L/kg (Ochs et al. 2016). Weak interaction with HCP was further observed in the case of small organic molecules, such as acetate and formate, with sorption values typically ranging between $10^{-3}$ and 1 L/kg (Wieland et al. 2016). Sorption of organic compounds was found to decrease in the order formate $>$ acetate $>$ formaldehyde $\approx$ acetaldehyde $>$ methanol $>$ ethanol (Wieland et al. 2016). It was suggested that weak, reversible adsorption of the organics results from electrostatic interaction onto partially positively charged surface sites of the cement phases or from hydrogen bonding. Nevertheless, selective, irreversible sorption of a small fraction of formate was observed in both the sorption and diffusion experiments reported by Wieland et al. (2016), thus suggesting the presence of sorption sites capable of strongly binding the anion, for example by SO$_4^{2-}$/HCOO$^-$ replacement in the ettringite structure.

2. Materials and methods

For the evaluation and modelling of the CI-D and CIM diffusion field experiments, tracer sorption studies were performed using site-specific sample material. Batch sorption tests using a tracer cocktail containing $^{36}\text{Cl}$, HTO and $^{125}\text{I}$ were carried out with each material, i.e. CI-D and CIM, as well as with fresh hardened OPC paste after 30 days of hydration for comparison. In addition, sorption tests with $^{14}\text{C}$ in the chemical form of formic acid were performed on CIM only in order to provide laboratory data in support of the respective field experiment.
2.1 Materials

The sorption experiments were carried out using three different sample materials: OPC mortar core material (CIM), OPC concrete core material (CI-D) and freshly prepared hardened OPC cement paste (fresh OPC).

(1) CIM

The CIM material is an OPC mortar drill core from the Grimsel test site. The core was drilled after approximately 14 years of emplacement (backfilling of HPF large-diameter borehole) and was stored in a vacuum-sealed plastic bag. The core has a diameter of 43 mm. The chemical composition of the mortar was not determined.

(2) CI-D

The CI-D material is an OPC concrete based on the sulfate resistant cement Holcim Protego 4R (CEM I 42.5 R-HS) prepared with a water-to-cement (w/c) ratio of about 0.8 and containing aggregates having a size of < 16 mm. The chemical composition is listed in Table 1. This material was sampled from the Mont Terri test site after 10 years of emplacement and kept vacuum-sealed in cold storage. A mixture of three different CI-D samples was used in the sorption experiments. The first two samples were recovered from the BCI-6 borehole in 2017 (4th sampling campaign), i.e. BCI-22 borehole in Fig. 1. The samples are part of a 160 cm long core with diameter of 101 mm, comprised of intersections with Opalinus clay/OPC/Opalinus clay. Several samples were cut out of the core and a diameters of 43 mm. The chemical composition of the mortar was not determined.

(3) Fresh OPC

The OPC paste was prepared from a Holcim Protego 4R (CEM I 42.5 R-SR0) sulfate resistant cement (origin: Vils, Austria). The cement has a chemical composition close to the one used in the CI experiment, as determined by X-ray fluorescence (XRF). 120 g of water were mixed with 150 g cement using a mixer (w/c ratio = 0.8). After mixing, the paste was cast in a 0.25 L PE-bottle with a screw cap and sealed with Paraffin film to exclude CO₂ contamination and water evaporation. The sample was then placed on a shaker for 24 h to prevent water segregation. The paste was cured for 30 days at room temperature in a vapor-tight box at high relative humidity.

(4) Chemicals and radiotracers

Throughout this study, Fluka or Merck Emsure (Germany) analytical grade chemicals and a high-purity deionized water (18.2 MΩ·cm resistivity) generated by a Milli-Q Gradient A10 System (Millipore, USA) were used. All sorption experiments were carried out in duplicate samples in a glovebox under a N₂ atmosphere (O₂ and CO₂ < 2 ppm) at ambient temperature (T = 23°C). The experiments were carried out in 40 mL polyallomere centrifuge tubes (Beckman Coulter, USA), which were cleaned in 0.1 M HNO₃ and thoroughly rinsed with deionized water before use.

The radionuclides used in the sorption tests were ¹²⁵I as NaI in 0.1 M NaOH (PerkinElmer Inc, USA), ³⁵Cl as KCl in H₂O (Eckert & Ziegler, Germany), HTO (GE Healthcare, UK), diluted with 0.3 M NaOH and ¹⁴C-labeled formic acid (Na¹⁴COOH), dissolved in 10 mL ethanol/water (7:3) solution (American Radiolabeled Chemicals, Inc., USA).

Table 1 Chemical composition, determined by XRF analysis, of the CEM I 42.5 R-SR0 cement used for the fresh OPC paste compared to the chemical composition of the OPC cements from the CI experiment.

| Component  | CIM Jan 20 | CI experiment Nov 05 to Mar 06 | OPC CEM Jan 12 |
|------------|------------|-----------------------------|---------------|
| SiO₂       | 19.46      | 18.9                        | 19.3          |
| Al₂O₃      | 3.53       | 4.7                         | 3.4           |
| Fe₂O₃      | 5.64       | 6.9                         | 5.2           |
| Cr₂O₃      | 0.011      | -                           | -             |
| MnO        | 0.057      | -                           | -             |
| TiO₂       | 0.20       | -                           | -             |
| P₂O₅       | 0.22       | -                           | -             |
| CaO        | 61.99      | 63.8                        | 59.4          |
| MgO        | 3.36       | 2                           | 4             |
| K₂O        | 0.55       | 0.87                        | 0.73          |
| Na₂O       | 0.15       | 0.62                        | 0.28          |
| SO₃        | 3.40       | 2.5                         | 3.3           |
| LOI        | 1.27       | 3.5                         | 2.6           |
| TC         | 0.26       | -                           | -             |

TC: Total carbon.
2.2 Methods

(1) Analytical methods
XRF analyses were performed on an energy dispersive Bruker Explorer S4 instrument (maximum power = 1 kW; LiF200, PET, OVO-55, OVOB as analyzing crystals) according to DIN EN 196-2: 2013-10 using fused beads. Total carbon content (TC) was quantified by dry combustion analysis according to DIN ISO 10694: 1996-08. X-ray diffraction (XRD) was performed with a PANalytical X’Pert Pro MPD diffractometer, using CuKα radiation and an X’Celerator detector. Diffraction data were collected between 5 and 75° (2θ). An external standard (CaF2) was measured during the same week of the measurements in order to quantify the amount of inert aggregates, cement crystalline phases and the amorphous content. Rietveld refinement of the XRD patterns was performed using X’Pert Highscore Plus v. 4.7 and the mineral phase structures detailed in Snellings (2016). Thermogravimetric analyses (TGA) were carried out on a TGA/SDTA 851 instrument (Mettler Toledo, Switzerland). The samples were heated under a N2 atmosphere between 30 and 980°C at a heating rate of 20°C/min. Thermogravimetric analyses (TGA) and X-ray diffraction (XRD) were performed using a TGA/SDTA 851 instrument (Mettler Toledo, Switzerland). The samples were heated under a N2 atmosphere between 30 and 980°C at a heating rate of 20°C/min.

