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Abstract

The potential effects of alkaline degradation products of the fibre mass UP2 on metal sorption onto fresh and degraded cement have been investigated. For this purpose, crushed cement have been leached to support material for the subsequent batch sorption experiments.

Alkaline leaching of UP2 were also made, which gave leaching solutions of 30 ppm DOC after 300 days. These solutions were used in the batch experiments. Continued leaching shows that even higher concentrations can be expected: 45 ppm DOC in the leaching with a low-alkaline (pH 12.5) artificial cement pore-water and 150 ppm DOC with a high alkaline (pH 13.3) artificial pore-water.

Batch sorption experiments with ^{134}Cs and ^{60}Co show no effects on metal sorption onto leached or fresh cement when the 30 ppm DOC leaching solutions of UP2 were used as liquid phase. The measured R_d values were 10^{-3} m^3/kg for Cs and in the range of 0.03–0.1 m^3/kg for Co.

Separate experiments with other organics ligands were also made: EDTA, ISA and citric acid with maximum concentrations of 500, 300 and 300 ppm DOC, respectively. Also here no effects on Cs and Co sorption onto leached and fresh cement were established.

Batch experiments of ^{152}Eu were not successful since results were above detection level of about 2–3 m^3/kg. The addition of the aforementioned 30 ppm UP2 leaching solution or the other organic ligands did not affect the detection level.

Measurements of background concentrations of total Eu show a peculiar result of Eu apparantly increasing in batch experiments with cement to final values of about 5–10 nM. The underlying reason for this effect, whether real or artificial, could not be established.

Background concentrations of Th were about 1 nM in both cement and blank samples.

Background concentrations of Zr were about 100–700 nM in both cement and blank samples, the high values were measured acidic blanks, which suggests either acidic leaching from tube walls or contamination from the acid itself.

No effects from the leaching products of UP2 or the other organic ligands on the background concentrations of Eu, Th and Zr could be confirmed.

Sammanfattning

De förmodade effekterna av produkterna från den alkaliska degraderingen av fibermassan UP2 på metallers sorption på färsk och lakad cement har undersökts. För detta ändamål har krossad cement lakats för att ge material till de efterföljande batchsorptionsförsöken.

Alkalisk lakning av UP2 har också gjorts , vilket gav laklösningar om 30 ppm DOC efter 300 dagar. Dessa lösningar användes sedan i batch experimenten. Fortsatt lakning visar att ännu högre koncentrationer kan förväntas: 45 ppm DOC vid lakning med ett låg-alkaliskt (pH 12.5) artificiellt cementporvatten och 150 ppm DOC vid lakning med ett hög-alkaliskt (pH 13.3) artificiellt cementporvatten.

Batchsorptionsexperiment med ^{134}Cs och ^{60}Co visar att inga effekter fås på metallernas sorption på lakad eller färsk cement när UP2-laklösningen om 30 ppm DOC används som vattenfas i försöken. Uppmätta R_d värden var 10^{-3} m^3/kg för Cs och i intervallet 0.03–0.1 m^3/kg för Co.

Separata försök har även gjorts med andra organiska ligander som tillsats: EDTA, ISA och citronsyra med högsta koncentrationer om respektive 500, 300 och 300 ppm DOC. Även här noterades inga effekter på Cs eller Co sorption på vare sig lakad eller färsk cement.

Batchförsök med ^{152}Eu var generellt ej lyckade då resultaten var över detektionsnivån på 2–3 m^3/kg. Tillsatserna av de förut nämda 30 ppm laklösningen av UP2 eller de andra liganderna gav ingen effekt på detektionsnivån.

Mätningar av bakgrundshalt av total Eu visar en märklig effekt av Eu som till synes ökar i de batch experiment som innehöll cement. Slutlig koncentration var i området 5–10 nM. Den underliggande orsaken till denna effekt, om den är verklig eller artificiell, kunde inte bestämmas.

Mätningar av bakgrundshalt av total Th visar värden omkring 1 nM, både i försök med cement och i blanker.

Mätningar av bakgrundshalt total Zr visar värden i området 100–700 nM, både i försök med cement och i blanker. De högsta värdena uppmättes i de surgjorda blankerna, vilket tyder på antingen en utlakning från plaströren eller en kontamination från syran.

Inga effekter av UP2 lakprodukterna eller de andra organiska liganderna på bakgrundshalterna av Eu, Th och Zr kunde konstateras.

Contents

1 Introduction

The fibre mass Ricem UP2 (hereafter abbreviated UP2), an acrylonitrile polymer used as filtration aid in condensate cleanup in Nuclear Power plants (Dario et al. 2004b), and cellulose are two examples of organic materials that will be deposited in the Swedish SFR repository for short-lived low to intermediate-level radioactive waste (LILW) (Riggare and Johansson 2001). The formation of isosaccharinic acid (ISA), the major alkaline degradation product from cellulose, and its complexation capability of typical metals found in a waste inventory are now fairly well documented in the literature (Börstell 2006)[1].

However, for UP2 the corresponding knowledge database is considerably smaller, the article and report by Dario et al. (2004a, b) and the report by Duro et al. (2005) are the only, to us known, experimental investigations that report on the metal complexation capability of UP2 alkaline degradation products.

In the works by Dario et al. (2004a, b) alkaline degradation of 20 g/L UP2 at pH 12.5 and 60°C, with or without the addition of 0.01M $CaOH_2$, were studied. Results for $CaOH_2$ free solution gave 80 mM dissolved organic carbon (DOC) after about 100 days of leaching, while the solution that included $CaOH_2$ gave 120 mM DOC after about 50 days (Dario et al. 2004a, b). However, from the appearance of the evolution of DOC with time in these experiments, the concentrations would still be increasing after these points, which were the last analysed data.

In the same work, batch experiments with Eu sorption onto cement and TiO_2 powders were also made, by the use of diluted UP2 leaching solutions, adjusted to pH12.5, as liquid phase. Distribution coefficient R_d (m^3/kg) values were measured, most of them as results from 1 day of sorption and fewer as results from longer period studies, of up to 400 days.

However, a general problem with the use of results from 1 day of sorption is that there will not be enough time to reach equilibration, especially in a complex system, which consists of liquid phase with dissolved metal, hydroxide and organic ligands and two solid phases (the solid added and the tube wall). An interpretation of initial results as an indication of the final distribution is usually not meaningful, even less so when used as data for building sorption models.

The results reported (Dario et al. 2004a, b) for the long-term experiments illustrates this problem, as they generally show an initial steep increase in R_d values with time, followed by a levelling out to limiting values.

The long-term results for Eu sorption onto cement with 3 mM and 0.3 mM in DOC dilution of UP2 leaching products gave limiting log R_d values of 0.7 and 3.5, respectively (Dario et al. 2004a, b). For these particular experiments it is noteworthy that the initial phase in the evolution of R_d with time is much steeper with the lower concentration of organics. The first points of respective experiment, after 1 day, are quite close to each other and, consequently, give no indication whatsoever of what the final limiting values will be, which, in the end, turn out to differ by three orders of magnitude.

In the cited works, similar sorption experiments with the direct addition of dissolved organic ligands, for example EDTA, ISA and citric acid were also made.

Long-term results for Eu sorption onto cement with 10 mM EDTA, 3 mM ISA and 10 mM citric acid gave limiting log R_d values of – 0.4, 2.0 and 2.3, respectively (Dario et al. 2004a, b). Corresponding DOC concentrations are 100 mM EDTA (C_{10}), 18 mM ISA and 60 mM citric acid (both C_6).