HTO, 36Cl, 125I and 14C-formate sorption was quantified by measuring the partitioning of the radionuclides between the solid and the liquid phases. The sorption of the first three tracers was studied in triple labeled experiments while 14C sorption was studied in separate experiments labeled only with 14C-formate. The activities in the triple labeled samples were determined both by gamma counting using a Packard Cobra 5003 gamma-counter (PerkinElmer, USA) and by liquid scintillation counting using a Tri-Carb A2750 liquid scintillation counter (LSC) (Perkin Elmer, USA). The 14C activity was measured by LSC only. Samples for LSC were prepared by mixing 5 mL aliquots of the supernatant solutions with 15 mL Ultima Gold XR, Perkin Elmer, USA). Standards were prepared by mixing aliquots (10 to 90 μL) of tracer solution with 5 mL 0.3 M NaOH and 15 mL of Ultima Gold XR, with a targeted activity of 2000 to 3000 cpm/20 mL. Blanks were prepared by mixing 5 mL 0.3 M NaOH with 15 mL Ultima Gold XR. 14C labeled samples were measured by LSC using three energy windows: A: 4 to 65 keV, B: 0 to 65 keV, C: 0 to 2000 keV.

In the case of the triple labeled samples, energy windows for LSC were set at A: 0 to 20 keV, B: 20 to 600 keV and C: 0 to 2000 keV, allowing for a relatively good separation between HTO and 36Cl spectra, as window A contains mostly HTQ counts and window B mainly 36Cl counts. However, 125I energy spectra strongly overlap with those of HTO and to a lesser extent with those of 36Cl. Therefore, data evaluation of the triple labeled samples required first the development and validation of an analytical approach allowing the determination of the individual activities for each of the three tracers (125I, 36Cl, HTO) present in the same sample. Since 125I was the only radionuclide of the three that undergoes gamma decay, its gamma activity was measured in a gamma counter using the spectral window C (15 to 2000 keV). With the help of 125I standards with known activity, conversion factors were determined to convert the 125I gamma activity measured in the unknown samples into beta activities in the beta windows A and B as follows:

\[
F_{\text{GB}}^B = \frac{A_{\text{B}}^{\text{std}}}{C_{\text{G}}^{\text{std}}} \quad (1)
\]

\[
F_{\text{GB}}^C = \frac{B_{\text{B}}^{\text{std}}}{C_{\text{G}}^{\text{std}}} \quad (2)
\]

where \[A_{\text{B}}^{\text{std}}\]: 125I beta activity in window A in standard solution [cpm/mL tracer], \[B_{\text{B}}^{\text{std}}\]: 125I beta activity in window B in standard solution [cpm/mL tracer], \[C_{\text{G}}^{\text{std}}\]: 125I gamma activity in window C in standard solution [cpm/mL tracer], \[F_{\text{GB}}^B\]: factor for conversion of gamma activity to beta activity in window A and \[F_{\text{GB}}^C\]: factor for conversion of gamma activity to beta activity in window B. In addition, 125I activities had to be corrected for radioactive decay (t1/2 = 60.14 d). The 125I contribution in the beta windows A and B of the unknown sample was obtained using the following expressions:

\[
A_{\text{B}}^i = C_{\text{G}}^i \times F_{\text{GB}}^A \quad (3)
\]

\[
B_{\text{B}}^i = C_{\text{G}}^i \times F_{\text{GB}}^C \quad (4)
\]

where \[C_{\text{G}}^i\]: total 125I gamma activity in window C in unknown sample [cpm/5 mL sample], \[A_{\text{B}}^i\]: contribution of 125I beta activity in window A in unknown sample [cpm/5 mL sample] and \[B_{\text{B}}^i\]: contribution of 125I beta activity in window B in unknown sample [cpm/5 mL sample]. \[A_{\text{B}}^i\] and \[B_{\text{B}}^i\] were then subtracted from the activities measured in each window:

\[
A_{\text{B}}^{\text{HTO+Cl}} = A_{\text{B}} - A_{\text{B}}^i \quad (5)
\]

\[
B_{\text{B}}^{\text{HTO+Cl}} = B_{\text{B}} - B_{\text{B}}^i \quad (6)
\]

where \[A_{\text{B}}^{\text{HTO+Cl}}\]: beta activity in window A in unknown sample [cpm/5 mL sample], \[B_{\text{B}}^{\text{HTO+Cl}}\]: beta activity in window B in unknown sample [cpm/5 mL sample], \[A_{\text{B}}^{\text{HTO+Cl}}\]: contribution of HTO and 36Cl beta activity in window A in unknown sample [cpm/5 mL sample] and \[B_{\text{B}}^{\text{HTO+Cl}}\]: contribution of HTO and 36Cl beta activity in window B in unknown sample [cpm/5 mL sample]. The deconvolution of the HTO and 36Cl beta activities was done based on a set of standards measurements containing HTO and/or 36Cl of known activity, from which the counting efficiency of HTO and 36Cl in each window were determined:

\[
h_A = A_{\text{std}}^{\text{HTO}} / C_{\text{std}}^{\text{HTO}} \quad (7)
\]

\[
h_B = B_{\text{std}}^{\text{HTO}} / C_{\text{std}}^{\text{HTO}} \quad (8)
\]

\[
C_{\text{std}}^{\text{HTO}} = A_{\text{std}}^{\text{HTO}} / C_{\text{std}}^{\text{HTO}} \quad (9)
\]
\[ c_{\text{h}} = \frac{B_{\text{h}}^{\text{B}}}{c_{\text{cl}}} \]  
(10)

where \( h_{\text{h}} \): HTO beta efficiency in window A [cpm/5 mL sample], \( h_{\text{B}} \): HTO beta efficiency in window B [cpm/5 mL sample], \( c_{\text{cl}} \): \(^{36}\text{Cl}\) beta efficiency in window A [cpm/5 mL sample] and \( c_{\text{cl}} \): \(^{36}\text{Cl}\) beta efficiency in window B [cpm/5 mL sample]. Finally, HTO and \(^{36}\text{Cl}\) beta activities were calculated according to the following equations:

\[ H = \frac{A_{\text{B}}^{\text{HTO-CI}} \cdot c_{\text{h}} - B_{\text{B}}^{\text{HTO-CI}} \cdot c_{\text{cl}}}{h_{\text{h}} \cdot c_{\text{h}} - h_{\text{B}} \cdot c_{\text{cl}}} \]  
(11)

\[ CL = \frac{B_{\text{B}}^{\text{HTO-CI}} \cdot c_{\text{h}} - A_{\text{B}}^{\text{HTO-CI}} \cdot h_{\text{B}}}{c_{\text{h}} \cdot h_{\text{h}} - c_{\text{cl}} \cdot h_{\text{B}}} \]  
(12)

The method was tested with a set of triple labeled standards, resulting in good reproducibility and a small analytical error (see Table A1 of the Appendix).

(2) Preparation of the artificial cement pore water
All sorption tests were performed with suspensions of the three sample materials in artificial cement pore waters (APW). The composition of each of the APWs reflects the composition of a pore water in chemical equilibrium with the respective solid material (recipes in Table A2 of the Appendix). APW for OPC was prepared following the synthesis procedure described in Wieland et al. (1998) with an excess of CaCO\(_3\) and Ca(OH)\(_2\) added to the solution, which was shaken for one week and then filtered under N\(_2\) atmosphere. The composition of the APW for CIM corresponds to the measured composition of the pore solution extracted from the same material, determined in a previous set of experiments performed at Empa, Switzerland (Lothenbach 2019). The extracted pore solution showed a pH value of 13.3 and contained mainly K\(^+\), Na\(^+\) and hydroxide. Formic and acetic acid in mM concentrations were also present, originating from organic cement admixtures, added to the mortar during its preparation (Lothenbach 2019). APW for CI-D was prepared based on the recipe currently used in the field (Lothenbach 2019). APW for CI-D was prepared based on the recipe currently used in the field experiments, consisting mainly of K\(^+\) and Na\(^+\) as well as minor concentrations of Ca\(^{2+}\) and SO\(_4^{2-}\).