In a follow-up study by Duro et al. (2005)[2], 25 g/L UP2 leaching experiments at room temperature and at pH 12.5 and 13.4 were studied. Results after 700 days show that the yield of degradation products now was considerably lower, 0.7 mM and 2.5 mM in DOC, respectively, despite the

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[1] **Börstell L, 2006.** Organic ligands in a respository for low and intermediatelevel radioactive waste. Unpublished report.

[2] **Duro L, Grivé M, Gaona X, Bruno J, Andersson T, Borén H, Dario M, Allard B, Hagberg J, 2005.** Study of the effect of the fibre mass UP2 degradation products on radionuclide mobilisation. Unpublished report.

slightly higher initial loading than in the previous study and the longer leaching time. At least for the pH 13.4 experiment the results indicate increasing concentration after the last point.

From comparison with the previous studies (Dario et al. 2004a, b) it can be concluded that the temperature is obviously a decisive factor for the yield of the UP2 degradation products from leaching.

In the same study (Duro et al. 2005), a long-term batch sorption study of Eu onto cement, in the presence of the above mentioned pH 13.4 leaching solution diluted to 0.9 mM in DOC, was also made. The limiting log R_d value was about 1.5 after 50 days (Duro et al. 2005). It is noteworthy that this result fits in between the two limiting log R_d values for the 0.3 and 3 mM concentrations, cited above.

From the cited studies (Dario et al. 2004a, b, Duro et al. 2005) it can be concluded that the UP2 leaching products seem to form rather strong complexes with Eu and thereby reduce Eu sorption onto cement, provided that the concentration of them is high enough.

To extend the knowledge database on the subject, the present project "Studies of the complexation properties of degradation products of UP2 and Cellulose" was started in 2004 at Chalmers, Nuclear Chemistry.

At that time, however, the project had the title "Preparation of models to handle organic ligands in Safety Studies" and from the Project Plan the work was intended to consist of four parts:

1) Literature study of organic ligands and their complexation capability.
2) Hypothesis for complexation, based on the literature study.
3) Experimental studies, for hypothesis testing.
4) A final model, considering all previous findings.

The first part, the literature study, was reported in 2006 (Börstell 2006)[3].

The third part of the work, the experimental studies, were then started but unfortunately never concluded, due to personel changes within the project in the beginning of 2007.

The latest project plan was therefore considerably reduced in order to conclude the experimental studies (corresponding to Part 3 of the original project plan) that had been started. The current project plan therefore consists of:

- Alkaline degradation of UP2 filter mass at room temperature.
- Leaching of cement paste to simulate degraded (pH 12.5) conditions.
- Using these materials in Cs, Co, Eu and Th/Zr batch sorption experiments.

In an intermediate work report it was concluded that final reporting of Eu sorption results were impossible because the radionuclide ^{152}Eu was not measurable with the gamma detecting HPGe method in samples where cement was present. It was therefore suggested in the report to try to obtain results for Eu, together with Th/Zr, by using ICPMS measurements of the total concentrations.

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[3] **Börstell L, 2006.** Organic ligands in a respository for low and intermediatelevel radioactive waste. Unpublished report.

2 Objective and Scope

The primary purpose of this work is to measure partitioning coefficients as a function of time for ^{134}Cs (I), ^{60}Co(II), ^{152}Eu(III) and ^{232}Th(IV) (alternatively using natural Zr as metal of IV oxidation state) sorption onto fresh and degraded cement paste in the presence of alkaline degradation products of the fibre mass UP2. The conditions are valid for the Swedish SFR repository for LILW.

In a similar way that alkaline degradation of cellulose will produce isosaccharinic acid (ISA) (Börstell 2006), a potent metal complex forming ligand, the alkaline degradation of the fibre mass UP2 will yield shorter chain degradation products, mainly in the form of carboxylic acids.

The degradation mechanism and the resulting products have been thoroughly studied by Duro et al. (2005), both in the literature and by conducting own experiments. The studies show that forced leaching at elevated temperatures (60 and 85°C) yields other mixtures of degradation products of UP2 (henceforth abbreviated UDP) than degradation at room temperature.

As stated in the Introduction chapter above, literature data for Eu sorption onto cement in the presence of UDP, show that UDP solutions, obtained from alkaline leaching of UP2, are able to reduce the R_d values for Eu sorption with several orders of magnitude (Dario et al. 2004a, b, Duro et al. 2005).

A second aim for the present work is to compare the metal complex formation strength of UDP-containing leaching solutions with three more familiar ligands, namely: ISA, ethylenediamine-tetraacetic acid (EDTA) and citric acid (CA). The latter two ligands are also present in LILW.

The comparison is made by further batch experiments, repeating the radionuclide sorption onto cement experiments with similar ligand concentrations, measured as Non-Purgeable Organic Carbon (NPOC) in the water phase.

In order to obtain solutions for the sorption experiments with UDP mixture and concentration that is representative for repository conditions, leaching experiments of UP2 fibre mass at room temperature and inert atmosphere was conducted first. The conditions were selected as close as possible to the aforementioned study (Duro et al. 2005).

The solid selected for the sorption experiments is cement of the Ordinary Portland Cement (OPC) type. Two cases were considered here: fresh and leached OPC. In the latter case, the alkaline hydroxides of Na and K have been leached out from the material, which gives an altered solid material and water composition of the pore water. It is necessary to have the cement leached in order to maintain pH at 12.5, which will otherwise establish itself to about 13.4 for fresh cement (Andersson et al. 1989).

Hence, the UP2 leaching and radionuclide sorption experiments were also duplicated according to these two cases and the experimental work included also the preparation of the OPCs.

The present study is quite similar in experimental plan and methodology to what have already been done before as part of other work (Dario et al. 2004a, b, Duro et al. 2005). The scope of the present study is much more restricted regarding the number of many different metal complex formation ligands investigated, since it focus entirely on the UDP and the comparison of batch sorption data with EDTA, ISA and citric acid. The present study is, however, expanded compared with previous work with regard to the concentration range of the organic ligands and the number of metals studied.

The experimental methodology basically follows the SKB Method Description for Batch Sorption Measurements (SKB MD 540.002).

It should be noted that the methodology is designed for rock samples and not for cement. In the methodology the prescribed solid to liquid ratio is 1:4. However, in the present work this ratio was reduced to 1:20 since it can be assumed, based on literature data, that cement has a larger metal sorption capacity than rock samples.

The exception is Cs, which usually show stronger sorption onto rock minerals than onto cement. So for example, for batch experiments with similar size fractions (in the range 0.063–0.25 mm) and experimental duration (1 month) values of R_d=0.14 m^3/kg for granite (Byegård et al. 1998) and R_d =$2 \cdot 10^{-3}$ m^3/kg for cement (Holgersson et al. 1998) are reported. The addition of aggregate to cement to form concrete also enhances sorption, results for Cs sorption onto crushed concrete (<2 mm) with R_d =0.1 m^3/kg are reported (Hietanen et al. 1985).

A deviation from the SKB methodology is also that in the present investigation the number of experiments is limited to only one size fraction (0.063–0.125 mm) of the solid phase, while the standard methodology prescribes measurements with several fractions.

The metal tracers to be studied were representatives of different metal oxidation states: Cs(I), Co(II), Eu(III), Th(IV) and/or Zr(IV).

In order to keep the number of experiment multiplication factor down, it was desirable to use one tracer cocktail only, since the number of organic additives (four) and their concentrations (five) to be investigated already gave the experimental series large multiplication factors.

Therefore, all tracers were added together into one cocktail, the first three tracers added as ^{134}Cs, ^{60}Co and ^{152}Eu, intended to be measured with HPGe (High Purity Germanium) high resolution energy-discriminating gamma-detector, while the non-radioactive tracers Th and Zr, were added as natural elements, to be measured with an ICP-MS instrument.

However, as the experiments progressed, it was found that due to the strong sorption of Eu it was necessary to measure the higher total Eu concentration with ICPMS, instead of radiometric detection of ^{152}Eu. Because of the method of production, ^{151}Eu(n,γ)^{152}Eu, this radionuclide always has company of non-radioactive Eu “carrier” isotopes in excess of the radioactive nuclide.

The batch sorption experiments were accomplished by preparing batches of 0.5 g of crushed cement suspended in 10 mL artificial cement pore-waters in polypropylene centrifugation tubes. After a certain pre-conditioning period of the batch samples with water exchanges, the tracer mixture was added. Samples of the water phase were taken after 1 day, 1 week, 1 month, 3 months and 6 months of contacting time. All experiments were made in a nitrogen-flushed glove box.

The metal concentrations of tracer in the batch experiments were targeted to: 10^{-8} M for Co, 10^{-9} M for Eu, 10^{-10} M for Th and Zr. This was assumed to be low enough metal concentrations to go clear below metal hydroxide solubility limits. The tracers were also equilibrated with the artificial cement pore-waters and organic ligands before the start of the experiments.

A number of parameters that may affect metal sorption onto cement in the presence of organic ligands were investigated:

- Solid phases: one cement type OPC, 0.063–0.125 mm sieved fraction, in two states; fresh and leached.
- Organic Ligands:
  - UDP from UP2 leaching with two different artificial pore-waters.
  - ligands for comparison of UDP complexation strength: ISA, EDTA and citric acid (CA).
- Ligand concentrations:
  - Highest concentration will be DOC level as measured in UP2 leachings.
  - In addition, four different dilutions.
- Bulk water phases: artificial fresh and leached cement water for corresponding solid.
- Replicates: 2 (3 for references, 1 for acidic references).

3 Equipment

3.1 Description of Equipment

3.1.1 Equipment used in the cement degradation experiments

Cement samples were cast in 100 mL polypropylene beakers (Sarstedt 75.563). After the initial casting all work with the cement samples, except centrifugation and analyses, was done in a N_2 flushed glove-box. For the analyses of total alkalinity, N_2 bubbling was used in the titration vessel.

The cement samples were crushed with hammer, agate mortar and pestle. Sieving of the crushed cement was made with 0.063–0.125 mm geological sieves (Retsch). Leaching of cement was made in 250 mL polypropylene centrifugation bottles (Nalge 3120-0250). Phase separation at the analyses of liquid samples was accomplished with a centrifuge (Beckman J2-21 and JA-14 rotor).

Total alkaliny was measured using a titrator and a pH-electrode (Radiometer ABU-90 burette, TIM-90 controller and pHC3006-9 electrode). Major cationic constituents analyses were made using an ion chromatograph with conductivity detector (Dionex DX-100 system, CS-12A 4 mm cation exchange column, CSRS-Ultra II background suppressor, 20 mM methanesulfonic acid eluent).

Pure water in all applications was produced by running double-distilled water through a Milli-Q 185 Plus.

3.1.2 Equipment used in the UP2 degradation experiments

The preparation of synthetic concrete pore-water and UP2 leaching were made in a N_2 flushed glove-box. Paper filters of type Munktell 00H were used for filtering $Ca(OH)_2$ from the synthetic concrete water. 1L polypropylene centrifuge bottles (Nalge 3120-1000), previously washed with 3M HCl and rinsed with water, were used for water storage. The same type of bottles were also used for UP2 degradation experiments, except that they were wrapped in Al foil to minimize exposure of the content to light.

Analyses of total alkalinity and major cations in synthetic concrete water were accomplished with the same equipment as stated in 3.1.1. Phase separation at the analyses of UP2 leaching solution was made by filtration of small portions of the solutions through a Munktell 00H paper filter.

The samples were analyzed for Total Organic Carbon using an instrument of the type Shimadzu TOC-5000A. TOC measurements were made in the Non-Purgeable Organic Carbon (NPOC) mode, where volatile compounds are bubbled away from the acidified samples together with CO_2 before the measurement.

The NPOC mode is generally recommended for measurement of low level of organics because TOC is measured as the difference between measurements of Total Carbon (TC) and Dissolved Inorganic Carbon (DIC), while NPOC only requires one measurement.

Pure water in all applications was produced by running double-distilled water through a Milli-Q 185 Plus.

3.1.3 Equipment used in the batch sorption experiments

For the batch sorption experiments centrifugation tubes made of polypropylene (Sarstedt 60.541, non-sterile), with a nominal capacity of 13 mL were used.

The experiments, except the phase separation step and radiotracer measurements, were made in a N_2-atmosphere glove-box of an elderly type, with a constant N_2 overpressure flush. The glove-box was equipped with an oxygen scavenger (Anoxy-Cil). Equipment for measurement of oxygen levels inside the box were, however, not available.

40 mL polypropylene vessels (Sarstedt 62.555) were used for preparation of tracer/organics solutions.

For the phase separation, a Beckman J2-21 centrifuge, equipped with a JA-20.1 rotor, was used. The temperature control of the rotor was set to 20±5 °C.

For sampling, Gilson pipettes were used as well as a Mettler-Toledo balance (10 mg precision). The functioning of the balance was checked periodically with calibration weights.

For radiotracer measurements of ^{134}Cs, ^{60}Co and ^{152}Eu a High-Purity Germanium detector (HPGe) of the type Canberra Gamma Analyst with Genie 2000 software was used.

For measurements of total Eu, Th and Zr and additional background measurements of Cs, Co, Eu, Th and Zr, an Inductively Coupled Plasma Mass spectrometer (ICPMS) of the type PerkinElmer Elan 6000 was used.

Background measurements of NPOC were also made, the instrumentation is described in Section 3.1.2.

Pure water in all applications was produced by running double-distilled water through a Milli-Q 185 Plus.

3.2 Description of interpretation tools

3.2.1 Evaluation of sorption coefficients

The evaluation of sorption coefficients R_d(m^3/kg) was made by a methodology which is largely identical with the SKB Method Description for evaluating batch sorption measurements with minerals (SKB MD 540.002).

The only deviation from the standard method is how wall sorption data is interpreted and used for correcting results for the actual batch measurements. Wall sorption is the amount of tracer that sorbs on the walls of the container used in the batch sorption experiments. In the modified evaluation method used here, R_d values *for the wall* is extracted from the separate wall sorption measurements and these values, here labeled L_d, are subsequently used for correcting the batch sorption results. The equation for calculating R_d is:

$$R_d = \left(\frac{\overline{C} \cdot V_{stam} \cdot V_{utt,n}}{A_{utt,n}} - \left(V_0 - \sum_{i=1}^{n-1} V_{utt,i} \right) - L_d - \frac{V_{utt,n} \cdot \sum_{i=1}^{n-1} A_{utt,i}}{A_{utt,n}} \right) \cdot \frac{1}{10^6 \cdot m} \qquad (3\text{-}1)$$

The parameters are:

$\overline{C}$: mean concentration of the radiotracer stock solution (in cpm/mL), as measured in separate acidic reference experiments

V_{stam}: the volume of tracer initially added (mL)

$V_{utt,\,n}$: volume of sample taken at sampling n (mL)

$A_{utt,\,n}$: counting rate or mass of sample, taken at sampling n (cpm)

V_0: volume at start of experiment (mL)

L_d: R_d for wall times the mass of the tube involved in wall sorption (mL), as measured in separate wall sorption experiments

m: dry mass of cement (kg)

Note that the mass of the wall involved in wall sorption is unknown, therefore the wall sorption coefficient R_d times mass of wall is collected together as L_d.