(3) Sample preparation
The preparation of powder material, suitable for batch sorption experiments, included several steps (a flow chart is shown in Fig. A1 of the Appendix). First, the core samples and the fresh OPC paste were crushed using a rock crusher. In a second step, a hydration stoppage was performed for each material in order to remove any remaining free pore solution. This enabled sample storage and manipulation outside the glovebox and minimized carbonation. The free water was removed by the solvent-exchange method: the crushed sample was first immersed in isopropanol for about 15 min, filtered by vacuum filtration and then rinsed with diethyl ether for another 5 min to remove the isopropanol. After that, the sample was dried in the oven for 10 to 20 min at 40\(^\circ\)C. After drying, the CIM and the fresh OPC sample materials were ground by hand down to < 63 \(\mu\)m in an agate mortar. To ensure that a homogeneous powder was used for the sorption experiments, the entire sample material was ground before the start of the experiments. Special care was taken in the case of the heterogeneous CIM material that no segregation occurred. The grinding took several days for each material. During that time, the material was stored in a desiccator over a saturated NaOH solution to minimize carbonation. Prior to use in the sorption experiments, each powder material was analyzed by TGA and XRD. Sample preparation of the CI-D material required an additional step in which the large aggregates were separated from the matrix. This was done by sieving, separating a < 250 \(\mu\)m fraction from each of the three borehole samples. Each < 250 \(\mu\)m fraction was analyzed separately by XRD and TGA to determine its mineralogical composition, after which they were combined to prepare a homogenous powder material (CI-D) used in the sorption experiments. The mixed CI-D powder was once again analyzed by XRD and TGA prior to use.

(4) Sorption experiments
\(^{36}\text{Cl}\), \(^{125}\text{I}\), HTO and \(^{14}\text{C}\)-formate sorption was quantified by measuring the partitioning of the radiotracers between the solid and the liquid phases in batch sorption experiments. The experiments were carried out in duplicate using either a tracer cocktail containing \(^{36}\text{Cl}\), \(^{125}\text{I}\) and HTO (for CIM, CI-D and OPC) or \(^{14}\text{C}\)-labeled formic acid (for CIM only). For the triple labeled samples, solutions with stable I and Cl, prepared with NaI and KCl salts dissolved in 0.3 M NaOH, were used to vary the starting \([\text{I}]_{\text{tot}}\) and Cl \([\text{Cl}]_{\text{tot}}\) concentrations: with \([\text{I}]_{\text{tot}}\) = 10\(^{-6}\) M to 10\(^{-3}\) M for CIM and OPC; and \([\text{Cl}]_{\text{tot}}\) = 10\(^{-4}\) M to 10\(^{-1}\) M for CI-D. The \(^{36}\text{Cl}\), \(^{125}\text{I}\) and HTO tracers were then added to the solutions and left equilibrating overnight. The sorption kinetic series with \(^{14}\text{C}\) was performed with stable solutions prepared with Na-acetate dissolved in 0.3 M NaOH with \([\text{C}]_{\text{tot}}\) of 10\(^{-6}\) M. Acetate was added to the solution in order to match the composition of the pore water, extracted from the mortar as well as the solution used in the field experiments. The total amount of activity per sample was about 500 Bq.

For the sorption experiments, multiple aliquots of cement powder suspensions were prepared in centrifuge tubes. In the case of the CIM material and the OPC paste, 4 g of cement powder were immersed in 25 mL APW and equilibrated on an end-over-end shaker for 24 h. After equilibration, 5 mL of radiolabeled CI/I/HTO or C (for CIM only) solutions of known concentration and activity were added to the suspension obtaining a solid-to-liquid ratio (S/L) of 0.13 kg/L. In the case of CI-D, due to the limited amount of crushed material available, the suspensions were prepared with 2 g of powder, 12.5 mL APW and 5 mL of radiolabeled I/CI/HTO solutions,
resulting in a S/L of 0.11 kg/L. It should be noted that the addition of 0.3 M NaOH to the suspension might have influenced the stability of the cement minerals in the samples, possibly leading to some mineral dissolution or recrystallization. In addition to the radiolabeled suspensions, two samples from each material were prepared using only stable Cl and I solutions in the same concentration range to be analyzed by XRD for possible changes in their mineral composition after the sorption experiments are complete.

The sorption behavior of 36Cl and 125I was studied in two sets of experiments: as a function of time (kinetics) and as a function of concentration (sorption isotherm). The sorption of HTO and 14C was studied as a function of time (kinetics) only. For the sorption isotherms, the suspension samples were kept on an end-over-end shaker for 7 days. Samples for the kinetic studies were equilibrated for 1, 3, 5, 14 or 30 days (Table 3). After the equilibration time, the solid and the liquid phases were separated by centrifugation (1 h at 28000 rpm and 95000 g maximum). An aliquot (5 mL in the case of CIM and OPC; 2.5 mL diluted with 2.5 Milli-Q H2O in the case of CI-D) of the supernatant solution from each sample were prepared for radio analysis.

Measured activities in the samples were used to determine the partitioning of the studied radionuclide between the solid and the liquid phase, which was expressed in terms of the distribution ratio R_d [L/kg]:

\[ R_d = \frac{\{An\}}{\{An\}_o} = \left( \frac{A_{\text{sup}} - A_{\text{eq}}}{A_{\text{eq}}} \right) \times \left( \frac{V}{m} \right) \]  

where \( \{An\} \) is the amount of anion (I', Cl', HCOO') sorbed [mol/kg] and \( \{An\}_o \) the anion concentration in solution [M] at equilibrium, respectively. Both terms were obtained from the total radionuclide activity added to the suspension, \( A_{\text{sup}} \) [cpm/L], and the radionuclide activity in the equilibrium solution, \( A_{\text{eq}} \) [cpm/L]. V is the suspension volume [L] and m is the mass of the solid [kg].

### 3. Results

#### 3.1 XRD and TGA results

(1) CIM

XRD data of CIM showed that the material primarily consists of calcite, dolomite and quartz belonging to the aggregates/fillers added during the preparation of the ready-mix mortar [Fig. 2(a)]. Portlandite was the main crystalline cement phase present along with some ettringite and monocarbonate. TGA [Fig. 2(b)] confirmed the observations made with XRD and further indicated the presence of some C-S-H, not visible in XRD due to its amorphous nature. The total measured weight loss amounted to 39.5 wt.% from which 1.2 wt.% can be attributed to the dehydration of portlandite and 30.9 wt.% were lost as CO2 bound in calcite and dolomite. From the measured values it was roughly estimated that the material consists of about 60 wt.% calcite and dolomite. Ettringite and C-S-H dehydrated in the same temperature region resulting in an overlap in their signals. Therefore, their exact amount in the sample could not be quantified solely based on TGA measurements. In addition, Rietveld quantification was performed using the XRD pattern and information from TGA analysis. The Rietveld data showed similar amounts of crystalline ettringite and monocarbonate of about 3 to 4 wt.% (Table 2). The amount of amorphous/nanocrystalline phases summed up to about 40 wt.%. Amongst them, C-S-H is considered as the main cement phase, contributing to the residual

### Table 2. Estimated composition, based on XRD and TGA data for the three materials (CIM, CI-D and OPC), used in the sorption experiments.