A detailed deduction of (3-1) can be found elsewhere (Andersson et al. 2008). In the standard methodology the wall sorption correction is made by assuming that the measured amount of tracer sorbed in the separate wall sorption experiments is the same as in the batch experiments, without assuming R_d values for wall sorption, which means that any feedback on wall sorption from batch sorption onto the solid phase is omitted.

3.2.2 Evaluation of detection levels for sorption coefficients

The methodology for calculating theoretical detection levels for radiometric measurements is based on counting statistics only, where the error associated with the number of counts is the square root of this value. Measurement errors associated with volume and mass measurements are not considered.

When measuring of R_d coefficients with the batch method there are actually no less than five detection levels (DL) to consider: upper and lower DL for the supporting L_d experiment, the "critical" value of L_d beyond where no R_d values can be evaluated and finally, upper and lower DL for R_d itself.

Starting with L_d, it is clear that there is an upper DL when the counting rate in the sample approaches background values, due to strong sorption onto the tube wall. At the one sigma confidence level, the criterion for detection is here taken as

$$P = B + \sqrt{B} + \sqrt{P} \qquad (3\text{-}2)$$

P is the number of counts in the sample and B is the corresponding value for the background.

This L_d upper DL is then calculated as

$$L_{d,Limit} = \left(\frac{R_0 - P}{P - B} \right) \cdot V_{0,ref} \qquad (3\text{-}3)$$

Where

$$R_0 = \frac{V_{utt,ref} \cdot \overline{C} \cdot V_{stam,ref} \cdot t_{count}}{V_{0,ref}} \qquad (3\text{-}4)$$

R_0 is the number of counts in the acidic reference, t_{count} is the counting time, and the other parameters $V_{0,ref}$, $V_{utt,ref}$, $V_{stam,ref}$ have the same meaning as defined in the previous section, but are now with respect to a wall sorption reference experiment (without solid phase). The sample volume $V_{utt,ref}$ taken from acidic and wall sorption tubes is assumed to be the same.

However, although this upper level of L_d do have importance for judging how strong wall sorption that can be detected, it will not have any importance if a R_d value for a solid phase shall be calculated as well.

To be able to calculate R_d, the acidic reference must first be corrected for wall sorption

$$R = R_0 - L_d \cdot (P - B) / V_0 \qquad (3\text{-}5)$$

Here R is used for the corrected value.

In addition, the criteria for detection are now chosen as

$$\begin{aligned} P &= B + \sqrt{B} + \sqrt{P} \\ R &= P + \sqrt{R} + \sqrt{P} \end{aligned} \qquad (3\text{-}6)$$

Again using eq. (3-3) and solving the equation system for L_d yields the “critical” $L_{d,crit}$, the largest value of the wall sorption coefficient where R_d values of solid phase sorption coefficients can be calculated.

Turning now to the other end of the measurable range, it is also clear that there is a lower DL for L_d, where the difference between acidic reference and wall sorption reference is small.

The criteria for detection is then taken as

$$P = R_0 - \sqrt{R_0} - \sqrt{P} \tag{3-7}$$

Using eq. (3-7) for P the L_d lower DL can then be calculated with the eq. (3-3), above.

The upper and lower DL of R_d will depend on which L_d that is measured, as long as this value is below the “critical” L_d.

The detection levels for R_d are calculated as

$$R_{d,Limit} = \frac{(R-P)\cdot V_0}{(P-B)\cdot m} \tag{3-8}$$

For upper DL the criterion for detection is the same as for L_d, that is eq. (3-2). However, for the lower DL the criterion is now

$$P = R - \sqrt{R} - \sqrt{P} \tag{3-9}$$

where the wall-sorption corrected reference R from eq. (3-5) is used and inserted in eq. (3-7) instead of R_0 .

For non-radiometric measurements (i.e. ICP-MS), the method described above was also used but the number of counts is replaced by the measured average mass intensity and the error associated with that measurement. The error associated with the average mass intensity was taken as 1% of the measured mass intensity, as a typical value.

For results of DL calculations, see Results section 5.3.2.

4 Execution

4.1 Cement degradation experiments

4.1.1 Preparation of cement paste samples

400 g of OPC paste (Degerhamn Anläggningscement) and 200 g water was mixed for 15–20 min. and 75–80 mL then poured into each of three 100 mL plastic beakers. The following day the beakers with cement were placed in a N_2 filled glove-box, with the beaker lids only loosely fitted, to allow contact between the content and the inert atmosphere.

During the initial curing time it was found that some water had to be added in order to have a few mm of water standing above the surface of the cement and thereby to ensure continued hydration. The cement samples were cured for totally five months.

Two cement samples were smashed to smaller pieces with a hammer and then allowed to superficially dry, by placing them in front of a fan overnight. Then, the pieces were crushed further, using a mortar and pestle. The resulting cement powder was sieved to the 0.063–0.125 mm fraction.

One intact cement sample was placed in an oven at about 40°C for a week and thereafter weighed for density measurement.

4.1.2 Cement degradation

For the leaching of cement, two 12.5 g samples of cement powder were transferred to 250 mL polypropylene centrifuge flasks and 250 mL water was added to each flask. In addition, a 5 g sample was added to 100 mL water. The smaller batch was prepared for monitoring of the long-term approach of equilibrium in the initial leaching water (without water exchange).

4 mL of samples were taken from each of the three leaching solutions once a week and analysed for 1) total alkalinity, using 0.1 mL sample diluted to 40 mL and titrated with 0.01 M HCl (Fixanal), and 2) major cations, using 0.1 to 30 mM solutions of p.A quality Na, K and Ca salts as standards.

After about 1 month of sampling, the two 250 mL flasks were centrifuged at 9,000 rpm (10,000 g) at 30 min and the leaching solution was exchanged for fresh Milli-Q water. Sampling for total alkalinity and major cations was then continued, as above.

Based on the outcome of results, the procedure of water replacement was repeated two more times.

The cement was then completely separated from the solution by centrifugation, as above, and left to dry for several days in N_2. However, it was found to be necessary to also use gentle heating (50°C) to completely dry the leached cement powder.

4.2 UP2 degradation experiments

4.2.1 Preparation of synthetic cement pore-water

Since alkaline conditions are to be expected in cement pore-water, an artificial Fresh Cement Pore-Water (FCPW) was prepared from a recipe based on pore-water pressings of Standard Portland cement paste (Andersson et al. 1989).

The FCPW was made by dissolving 2.6494 g/L NaOH (AkzoNobel, 98.5%) and 6.0776 g/L KOH (AkzoNobel, 85%) in Milli-Q water. Then 1.25 g/L $Ca(OH)_2$ (p.A. , Merck, 96%) was added, which is enough to saturate the water. After 24 hours of stirring the excess $Ca(OH)_2$ was removed by filtering the suspension.

For a corresponding artificial Leached Cement Pore-Water (LCPW), the alkalis were simply omitted from the recipe and the water was only saturated with $Ca(OH)_2$ and filtered, as above.

The synthetic waters were analyzed for total alkalinity and major cations. 0.1–0.4 mL samples were diluted to 40 mL for the titrations with 0.1 M HCl (Fixanal). For ion chromatography, samples of FCPW and LCPW were diluted to 1:10 and 1:5, respectively, and solutions of 0.5 to 10 mM of p.A quality Na, K and Ca salts were used as standards.