|        | CIM    | CI-D   | OPC    |
|--------|--------|--------|--------|
|        | [wt.%] |        | [wt.%] |        |
| Aggregates | 51     | 45     |        | 30.1   |
| Calcite   | 15     | 14     |        | 13     |
| Dolomite  | 33     | 5      |        | ≥ 8.8  |
| Quartz    | 3      | 22     |        | ≥ 6.5  |
| Cryst. cement phases | 9       | 4      |        | MgO 1.0 |
| Portlandite | 2      | 12     |        | Calcium 0.8 |
| Ettringite | 3      | 4      |        |        |
| Monocarbonate | 4      | 5      |        |        |
| Amorphous phases | 40    | 3      |        | 69.9   |
|        |        |        |        |        |
| Cryst. cement phases | 18     | 22     |        |        |
| Portlandite | 4      | 7      |        |        |
| Ettringite | ≥ 6    | ≥ 9    |        |        |
| Monocarbonate | ≥ 8   | ≥ 5    |        |        |
| Amorphous phases | 82    |        |        | 78     |

*Quantification error: ± 5 wt.% on the aggregate/cement fraction. No specific extractions were performed to quantify the Si-hydrogarnet; if present, it is accounted as a part of the amorphous fraction. AFm phases, AFt phases and hydrotalcite could also be components of the amorphous fraction.
Table 3 Summary of experimental conditions and obtained $R_d$ values for $^{36}$Cl, $^{125}$I, HTO and $^{14}$C for the three studied OPC materials: CIM, CI-D and fresh OPC paste.

| Kinetic series | $^{36}$Cl | $^{125}$I | HTO | $^{14}$C |
|----------------|----------|----------|-----|---------|
| Material       | OPC      | CIM      | CI-D| OPC     | CIM      | CI-D    | OPC     | CIM     |
| S/L [kg/L]     | 0.13     | 0.13     | 0.11| 0.13    | 0.13     | 0.11    | 0.13    | 0.11    |
| Time [d]       | 1, 3, 5, 14, 30 |        |     |         |          |         |         |         |
| Conc. [M]      | $10^{-6}$| $10^{-4}$|     |         |          |         |         |         |
| max. $R_d$ [L/kg] | 23 ± 7   | 3.8 ± 1.9| 2.3 ± 1.1| 24 ± 7   | 5.0 ± 2.5| 6.1 ± 3.0| 1.3 ± 0.6| 1.9 ± 0.9| 0.23 ± 0.11| 0.89 ± 0.44| 0.54 ± 0.34| 0.24 ± 0.12|

| Sorption isotherm series | $^{36}$Cl | $^{125}$I |
|--------------------------|----------|----------|
| Material                 | OPC      | CIM      | CI-D    |
| S/L [kg/L]               | 0.13     | 0.13     | 0.11    |
| Time [d]                 | 7        |          |         |
| Conc. [M]                | $10^{-6}$ to $10^{-1}$| $10^{-4}$ to $10^{-1}$| $10^{-6}$ to $10^{-1}$|
| min. $R_d$ [L/kg]        | 0.29 ± 0.09| 0.96 ± 0.48| 0.14 ± 0.07|
| max. $R_d$ [L/kg]        | 17 ± 5   | 3.4 ± 1.7| 1.7 ± 0.9| 14 ± 4   | 4.6 ± 2.3| 5.3 ± 2.7|

non-crystalline fraction. However, nanocrystalline AFm and AFT as well as hydrotalcite could also contribute to the amorphous fraction.

(2) CI-D

For the sorption experiments, a < 250 µm powder fraction obtained by sieving from three borehole samples was used as it contained the highest amount of portlandite and thus of the cementitious matrix, and the least amount of quartz, albite and calcite. XRD and TGA analyses of the < 250 µm fractions of each of the three samples as well as of the mixture of the three (CI-D, the powder ultimately used in the sorption experiments) are shown in Fig. 3. Quartz, albite, calcite, portlandite, ettringite and hydrotalcite were the mineral phases observed in each of the XRD patterns, present in slightly different proportions. TGA showed additionally the presence of C-S-H and monocarbonate in all three samples. The amount of portlandite in the CI-D powder mix determined by TGA was 5.6%. Rietveld refinement resulted in a slightly lower value of 4 wt.%. The crystalline ettringite content summed up to about 5 wt.%. The amount of AFm phases and hydrotalcite could not be determined separately due to the overlap of their reflection peaks. Both phases together accounted for about 3 wt.% of the CI-D material (Table 2).

(3) Fresh OPC

XRD and TGA measurements were performed on the unhydrated cement as well as on the HCP after 30 days of hydration (Fig. 4). The unhydrated cement mainly consisted of gypsum, anhydrite and the clinker phases alite, belite, aluminate and ferrite. XRD analyses of the OPC after 30 days of hydration showed that the material has been fully hydrated and no remnants of the clinker phases could be detected. The OPC contained portlandite, ettringite, hydrotalcite, C-S-H and some calcite. The total mass loss determined by TGA was 24.5 wt.% from which 4.9 wt.% arose from water loss in portlandite. The refined amount of portlandite contained in the OPC was 13 wt.% (Table 2). AFm phases and hydrotalcite together accounted for about 6.5 wt.% of the fresh OPC. The calculated ettringite content was 9 wt.%. Rietveld refinement showed additionally the presence of some unreacted MgO (1 wt.%),

![Fig. 2 XRD (a) and TGA/DTG (b) of the mortar material (CIM). C: calcite, D: dolomite, Ett: ettringite, Mc: monocarbonate, prt: portlandite, Q: quartz.](image-url)
as well as traces of calcite (≈ 0.8 wt.%). Amorphous phases accounted for about 70 wt.% of the hardened OPC paste.

The main goal of the Rietveld refinement performed was to quantify the amount of aggregates present in the CIM and CI-D materials. Due to the high content of amorphous/nanocrystalline fraction in the three cement materials, only a minimum estimate for the cement phases is given in Table 2. C-S-H is the main amorphous phase in hydrated cement. However, other poorly crystalline cement phases, for example, ettringite (Pedersen 2018) could be also contained. It should be noted that overgrinding could also lead to partial amorphization of the softer cement phases (Snellings 2016).

### 3.2 Sorption experiments

The sorption of $^{36}\text{Cl}$, $^{125}\text{I}$, HTO and/or $^{14}\text{C}$ was investigated in a series of batch sorption experiments on the three different materials, i.e. the fresh hardened OPC paste and the aged CIM and CI-D materials, in APW with pH ranging between 13.04 and 13.37 (Table A2 of the Appendix). To allow direct comparison between the sorption properties of fresh OPC, and of the CIM and CI-D materials, measured sorption data for CIM and CI-D have been recalculated to account for a 100% cementitious matrix excluding the aggregates (crystalline cement phases + amorphous cement phases = 100 wt.%), based on the results from the Rietveld refinement. Due to the addition of the analytical uncertainties caused by the Rietveld refinement and by the analytical error, a large error of 50% was assigned to the experimental sorption data. The results are summarized in Figs. 5, 6 and Table 3.

1. **Sorption kinetics**

The kinetics of $^{36}\text{Cl}$ uptake was determined at a total aqueous Cl concentration of $10^{-6}$ M for the CIM material and the fresh hardened OPC paste. Due to the high Cl content of the CI-D material, kinetic $^{36}\text{Cl}$ sorption experiments were carried out at a significantly higher...
aqueous Cl concentration of $10^{-4}$ M. It should be noted that, in general, $R_d$ values were found to decrease with increasing aqueous Cl $^-$ concentration (Ochs et al. 2016); see also Fig. 6. Hence, the $R_d$ value is expected to be lower for CI-D as compared to OPC and CIM. $^{36}$Cl uptake for all three materials is relatively fast and equilibrium was reached after 5 to 10 days [Fig. 5(a)]. From the three studied materials, fresh OPC showed the strongest sorption with $R_d$ values ranging between $14 \pm 4$ L/kg and $17 \pm 5$ L/kg for the first 7 days, and 22 to 23 $\pm$ 7 L/kg after two to four weeks of equilibration time. Hence, a trend to slightly stronger uptake with time is observed while the difference in the $R_d$ values is hardly significant within the given uncertainty. At similar equilibrium Cl concentrations, $^{36}$Cl uptake was about a factor 5 to 6 lower on CIM as compared to OPC. Calculated $R_d$ values ranged between $2.8 \pm 1.4$ L/kg and $3.8 \pm 1.9$ L/kg for CIM. $R_d$ values amounted to $1.4 \pm 0.7$ L/kg and $2.3 \pm 1.1$ L/kg for CI-D at the higher [Cl]$_{eq}$ of $10^{-4}$ M.

$^{125}$I showed a similar sorption pattern as $^{36}$Cl with comparatively fast sorption kinetics [Fig. 5(b)]. OPC was the material showing strongest uptake of $^{125}$I with a maximum $R_d$ value of $24 \pm 7$ L/kg after 30 days of equilibration. Interestingly, $^{125}$I uptake by CIM and CI-D was again weaker as observed in the case of $^{36}$Cl uptake. Maximum measured $R_d$ values were $5.0 \pm 2.5$ L/kg for CIM and $6.1 \pm 3.0$ L/kg for CI-D. The difference in the sorption values between fresh OPC paste and the aged CIM and CI-D materials was a factor of about 4 to 5.

HTO sorption was very weak with measured values close to the limit of quantification. The large scatter is associated with the small difference observed between total HTO activity added and the HTO activity in solution at equilibrium [Fig. 5(c)]. HTO uptake by fresh OPC and CIM seems to be slightly higher than the one determined on CI-D with $R_d$ values ranging between $0.26 \pm 0.13$ and $1.9 \pm 0.9$ L/kg. $R_d$ values for CI-D ranged between $0.04 \pm 0.02$ and $0.23 \pm 0.11$ L/kg. The uptake of HTO by all three materials was fast and equilibrium was instantaneously reached. The observed trend to lower $R_d$ values with time (after 30 days) for fresh OPC and CI-D could possibly be the result of loss of tracer due to
evaporation.

The uptake of $^{14}$C in the chemical form of formic acid by CIM was studied in the presence of $10^{-6}$ M acetate. Similarly to HTO, sorption kinetics of $^{14}$C was fast and equilibrium was instantaneously reached. Extending the time of equilibration did not significantly influence formate sorption and measured $R_d$ values after 1 day of equilibration and after longer equilibration times were nearly identical ranging between $0.58 \pm 0.29$ L/kg and $0.89 \pm 0.44$ L/kg [Fig. 5(d)].

(2) $^{36}$Cl and $^{125}$I sorption isotherms

$^{36}$Cl sorption on all materials was non-linear and decreased with increasing $[\text{Cl}]_{eq}$ [Figs. 6(a) and 6(b)]. In particular, non-linear sorption is evidenced by the decrease in the $R_d$ values with increasing $[\text{Cl}]_{eq}$. Strongest sorption was observed for OPC with a maximum $R_d$ value of $17 \pm 5$ L/kg at the lowest $[\text{Cl}]_{eq}$ of $10^{-6}$ M. $^{36}$Cl sorption on CIM was significantly weaker at the same $[\text{Cl}]_{eq}$ with a maximum $R_d$ value of $3.4 \pm 1.7$ L/kg. At the highest $[\text{Cl}]_{eq}$ loading of $1.7 \times 10^{-3}$ M, the measured $R_d$ values were negative, indicating very weak sorption below the analytical error (data not shown in Fig. 6). The $^{36}$Cl sorption isotherm on CI-D seems to be closer to the one obtained for OPC in the concentration range in which they overlap. This suggests, overall, a stronger $^{36}$Cl sorption on CI-D than on CIM while $^{36}$Cl sorption on fresh OPC and CI-D were comparable. Calculated $R_d$ values for $^{36}$Cl were between $0.14 \pm 0.07$ L/kg and $1.7 \pm 0.9$ L/kg. The shape of the sorption isotherm for OPC indicated a saturation effect at high $[\text{Cl}]_{eq}$, whereas for CIM and CI-D no saturation effect was observed. Furthermore, the isotherms did not indicate precipitation of Cl-bearing solid phases.

$^{125}$I sorption revealed a similar, non-linear sorption trend as the one observed for $^{36}$Cl [Figs. 6(c) and 6(d)]. All materials showed similar affinity for $^{125}$I uptake in the low to moderate I concentration range with a maximum measured $R_d$ value of $14 \pm 4$ L/kg at low $[\text{I}]_{eq}$. At increasing $[\text{I}]_{eq}$, however, $R_d$ values tend to be somewhat

Fig. 6 Sorption isotherms and corresponding $R_d$ values for $^{36}$Cl (a, b) and $^{125}$I (c, d) on the three studied OPC materials: CIM, CI-D and fresh hardened OPC paste. Plotted sorption data for CIM and CI-D are normalized to 100 wt.% HCP. Dashed line in (a) and (c) indicates a slope of 1. Open triangle in (a) is a single outlier, considered to be the result of an experimental error.
higher for CIM than for the two other materials. The $^{125}$I sorption isotherm revealed no saturation effect and further, no precipitation of I-bearing solid phases was indicated in these conditions.

### 4. Discussion

#### 4.1 Alteration of cement matrices

An attempt was made to determine the mineralogical composition of the three studied materials by a combination of TGA, XRD and Rietveld analyses. Note, that the amorphous fraction in the three cement samples is substantial. This fraction can contain nanocrystalline AFm and AFt as well as hydrotalcite. Thus, the mineral compositions are only a rough approximation of the real compositions of the pastes. Nevertheless, a comparison based on the amount of cement minerals related to 100% HCP, i.e. excluding the presence of aggregates, reveals differences in the mineral composition between fresh and aged hardened cement pastes. In all materials, the main cement hydrates are C-S-H, portlandite, ettringite, AFm phases (and hydrotalcite). A very small portion of calcite is present in the fresh hardened OPC paste, assigned to the aggregate fraction in the case of the CI-D and CIM materials.

The CIM material has a low portlandite content and a relatively high amount of monocarbonate. It shows no traces of Mg-bearing phases, while fresh OPC paste and the aged CI-D material are MgO-rich, reflected by the relatively high amount of hydrotalcite (Table 2). Previous pore solution analysis on CIM indicated no significant signs of degradation of the material (Lothenbach 2019). After 14 years of contact time with the granodioritic host rock at the test site, the pore solution still has a high pH of 13.3 and a high alkali content, typically found in unaltered HCP.