4.2.2 UP2 degradation experiments

One batch of UP2 leaching was started with 19 g fibre mass suspended in each of two bottles of respectively 0.8 L FCPW and LCPW (24 g/L). Corresponding reference experiments with no UP2 addition were also started, in order to measure any background contribution of organic materials. Another batch of four bottles with exactly the same composition was started about one month later.

5 mL samples from the two batches were taken using filtration for the phase separation. Samples were taken between about 200 and 300 days of leaching at four different occasions and analyzed for NPOC. One additional sample was taken at 1,200 days. The samples were acidified with HCl to pH 2 and allowed to stand for one week before measurements (see results Section for outcome of procedure testing). Standard solutions of 1, 5, 10 and 30 ppm C were prepared by diluting a 500 ppm C solution with FCPW. Thereafter these solutions were acidified to pH 2 with HCl. The 500 ppm solution was prepared by dissolving p.A. quality potassium hydrogen phtalate in water.

4.3 Batch sorption experiments

4.3.1 Overview

An overview of the experiments, considering also reference experiments for 1) total added tracer (acidic references), and 2) corrections for wall sorption on the sample tubes (wall references), is shown in Table 4-1. In total, 214 separate experiments were made.

4.3.2 Preparation of acidic tracer cocktail

For preparing the tracer solutions an acidic concentrated cocktail of the tracers were prepared in 1 M HCl. The tracer stock solutions used were for ^{60}Co: $1.0 \cdot 10^{-6}$ M Co, ^{134}Cs: $5.6 \cdot 10^{-2}$ M Cs and ^{152}Eu: $9.5 \cdot 10^{-6}$ M Eu in total concentrations (including carrier isotopes). The total concentrations of the Co and Eu stock solutions have previously been analyzed by ICPMS. For Cs a specification sheet was still available (Polatom, CsCl solution).

For the non-radioactive tracers Th and Zr, 10^{-7} M solutions in 1 M HCl were prepared from $Th(NO_3)_4$ and $Zr(NO_3)_4$ salts.

The final concentrations in the 2.47 mL mixed stock solution in 1 M HCl were calculated to $8 \cdot 10^{-4}$ M Cs, $4 \cdot 10^{-7}$ M Co, $4 \cdot 10^{-6}$ M Eu and $8 \cdot 10^{-7}$ M Th and Zr. This would be further diluted when the cocktail was added to the solution of organic additives (see section 4.3.5. below).

Table 4-1. Experimental schedule for the batch sorption experiments, multiplication factors (normal) and number of experiments (bold).

	Acidic ref.	Acidic ref +ligand	Wall ref.	Wall ref. +ligand	Wall+solid	Wall+solid +ligand
Sol.phases	–	–	–	–	2	2
Liq. Phases	2	2	2	2	1*	1*
Ligands	–	4	–	4	–	4
Ligand conc.	–	5	–	5	–	5
Replicates	1	1	3	2	3	2
Total	**2**	**40**	**6**	**80**	**6**	**80**

*corresponds to solid phase, no further multiplication.

4.3.3 Preparation of organic additives

The preparation of synthetic cement pore-waters have already been described under Section 4.2.1 above.

The organic additives to cement pore-waters were prepared according the scheme presented in Table 4-2.

The UDP solutions were obtained from leaching of UP2, as described in Section 4.2.2 above. Leaching solution as obtained after about 300 days of leaching were used.

The ISA solutions were obtained from diluting a 0.5 M NaISA solution that have been made by purification and ion-exchange from commercial $Ca(ISA)_2$ (AlfaAesar), using a standard procedure (Allard and Ekberg 2006). EDTA and citric acid solutions were prepared from dissolving commercial products (Merck, p.A. quality) in water. The final dilutions were made in either FCPW or LCPW.

It was originally intended to have solution of the other ligands as 50 ppm DOC as the maximum concentration. However, by a mistake, the solutions were instead made as 50 ppm of the respective ligand. Since ISA and citric acid are C_6 molecules and EDTA is a C_{10} molecule this gave considerably higher concentrations of DOC for these ligands then what was originally intended.

It still makes it possible to compare sorption experiments of the ligands with the UDP experiments, but only the lowest concentrations (C4–C5) of the ligands are in the range of the highest UDP concentrations (C1–C2).

4.3.4 Preparations of solid phases

Fresh and leached cement was obtained as described under Section 4.1 above.

Before the actual sorption experiments were started, the cement was washed with FCPW or LCPW in the following way. The empty 13 mL polypropylene sample tubes were weighed, then 0.5 g of solid phases of fresh or leached cement was added and finally 10 mL FCPW or LCPW was added and the tubes shaken.

After about one week the samples were centrifuged at 8,000 rpm (8,000 g) at 30 min. 9 mL of the water phase was removed and exchanged for the same amount of new FCPW/LCPW.

This water exchange procedure was repeated two times before the actual sorption experiments were commenced.

Background levels, originating from cement or centrifugation tubes, in some of the washings, were measured in respect of: 1) NPOC with TOC instrument and 2) Cs, Co, Th and Zr with ICPMS.

The procedure for NPOC measurements have already been described in Section 4.2.2.

For the ICP-MS analyses all samples were diluted 100 times with 1 M HNO_3 (Merck, Suprapur) and internal standards of 2.5 ppb Bi and In (High-Purity Standards, same brand also for Cs, Co, Th, Zr) were added.

Table 4-2. 1 Dilution scheme for the organic additives in the sorption experiments, concentrations Dissolved Organic Carbon (ppm), measured as Non-Purgeable Organic Carbon for UDP, otherwise calculated from prepared solutions.

additive	water	C1	C2	C3	C4	C5
UDP	FCPW	33	16.5	8.3	4.1	2.1
	LCPW	27	13.5	6.8	3.4	1.7
ISA, CA	FCPW	300	150	75	38	19
	LCPW	300	150	75	38	19
EDTA	FCPW	500	250	125	63	31
	LCPW	500	250	125	63	31

These samples were run with the standard addition method: a given sample was split into three 0.5 mL samples where the last two had a standard addition, 0.05 and 0.25 mL of 100 ppb standard of the element to be measured. All samples were then diluted to 5 mL with 1M HNO_3.

4.3.5 Batch sorption experiments

Before starting the sorption experiments, a 37 mL batch of a particular organic solution (see Section 4.3.3) was taken to a 40 mL polypropylene vessel and 37 µL acidic tracer solution (see section 4.3.2) was added. The resulting 1,000 times diluted tracer cocktail (calculated values $8\cdot10^{-7}$ M Cs, $4\cdot10^{-10}$ M Co, $4\cdot10^{-9}$ M Eu and $8\cdot10^{-10}$ M Th and Zr) with organic ligand in FCPW or LCPW, was allowed to equilibrate over night.

Then, the water in the centrifugation tubes, with or without cement, was exchanged, as have been described in Section 4.3.4 above, but at this time the exchange water was the tracer and organics cocktail.

In addition, acidic references for measurement of tracer concentration were prepared by taking 1 mL of the tracer/organics cocktail to a sample tube and then add 5 mL 1 M HCl.

All tubes with their content were weighed before and after the addition of tracer cocktail.

Sampling of the water phase was made at 1 day, 1 week, 1 month, 3 months and 6 months. The sampling procedure was made as follows. For phase separation, the tubes were centrifuged outside the glove-box at 8,000 rpm (8,000 G) for 30 min. Then, the tubes were returned to the box and two 0.1 mL samples were taken: one for HPGe gamma measurements and one for ICPMS to separate sample tubes. All samples taken were weighed.