The mineral composition of the aged CI-D material can be compared with that of fresh hardened CI paste reported earlier by Lothenbach (2011, 2017). The latter paste was prepared with a CEM I 42.5 R-HS Holcim Protogo 4R cement of the same cement line as the one used in the CI field experiment (similar chemical composition to the cement used in the period Nov 05 to Mar 06, see Table 1) and the same w/c ratio of 0.8. The CI-D material used in this study was located about 10 cm away from the interface and had no direct contact with OPA. Nevertheless, when comparing the observed mineral compositions of the fresh OPC paste and the aged CI-D material with the one of the CI paste after 9 years of hydration in a closed system (Lothenbach 2011, 2017), it was noticed that a closer resemblance exists between the mineral compositions of the CI paste with fresh OPC paste rather than the aged CI-D material. Despite the fact, that the CI paste had been prepared from the same cement as the one used in the field experiments (Lothenbach 2011, 2017), its mineral assemblage, in particular the portlandite content, is comparable to fresh OPC paste, which has not been exposed to interactions with its service environment (in this case to OPA pore water). However, chemical and microstructural studies of CI-D samples, belonging to the same borehole and collected at the tip of it, i.e. at the interface with OPA, have shown changes in the mineralogical composition as a consequence of ageing.

Experimental data as well as thermodynamic modeling of the hydration process of the CI paste in a closed system showed a relatively constant portlandite/ettringite (P/E) ratio (of $\approx 1.33$) after a curing time of 30 days (Lothenbach 2011, 2017). Similar P/E ratio (of $\approx 1.48$) exhibits the fresh OPC paste used in this study. By contrast, the aged CI-D and CIM materials have significantly lower P/E ratios of $\leq 0.80$ and $\leq 0.67$, respectively, indicating a lower content of portlandite, which is also evident from the TGA data. Thus, a lower P/E ratio with ageing indicates the dissolution of portlandite and possibly one or more of the following processes: i) its subsequent leaching, ii) its precipitation into calcite and/or, iii) its conversion into other cement phases, such as C-S-H. Portlandite conversion into C-S-H phases could occur due to a pozzolanic reaction with SiO$_2$ released as a result of the dissolution of quartz aggregates in hyperalkaline cement pore water. It should be noted that aggregate reactivity was considered to have an impact on the mineral composition of cementitious materials with time in previous studies (Kosakowski et al. 2020; Wieland et al. 2020). A more detailed assessment of the conversion of portlandite into secondary phases would require a more precise quantification of C-S-H phases in the aged cements.

Pore solution data of the CI paste studied in a closed system showed high pH (13.3) and high alkaline content (90 mmol/L Na and 200 mmol/L K) after 9 years of hydration (Lothenbach 2017). Chemical characterization of the pore solution in a CI-D sample, located several cm away from the CI-D sample used in the sorption experiments, revealed a decrease in the alkali content ($\approx 75$ mmol/L Na and $= 35$ mmol/L K), increase in the CI ($\approx 150$ mmol/L) and lowering of the pH ($\approx 12.5$). The changes in the pore solution were assigned to the infiltration of the OPA pore water, which is characterized by a high Cl (230 to 250 mmol/L) content and low pH of $\approx 7.6$ and which is often associated with portlandite dissolution (Jenni et al. 2014; Mäder et al. 2017).

#### 4.2 Uptake of radionuclides

The radioactive isotope $^{36}$Cl is considered as one of the potentially dose-determining radionuclides in many disposal scenarios and therefore its interaction with the cement-based engineered barrier is of particular relevance as has been reported, for example, by Nagra (2002). In the repository environment the retention of $^{36}$Cl is expected to occur mainly due to interaction with cement phases as readily soluble CI-bearing phases, such as Friedel’s salts or calcium oxychlorides, only precipitate at Cl concentrations exceeding the millimol level (Ochs et al. 2016). The isotherm data, however,
show that the Cl− concentration allowing precipitation of a solubility-limiting CI-bearing phase, which fixes the aqueous Cl− concentration at constant value, was not reached up to an aqueous Cl− concentration of 0.1 M (Fig. 6). For this reason, sorption on cement phases is considered as the dominant binding mechanism in the Cl− concentration range covered in this study.

Amongst the components of the HCP, C-S-H, AFm phases, ettringite as well as hydrotalcite are the cement hydrates with the highest sorption potential for radionuclides, due to their abundance and/or favorable structural sorption sites (Wieland 2014; Ochs et al. 2016). Their presence/absence or relative proportion in the three studied materials could therefore have a direct effect on the observed sorption behavior. The three studied materials have a substantial nanocrystalline fraction, suggesting a large amount of C-S-H. In the case of a C-S-H with high C/S ratio, a strong Cl− sorption is expected (Wieland 2014). Monocarbonate, which readily reacts with Cl− to form solid solutions (Nielsen et al. 2005; Balonis et al. 2010), is present in all three materials, with the CIM paste containing the highest amount of the AFm phase. Fresh OPC and the CI-D material, on the other hand, contain hydrotalcite, which is completely absent in the CIM material. Hydrotalcite has been shown to have a relatively high sorption capacity for Cl− (Aggarwal et al. 2000), which could explain the stronger Cl− sorption observed for fresh OPC and CI-D compared to the CIM paste (Fig. 6). Ettringite is present in all three materials in slightly different proportions; however, since Cl− is a monovalent anion, only a weak interaction with ettringite is expected (Wieland 2014) so that variations in the ettringite content would have a negligibly small effect on the Cl− binding.

The sorption values determined at a Cl− concentration of 10−4 M on fresh OPC, i.e. ≈ 20 L/kg after two to four weeks of equilibration time at pH ≈ 13.4, are in line with previously reported values [see Fig. A2 of the Appendix and the review by Ochs et al. (2016)]. In the latter study, Rd values for hardened OPC paste in the stage I of the cement degradation (i.e. pH 13.3) were reported to range in value between ≈ 10 and ≈ 60 L/kg. Nevertheless, a Rd value ≈ 3 L/kg, as observed in the case of the CIM material at a Cl− concentration of 10−6 M, is at the lower limit of previously reported values and therefore is likely the result of the ageing process. In addition, an Rd value of about 2 L/kg determined for the CI-D paste at the higher aqueous Cl− concentration of 10−3 M also appears to be at the lower bound of previously reported values. Rd values determined on fresh OPC at high Cl− concentrations are expected to range in value between 10 and 100 L/kg as described by Ochs et al. (2016) and references therein. Hence, the sorption studies on the aged materials provide substantial evidence that 36Cl retention tends to be lower on aged pastes than fresh pastes (Table 3).

Another important observation concerns non-linearity of the sorption isotherm, which is the consequence of reduced sorption with increasing Cl− concentration in the pore water. This is a well known phenomenon discussed in detail elsewhere (Nielsen et al. 2005; Ochs et al. 2016). Non-linearity of sorption isotherms commonly indicates the presence of different sorbing sites on a solid surface exhibiting different affinities for radionuclide sorption. Nevertheless, in the case of the complex cementitious matrices, it is also conceivable that several sorption processes occurring simultaneously on different cement phases in the paste account for the observed non-linearity. For example, formation of solid solutions between AFm phases may be the controlling sorption mechanism at low Cl− concentrations (Balonis et al. 2010), while at higher Cl− concentrations where the capacity of Cl− binding by the formation of solid solutions is exhausted, adsorption on C-S-H phases may become the dominant sorption mechanism, as has been reported by, for example, Kurumisawa and Nawa (2016). Note that AFm and C-S-H phases are constituents of the pastes observed in this study. In the case of an ongoing pozzolanic reaction, the C-S-H fraction would increase in the aged materials compared to fresh OPC paste. At the same time, C-S-H formed due to the reaction of pozzolanic materials with portlandite tends to have a lower C/S ratio as has been reported, for example, by Lothenbach et al. (2011), and is generally characterized with decreased sorption. Thus, the reduced 36Cl uptake by the aged materials could be the result of the interplay of several factors: in the event of an ongoing pozzolanic reaction, the effect of the increased C-S-H content could be counterbalanced by an overall low C/S ratio and/or effect of infiltrating groundwater (for CI-D). On the other hand, the lower Rd value for the aged materials despite the potentially higher C-S-H content could also suggests that C-S-H may not be the dominant cement phase governing Cl− sorption.