For gamma measurements, 0.5 mL of 0.1 M HCl was added to the sample and the counting rate measured for 3 hours. The net counts, which are background corrected values given by the detector software, at gamma energies 121, 605 and 1,173 keV for ^{152}Eu, ^{134}Cs and ^{60}Co, respectively, and also the given detector live time were used for calculation of count rates.

For ICPMS measurements, 5 mL of 1 M HNO_3 (Merck, Suprapur) with internal standards of 2.5 ppb Bi and In (High Purity Standards) for correcting instrument drift, was added to the sample. Standard solutions with 0.05, 0.1, 0.5 and 1 ppb Eu, Th and Zr, made from diluting 10 ppm commercial ICPMS standards (High Purity Standards) in 1 M HNO_3 with internal standards were used for the external calibration. The mass numbers measured were 153, 232 and 92, respectively.

The tubes with sorption experiments were shaken for complete mixing of cement and liquid phase after each sampling.

5 Results

5.1 Results of cement degradation experiments

The weight of one casted piece of cement with a defined volume was 127 g and the bulk density of the material was calculated to 1,639 kg/m^3.

Crushing and sieving of the other two pieces gave a yield of the 0.063–0.125 mm fraction of about 90 g (35% yield).

It was found that, in total, three water exchanges were needed to leach out the Na and K alkalis from the crushed cement of size fraction 0.063–0.125 mm.

The results of the cement leaching are collected in Tables 5.1-4 and shown as diagrams in Figures A1-1–A1-4 in Appendix 1.

Table 5-1. Total alkalinity $[OH]_{tot}$ in the leaching solution of cement (mM). Mean values of triplicate titrations.

Water	Days	Sample#1	Sample#2	Sample#3
1	7	32.3	35.5	41.3
	14	40.8	41.2	41.4
	21	45.3	45.9	45.7
	28	45.1	45.5	45.6
	35	45.4	46.1	44.9
	49	–	–	44.2
	56	–	–	45.8
2	7	33.7	33.3	
	14	37.1	37.5	
	21	37.8	37.9	
	28	38.7	38.4	
	35	39.6	39.6	
	111	37.5	36.3	
3	7	22.7	23.3	
	14	31.5	31.1	
	22	34.2	34.5	
	28	35.3	36.1	
4	5	22	21.1	
	12	30.5	28.9	
	19	33.5	34.2	
	26	35.2	36	
	33	36.4	37.1	

Table 5-2. Total calcium concentration [Ca]tot in the leaching solution of cement (mM). Mean values of duplicate results from cation chromatograms.

Water	Days	Sample#1	Sample#2	Sample#3
1	7	14.9	15.8	11.0
	14	17.1	17.9	18.2
	21	18.2	18.3	18.9
	28	17.9	18.4	18.3
	35	17.5	17.6	17.0
	49	–	–	9.2
	56	–	–	25.4
2	7	7.1	5.4	
	14	23.5	23.4	
	21	23.8	24.1	
	28	24.4	24.4	
	35	25.2	25.0	
	111	25.9	26.1	
3	7	16.7	16.1	
	14	22.8	23.5	
	22	24.4	25.3	
	28	30.2	30.4	
4	5	15.1	15.4	
	12	23.6	23.3	
	19	25.3	25.6	
	26	30.0	30.7	
	33	28.8	30.2	

Total alkalinity decreases with the water exchanges. The development of total alkalinity (i.e. out-diffusion of hydroxide) after a new exchange of water shows no change between water 3 and 4 (Appendix 1, Figure A1-1). This indicates that at this stage the Na and K alkalis have been removed from the cement pores and that $Ca(OH)_2$ (portlandite) is now the primary source of hydroxide.

Leaching of total calcium, on the other hand, shows increasing concentrations after consecutive water exchanges, up to the last exchange. Then, as with the total alkalinity, water 3 and 4 were as good as identical in the leaching development of total calcium (Appendix 1, Figure A1-2).

Sodium and potassium (Appendix 1, Figures A1-3 and A1-4) both show the expected decreasing concentrations after consecutive water exchanges. In the last water the concentrations were close to detection limits.

The additional sample 3, where only the initial water was monitored and where no exchanges were made, show some erratic behavior in the long term leaching development of calcium and sodium (potassium was not possible to analyze in the last two samples). This cannot be explained, but may be due to CO_2 ingress in the alkaline samples because of a mistake made by leaving the samples for ion chromatography outside the glove-box for a longer period of time. The separate samples for total alkalinity, titrated immediately after taken out from the glove-box, seem not to have been affected (Table 5-1).

Table 5-3. Sodium concentration in the leaching solution of cement (mM). Mean values of duplicate results from cation chromatograms.

Water	Days	Sample#1	Sample#2	Sample#3
1	7	1.1	1.1	1.1
	14	1.0	1.1	1.1
	21	1.1	1.2	1.1
	28	1.1	1.1	1.1
	35	1.1	1.1	1.0
	49	–	–	0.59
	56	–	–	0.40
2	7	0.11	0.13	
	14	0.08	0.07	
	21	0.08	0.08	
	28	0.09	0.08	
	35	0.09	0.09	
	111	0.15	0.14	
3	7	0.04	0.04	
	14	0.02	0.01	
	22	0.03	0.02	
	28	0.02	not detected.	
4	5	not detected	not detected	
	12	0.02	0.02	
	19	not detected	not detected	
	26	0.01	0.001	
	33	0.03	0.02	

Table 5-4. Potassium concentration in the leaching solution of cement (mM). Mean values of duplicate results from cation chromatograms.

Water	Days	Sample#1	Sample#2	Sample#3
1	7	3.8	3.8	3.4
	14	3.6	3.8	3.5
	21	3.8	3.8	3.5
	28	3.7	3.7	3.4
	35	3.7	3.7	3.3
	49	–	–	not analyzed
	56	–	–	not analyzed
2	7	0.45	0.47	
	14	0.48	0.47	
	21	0.48	0.47	
	28	0.49	0.48	
	35	0.49	0.47	
	111	0.54	0.53	
3	7	0.15	0.16	
	14	0.15	0.14	
	22	0.15	0.15	
	28	0.14	0.14	
4	5	0.15	0.16	
	12	0.04	0.03	
	19	0.04	0.04	
	26	0.02	not detected	
	33	0.05	0.04	

5.2 Results of UP2 degradation experiments

The results from analyses of the two types of synthetic cement pore-water, used in the leaching of UP2 and batch sorption experiments, are shown in Table 5-5.

The measured values were compared with PHREEQC calculations, based on analyzed Na and K concentrations together with the amount of Ca actually added (17 mmoles/L) and a condition of solution saturation with portlandite.

For FCPW the analyzed $[Ca]_{tot}$ and $[OH]_{tot}$ values are smaller than predicted. This may indicate some CO_2 ingression to have taken place, which can give this effect.

In the actual leaching experiments, numerous troubles were experienced with the TOC instrument before any samples could actually be measured, the first after about 160 days of leaching. Altogether the NPOC content of the leaching solutions were measured at five occasions, up to 1,200 days of leaching. The results are collected in Table 5.6.

The results of the NPOC measurements were initially scattered and especially the high levels found at the second sampling occasion, even in the reference bottles without UP2, were, at the moment of measurement, puzzling.

The measured high levels in references were later related to the standing time of acidified samples before measurement. Acidification of all samples and standards is necessary to remove inorganic carbon, in the form of carbonates, otherwise they will add to the measured signal. In the cases where high levels were found, in both references and leaching solutions, the samples were run at the same day that they were sampled and acidified. In the three last measurements the samples were measured first after one week after acidification.