The sorption kinetics of 36Cl and 125I are very similar and, overall, the trends in the sorption isotherms of the two radioisotopes agree well, except that 36Cl sorption tends to be lower on the aged materials at low Cl− concentrations compared to 125I (Table 3). In particular, non-linearity of the sorption isotherms of 36Cl and 125I support the idea that similar sorption mechanisms and in addition, the same cement phases control the uptake of the two radioisotopes by HCP. XRD analyses, performed after the sorption experiments were complete on samples, in which stable Cl− and I solutions in the same concentration range were used, confirmed that no new Cl− or I-bearing phases had precipitated, while the formation of solid solutions is possible. The XRD data are shown in Fig. A3 of the Appendix.

Measured HTO uptake by the three studied cementitious materials (CIM, CI-D and fresh OPC) shows fast sorption kinetics and generally low Rd values, which is consistent with previous studies (Tits et al. 2003; Ochs et al. 2016). Rd values determined on fresh OPC paste are in good agreement with a previously published Rd value of 0.8 ± 0.2 L/kg, obtained from batch sorption
experiments with HTO on non-degraded HCP (Tits et al. 2003). Furthermore, the results do not indicate a pronounced effect of ageing on HTO sorption (Table 3) as $R_s$ values for fresh OPC paste and the aged CIM paste agree, while only the sorption value for the CI-D material is somewhat lower. Possible uptake mechanisms for HTO by cement paste include isotope exchange reactions with chemically and physically bound water (bound protons, OH$^-$ ions and/or water molecules) as well as potential immobilization in dead-end pores (Tits et al. 2003; Ochs et al. 2016). Tits et al. (2003) demonstrated that even, if the entire amount of structural water bound by cement phases (e.g. AFt, AFm, C-S-H) is fully accessible to isotope exchange with HTO in solution, the resulting sorption values (0.18 L/kg to 0.32 L/kg) are not sufficient to explain the observed HTO uptake. The authors therefore suggested that an additional mechanism, such as diffusion in dead-end pores, needs to be taken into consideration in order to explain experimental sorption data. $R_s$ values for HTO may also be influenced by sample characteristics such as the w/c ratio and cement state, in which higher w/c ratios and the existence of partially hydrated phases in fresh cement paste may give rise to higher sorption values (Ochs et al. 2016). This could explain the higher $R_s$ values observed for the fresh OPC paste compared to CI-D.

Very limited quantitative information is presently available on the interaction of $^{14}$C-bearing organic compounds with HCP according to, for example, Wieland et al. (2016) and the references therein. In general, sorption of LMW organic compounds was found to be very weak with $R_s$ values typically < 1 L/kg. This study supports the notion of very weak interaction of LMW carbon compounds with cementitious materials. The $R_s$ value of $^{14}$C-bearing formate ranges between 0.58 ± 0.29 L/kg and 0.89 ± 0.44 L/kg (Table 3) which is in good agreement with previously reported data (0.22 ± 0.04 L/kg as given by Wieland et al. 2016). The latter authors postulated that the uptake of formate in pastes occurs mainly due to specific (electrostatic interaction) or non-specific (hydrogen bonding) adsorption on the cement phases, but partially also due to the replacement of sulfate by formate in the ettringite structure.

### 5. Conclusions

The present study on the interaction of $^{36}$Cl, $^{125}$I, HTO and $^{14}$C ($^{14}$C-labeled formate) with fresh OPC paste and pastes aged for 10 years (CI-D) and 14 years (CIM)emplaced in the granodiorite of the Grimsel Test Site indicates an effect of ageing on the mineral composition of the cement pastes and on the extent of radionuclide uptake by the aged materials. Batch sorption experiments conducted at pH ≈ 13.3 and S/L ratios ranging from 0.11 to 0.13 kg/L show strongest uptake of $^{36}$Cl and $^{125}$I by fresh OPC paste while sorption values tend to be almost an order of magnitude lower on the aged materials. The sorption values determined in this study for $^{36}$Cl and $^{125}$I on fresh OPC paste are in good agreement with sorption data reported in literature. HTO and $^{14}$C ($^{14}$C-labeled formate) are very weakly sorbing radionuclides and no effect of ageing on sorption is indicated. Also in case of the latter radionuclides, the sorption values determined in this study and those reported in literature agree very well.

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### List of notations

- $A_B$: beta activity in window A in unknown sample [cpm/5 mL sample]
- $A_B^{HTO+Cl}$: contribution of HTO and $^{36}$Cl beta activity in window A in unknown sample [cpm/5 mL sample]
- $A_B^{125}$I: beta activity in window A in standard solution [cpm/mL tracer]
- $A_{aq}$: radionuclide activity in the equilibrium solution [cpm/L]
- $A_{aq}^B$: contribution of $^{125}$I beta activity in window B in standard solution [cpm/5 mL sample]
- $A_{aq}^B$: amount of anion sorbed [mol/kg]
- $A_{aq}^B$: anion concentration in solution at equilibrium [M]
- $A_{aup}$: total radionuclide activity in the suspension [cpm/L]
- $B_B$: beta activity in window B in unknown sample [cpm/5 mL sample]
- $B_B^{HTO+Cl}$: contribution of HTO and $^{36}$Cl beta activity in window B in unknown sample [cpm/5 mL sample]
- $B_B^{125}$I: beta activity in window B in standard solution [cpm/mL tracer]
- $B_{B}^{125}$I: contribution of $^{125}$I beta activity in window B in unknown sample [cpm/5 mL sample]
- $C_G^{125}$I: gamma activity in window C in standard solution [cpm/mL tracer]
- $C_G^{total}$: total $^{125}$I gamma activity in window C in unknown sample [cpm/5 mL sample]
- $C_G^{125}$I: gamma activity in window C in standard solution [cpm/mL tracer]
- $C_G^{total}$: total $^{125}$I gamma activity in window C in unknown sample [cpm/5 mL sample]
- $C_{L}$: $^{36}$Cl beta activity [cpm/5 mL sample]
- $C_{L}^{125}$I: $^{36}$Cl beta efficiency in window A [cpm/5 mL sample]
- $C_{B}$: $^{36}$Cl beta efficiency in window B [cpm/5 mL sample]
- $F_{GB}$: factor for conversion of gamma activity to...
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Appendix

Table A1 Results for the triple labeled \(^{36}\text{Cl}, ^{125}\text{I}, \text{HTO}\) standards. The theoretical activity (HTO/CL/I theor.) was calculated based on the amount of added tracer. From the total measured activity in the samples the individual activities for each of the three tracers (HTO meas., CL meas. and \(A^*_B + B^*_B\)) was determined based on the calibration method described in the main text.

| No. | \(^{36}\text{Cl}\) µl | HTO µl | \(^{125}\text{I}\) µl | No. 1 | HTO meas. (cpm) | HTO theor. (cpm) | err.\(^*\) ( %) | CL meas. (cpm) | CL theor. (cpm) | err.\(^*\) ( %) | No. 1 | \(A^*_B + B^*_B\) (cpm) | I theor. (cpm) | err.\(^*\) ( %) |
|-----|-----------------|--------|-----------------|------|----------------|----------------|-------------|----------------|----------------|-------------|------|----------------|----------|-------------|
| 1-1 | 40              | 15     | -               | 926  | 983            | 5.8             | -           | -              | -              | -           | 977  | 989            | 1.2       |             |
| 1-2 | 40              | 15     | -               | 939  | 983            | 4.4             | -           | -              | -              | -           | 981  | 989            | 0.8       |             |
| 1-3 | 40              | 15     | -               | 914  | 983            | 7.0             | -           | -              | -              | -           | 990  | 989            | -0.1      |             |
| 2-1 | 40              | 30     | -               | 1932 | 1966           | 1.7             | -           | -              | -              | -           | 998  | 989            | -0.9      |             |
| 2-2 | 40              | 30     | -               | 1925 | 1966           | 2.1             | -           | -              | -              | -           | 998  | 989            | -0.9      |             |
| 2-3 | 40              | 30     | -               | 2177 | 1966           | -10.7           | -           | -              | -              | -           | 989  | 989            | 0.0       |             |
| 3-1 | 80              | 15     | 10              | 950  | 983            | 3.3             | -           | -              | -              | -           | 1973 | 1978           | 0.2       |             |
| 3-2 | 80              | 15     | 10              | 968  | 983            | 1.5             | -           | -              | -              | -           | 1991 | 1978           | -0.6      |             |
| 3-3 | 80              | 15     | 10              | 989  | 983            | -0.6            | -           | -              | -              | -           | 1993 | 1978           | -0.8      |             |
| 4-1 | 80              | 30     | -               | 1947 | 1966           | 0.9             | -           | -              | -              | -           | 2005 | 1978           | -1.4      |             |
| 4-2 | 80              | 30     | -               | 2051 | 1966           | -4.3            | -           | -              | -              | -           | 1963 | 1978           | 0.8       |             |
| 4-3 | 80              | 30     | -               | 2042 | 1966           | -3.9            | -           | -              | -              | -           | 1982 | 1978           | -0.2      |             |
| 5-1 | 40              | 15     | 10              | 951  | 983            | 3.3             | 1719        | 1730           | 0.6            | -           | 1001 | 989            | -1.3      |             |
| 5-2 | 40              | 15     | 10              | 997  | 983            | -1.5            | 1719        | 1730           | 0.6            | -           | 1007 | 989            | -1.8      |             |
| 5-3 | 40              | 15     | 10              | 889  | 983            | 9.5             | 1725        | 1730           | 0.3            | -           | 994  | 989            | -0.5      |             |
| 6-1 | 40              | 30     | 10              | 1945 | 1966           | 1.1             | 1733        | 1730           | -0.2           | -           | 1002 | 989            | -1.4      |             |
| 6-2 | 40              | 30     | 10              | 1904 | 1966           | 3.1             | 1723        | 1730           | 0.4            | -           | 1018 | 989            | -2.9      |             |
| 6-3 | 40              | 30     | 10              | 1976 | 1966           | -0.5            | 1718        | 1730           | 0.7            | -           | 1975 | 1978           | 0.1       |             |
| 7-1 | 80              | 15     | 10              | 884  | 983            | 10.0            | 1719        | 1730           | 0.7            | -           | 1976 | 1978           | 0.1       |             |
| 7-2 | 80              | 15     | 10              | 993  | 983            | -1.0            | 1716        | 1730           | 0.8            | -           | 1989 | 1978           | -0.5      |             |
| 7-3 | 80              | 15     | 10              | 1015 | 983            | -3.3            | 1726        | 1730           | 0.2            | -           | 1975 | 1978           | 0.1       |             |
| 8-1 | 80              | 30     | 10              | 1922 | 1966           | -1.3            | 1701        | 1730           | 1.4            | -           | 1972 | 1978           | 0.3       |             |
| 8-2 | 80              | 30     | 10              | 1982 | 1966           | -0.8            | 1704        | 1730           | 1.5            | -           | 2007 | 1978           | -1.5      |             |
| 8-3 | 80              | 30     | 10              | 1976 | 1966           | -0.5            | 1718        | 1730           | 0.7            | -           | 1975 | 1978           | 0.1       |             |

\*err. (\%) = (HTO theor./HTO meas.)/HTO theor. × 100.

Table A2 Recipes and corresponding calculated chemical compositions of the artificial pore water solutions used in the sorption experiments. The [Ca] value for OPC, marked with (*), gives the Ca content prior to filtration; the expected Ca concentration after filtration is \(1.6 \times 10^{-3}\) M approx. \((\text{Wieland et al. 1998})\).

| Recipe (\(^{36}\text{Cl}, ^{125}\text{I}, \text{HTO}\)) | CIM (\(^{14}\text{C}\)) | CI-D | OPC |
|----------------|-----------------|-----|-----|
| KOH            | 12.18           | 12.08 | 4.94 | 10.10 |
| NaOH           | 3.80            | 3.80  | 1.28 | 4.56  |
| Ca(OH)\(_2\)    | 0.134           | 0.134 | 0.148 | 1.00  |
| CaCO\(_3\)        | -               | -     | -    | 1.00  |
| Na\(_2\)SO\(_4\)   | 1.06            | 1.06  | 0.568 | 0.426 |
| Al\(_2\)(SO\(_4\))\(_3\)-16H\(_2\)O | 0.013         | 0.013 | 0.016 |       |
| KCl            | -               | -     | 0.130 |       |

| Recipe (\(^{36}\text{Cl}, ^{125}\text{I},^{14}\text{C}\)) | CIM (\(^{14}\text{C}\)) | CI-D | OPC |
|----------------|-----------------|-----|-----|
| KOH            | 217.0           | 109.9 | 1.81 | 7.50  | 0.040 | - | 13.37 |
| NaOH           | 217.0           | 109.9 | 1.81 | 7.50  | 0.040 | 1.75 | 13.37 |
| Ca(OH)\(_2\)    | 88.00           | 40.00 | 2.00 | 4.00  |       | - | 13.04 |
| CaCO\(_3\)        | 180.0           | 120.0 | 23.49* | 3.07  | 0.050 | - | 13.36 |
Fig. A1 Flow charts showing the different steps of the sample preparation and the sorption experiments.

Fig. A2 Comparison of measured $^{36}$Cl uptake by the three studied materials: CIM, CI-D and fresh OPC, with available literature data. Graph adapted from Ochs et al. (2016).
Fig. A3 XRD analyses of the three studied materials: CIM, CI-D and fresh OPC, showing the observed mineral compositions before and after the sorption experiments. The sorption experiments in this case were performed with stable Cl and I solution in the same concentration range as the radiolabeled samples. No changes in the mineral composition are observed, i.e. no precipitation of new Cl- or I-bearing phases, such as Friedel’s salt or monoiodide. The only exception is the CI-D sample with the lowest Cl and I loadings of 10^{-4} M and 10^{-6} M, respectively, where an additional peak at around 8.4 Å is visible (grey line), which was not present in the original CI-D material (red line). The peak could not be clearly assigned to a known phase. A: albite, C: calcite, D: dolomite, Ett: ettringite, Hc: hemicarbonate, htl: hydrotalcite, Mc: monocarbonate,prt: portlandite, Q: quartz.