The presumably substantial amount of carbonate in the samples, as measured at the second sampling occasion, is probably due to handling of alkaline samples outside the glove-box, without acidification.

A prolonged standing-time after acidification was therefore necessary to completely remove carbonate from the samples. Even as the initially alkaline samples are acidified to pH 2 (checked with pH sticks) it obviously takes a while for carbonate to be converted to CO_2 and thus possible to purge from solution.

The initial results in Table 5-6 therefore show the method development of the NPOC measurements, rather than any evolution with time in the leaching solutions. Only the three last measurements were judged as reliable of actual NPOC levels in the leaching solutions.

Table 5-5. Analyzed composition of the synthetic cement pore-waters (mM). Na and K concentrations were used to calculate pH at 20°C and 17 mM/L $Ca(OH)_2$ (saturated) conditions with the geochemical speciation code PHREEQC.

	Fresh Cement Pore-Water	Leached Cement Pore Water
$[OH]_{tot}$	155 ±5	28 ±1
$[Ca]_{tot}$	11 ±2	16 ±1
[Na]	73 ±14	3.6 ±0.3
[K]	98 ±17	3.5 ±0.0
pH*	13.3	12.6
$[Ca]_{tot}$*	14	14
$[OH]_{tot}$*	199	35
ionic strength*	191	42

*from PHREEQC calculations

Table 5-6. Measured NPOC in leaching solutions of UP2 and references, in ppm. Mean values of triplicate results.

Batch#	Days	FCPW+UP2	FCPW ref.	LCPW+UP2	LCPW+ref.
1	209	25.5	48.1	103	2.9
	307	283	179	183	228.1
	311	40.1	18.3	33.7	1.0
	319	33.1	0.4	28.0	0.9
	1,195	166	13	39.7	<0.08
2	167	25.5	67.8	89.5	2.8
	265	177.8	280.9	85.3	293.9
	269	38.4	0.8	28.0	0.8
	277	33.0	0.4	26.8	0.3
	1,153	145	<0.08	47.9	0.5

5.3 Results of batch sorption experiments

5.3.1 Measurements of background concentrations

The results of the NPOC measurements of background concentrations in cement and centrifuge tube washings are presented in Table 5.7.

According to the results from last washing, some contributions to organic amounts in the sorption experiments can be expected: about 1.5 ppm C from the centrifugation tubes and about 1.0 ppm C from the fresh cement. The organic contribution from cement has obviously disappeared during leaching.

The corresponding results of the ICPMS measurements of background concentrations are presented in Tables 5-8–5-11.

Table 5-7. Non-Purgeable Organic Carbon background concentrations(ppm) in the washings of cement and centrifugation tubes.

Washing	FCPW+cement	FCPW	LCPW+cement	LCPW
1	12.3	7.4	9.2	5.8
2	2.6	1.7	2.0	2.6
3	2.7	1.8	1.4	1.5

Table 5-8. Th background concentrations(nM) in washings of cement and centrifugation tubes. Additional background concentrations from tracer cocktail are given in parantheses.

Washing	FCPW+cement	FCPW	LCPW+cement	LCPW
input water	–	3.7 (0.08)	–	52 (0.08)
1	7,800	not measured	86	10
2	150	5.4	0.01	1.3
3	0.4	0.7	1.8	0.8

Table 5-9. Zr background concentrations(nM) in washings of cement and centrifugation tubes. Additional background concentrations from tracer cocktail are given in parantheses.

Washing	FCPW+cement	FCPW	LCPW+cement	LCPW
input water	–	46 (0.08)	–	110 (0.08)
1	430	not measured	700	8,700
2	140	69	140	3,200
3	15	39	11	5.8

Table 5-10. Cs background concentrations(nM) in washings of cement and centrifugation tubes. Additional background concentrations from tracer cocktail are given in parantheses.

Washing	FCPW+cement	FCPW	LCPW+cement	LCPW
input water	–	46 (800)	–	10 (800)
1	170	not measured	57	70
2	46	38	10	12
3	23	31	0.4	5.7

Table 5-11. Co background concentrations(nM) in washings of cement and centrifugation tubes. Additional background concentrations from tracer cocktail are given in parantheses.

Washing	FCPW+cement	FCPW	LCPW+cement	LCPW
input water	–	35 (0.4)	–	52 (0.4)
1	29	not measured	2,600	2.7
2	580	22	15	5.1
3	97	140	2.4	15

The results show that the elemental background concentrations after the three water exchanges are in all cases lower or similar to the input water. This will assure that the main contribution of tracer element is added in the start of the experiment and not leached from cement or tube walls.

The expected values of contribution from the tracers that will be added (1,000 time dilution of acidified tracer cocktail) to the input solution are given in parentheses.

For the non-radioactive tracers Th and Zr it seems that the addition of tracer to FCPW/LCPW is completely superfluous, since background concentrations of these elements are larger or comparable to added tracers, which should be of the same natural isotopic composition as the background.

5.3.2 Calculated detection limits for batch sorption experiments

The theoretical detection limits of R_d values for each radiotracer was calculated according to the methods described in Section 3.2.2, for some typical wall sorption coefficients L_d that was measured in the experimental series. The results are presented in Table 5-12 below.

Note that these are detection levels based on measurement statistics only, in practice however, the limits also depends on errors in volume measurements (usually giving negative L_d or R_d values when sorption is weak) or simply on a zero signal at the detection attempt (giving division by zero error when sorption is strong), hence the appearance of not detectable (=n.d.) values in the sections below.

Table 5-12. Calculated detection limits of sorption coefficients R_d(m³/kg) for some typical wall sorption coefficients L_d(mL), encountered in the batch sorption experiments. Boldface L_d values are calculated lower detection limits of wall sorption coefficient $L_{d,min}$, the corresponding detection limits in R_d are also given.

Series	L_d	$R_{d,max}$	$R_{d,min}$
Cs	**0.2**	**6**	**$3\cdot10^{-4}$**
	1	6	$4\cdot10^{-4}$
Co	**3**	**0.11**	**$7\cdot10^{-3}$**
	5	0.10	$7\cdot10^{-3}$
Eu	**0.5**	**2.7**	**$1\cdot10^{-3}$**
	150	2.5	$4\cdot10^{-3}$

In the following sections, all R_d or L_d values that are calculable and positive but below the calculated lower detection limits of the respective parameter are put between ( ) and all R_d values that are above the calculated upper detection limits are marked with *. The measured wall sorption was never near any upper detection limit.

Errors in R_d are given as standard deviations for replicate experiments. If no error is given, one of the replicates was not detectable. A zero error (±0)means that the error is smaller than the significant number of the associated R_d or L_d value, i.e 2±0.4 will be 2±0 but 2±0.5 will be 2±1.

5.3.3 Sorption of ^{134}Cs onto cement in the presence of UDP

The results for Cs sorption onto tube walls with UDP in FCPW, compared with reference case (no organics added), are shown in Table 5-13.

Table 5-13. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of UP2 degradation products (UDP) in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
1 week	0.3	n.d.	0.2	0.2	0.3	0.5
1 month	0.4	n.d	n.d.	(0.0)	(0.1)	0.4
3 months	0.7	n.d.	0.6	(0.1)	0.4	0.4
6 months	0.4	n.d.	n.d.	0.6	0.7	0.4

The results for Cs sorption onto cement with UDP in FCPW, compared with reference case (no organics added) are shown in Table 5-14.

Table 5-14. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of UP2 degradation products (UDP) in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3E–04)	n.d.	n.d.	n.d.	n.d.	n.d.
1 week	(3E–04)	n.d.	(3E–04)	n.d.	8 ±2E–04	n.d.
1 month	(2E–04)	n.d.	n.d.	4E–04	6 ±4E–04	(6E–05)
3 months	(6E–05)	n.d.	(1E–04)	(2E–04)	n.d.	1E–03
6 months	3 ±3E–03	n.d.	n.d.	n.d.	n.d.	4E–04

The results for Cs sorption onto tube walls with UDP in LCPW, compared with reference case (no organics added), are shown in Table 5-15.

Table 5-15. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of UP2 degradation products (UDP) in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	n.d.	(0.1)	(0.1)	0.8
1 week	0.6	n.d.	n.d.	0.2	n.d.	0.4
1 month	0.6	n.d.	n.d.	0.3	0.2	0.4
3 months	0.6	n.d.	n.d.	0.3	0.3	0.7
6 months	0.2	n.d.	n.d.	0.4	0.2	0.4

The results for Cs sorption onto cement with UDP in LCPW, compared with reference case (no organics added) are shown in Table 5-16.

Table 5-16. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of UP2 degradation products (UDP) in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	4E–04	6 ±3E–04	5 ±6E–04	n.d.
1 week	7E–04	n.d.	1E–03	6E–04	4 ±1E–04	n.d.
1 month	(2E–04)	n.d.	1 ±1E–03	2 ±0E–03	1 ±0E–03	2 ±0E–03
3 months	1 ±1E–03	(8E–05)	2 ±1E–03	1E–03	1 ±0E–03	2E–03
6 months	2± 0E–03	6E–04	n.d.	1E–03	4 ±1E–04	2 ±0E–03

The results are also shown as Figures A2-1 and A2-2 in Appendix 2.

5.3.4 Sorption of ^{134}Cs onto cement in the presence of EDTA

The results for Cs sorption onto tube walls with EDTA in FCPW, compared with reference case (no organics added), are shown in Table 5-17.

Table 5-17. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	0.2	n.d.	n.d	n.d.	0.2
1 week	0.3	1.0	0.6	1.9	0.9	1.4
1 month	0.4	(0.1)	n.d.	0.6	0.7	1.2
3 months	0.7	n.d.	n.d.	n.d.	n.d	n.d.
6 months	0.4	0.3	n.d	0.6	n.d.	n.d.

The results for Cs sorption onto cement with EDTA in FCPW, compared with reference case (no organics added) are shown in Table 5-18.

Table 5-18. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3E–04)	n.d.	n.d.	6E–04	(3E–05)	(7E–05)
1 week	(3E–04)	1 ±0E–03	4 ±5E–04	n.d.	n.d.	n.d.
1 month	(2E–04)	2 ±1E–03	1 ±0E–03	n.d.	9E–04	(2E–04)
3 months	(6E–05)	(3E–04)	n.d.	n.d.	n.d.	n.d.
6 months	3 ±3E–03	n.d.	n.d.	n.d.	n.d.	1 ±0E–03

The results for Cs sorption onto tube walls with EDTA in LCPW, compared with reference case (no organics added), are shown in Table 5-19.

Table 5-19. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	0.5	n.d.	n.d.	n.d.	(0.1)
1 week	0.6	(0.1)	0.4	1.0	(0.1)	0.5
1 month	0.6	n.d.	n.d.	1.2	0.8	0.3
3 months	0.6	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	0.2	n.d.	(0.1)	n.d.	n.d.	1.0

The results for Cs sorption onto cement with EDTA in LCPW, compared with reference case (no organics added) are shown in Table 5-20.

Table 5-20. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	2 ±0E–02	(1E–04)	n.d.	n.d.
1 week	7E–04	3 ±0E–03	5E–04	n.d.	1 ±1E–03	4 ±3E–04
1 month	(2E–04)	1 ±0E–03	3 ±1E–03	1 ±1E–03	4E–04	1 ±1E–03
3 months	1 ±1E–03	6 ±6E–04	n.d.	7E–04	8 ±4E–04	3 ±2E–03
6 months	2± 0E–03	2 ±1E–03	7E–04	1 ±1E–03	n.d.	n.d.

The results are also shown as Figures A2-3 and A2-4 in Appendix 2.

5.3.5 Sorption of ^{134}Cs onto cement in the presence of ISA

The results for Cs sorption onto tube walls with ISA in FCPW, compared with reference case (no organics added), are shown in Table 5-21.

Table 5-21. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	0.5	n.d.	n.d.	n.d.
1 week	0.3	0.2	0.8	0.6	0.6	0.7
1 month	0.4	n.d.	0.6	0.9	n.d.	n.d.
3 months	0.7	0.2	0.8	0.6	(0.1)	n.d.
6 months	0.4	0.2	(0.1)	0.5	n.d.	0.2

The results for Cs sorption onto cement with ISA in FCPW, compared with reference case (no organics added) are shown in Table 5-22.

Table 5-22. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3E–04)	n.d.	n.d.	5E–04	n.d.	n.d.
1 week	(3E–04)	6 ±6E–04	2E–03	6 ±4E–04	n.d.	n.d.
1 month	(2E–04)	n.d.	(2E–04)	n.d.	(3E–04)	n.d.
3 months	(6E–05)	(3E–05)	n.d.	n.d.	8E–04	(2E–04)
6 months	3 ±3E–03	n.d.	n.d.	n.d.	7 ±2E–04	9E–04

The results for Cs sorption onto tube walls with ISA in LCPW, compared with reference case (no organics added), are shown in Table 5-23.

Table 5-23. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1 week	0.6	0.2	0.3	0.3	0.4	0.4
1 month	0.6	0.7	0.9	0.4	n.d.	n.d.
3 months	0.6	(0.1)	0.3	0.7	0.8	0.3
6 months	0.2	0.3	0.8	0.8	(0.1)	0.5

The results for Cs sorption onto cement with ISA in LCPW, compared with reference case (no organics added) are shown in Table 5-24.

Table 5-24. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	(5E–5)	n.d.	n.d.	n.d.
1 week	7E–04	2 ±0E–03	2 ±0E–03	2 ±0E–03	1 ±0E–03	9 ±6E–04
1 month	(2E–04)	n.d.	n.d.	5 ±2E–04	2 ±2E–03	1 ±0E–03
3 months	1 ±1E–03	8E–04	8E–04	1 ±1E–03	5 ±3E–04	n.d.
6 months	2± 0E–03	2E–03	2E–03	n.d.	5 ±4E–04	(2E–04)

The results are also shown as Figures A2-5 and A2-6 in Appendix 2.

5.3.6 Sorption of ^{134}Cs onto cement in the presence of citric acid

The results for Cs sorption onto tube walls with citric acid in FCPW, compared with reference case (no organics added), are shown in Table 5-25.

Table 5-25. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	(0.1)	0.5	(0.1)	0.7	1.3
1 week	0.3	0.5	0.7	0.3	0.9	0.9
1 month	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	0.7	0.2	(0.1)	0.6	0.4	0.3
6 months	0.4	0.6	1.2	1.3	1.4	1.7

The results for Cs sorption onto cement with citric acid in FCPW, compared with reference case (no organics added) are shown in Table 5-26.

Table 5-26. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3E–04)	4 ±1E–04	2 ±0E–02	6 ±1E–04	1 ±0E–03	n.d.
1 week	(3E–04)	n.d.	n.d.	n.d.	9 ±6E–04	5E–04
1 month	(2E–04)	n.d.	n.d.	n.d.	n.d.	7E–04
3 months	(6E–05)	n.d.	n.d.	n.d.	n.d.	(9E–05)
6 months	3 ±3E–03	n.d.	n.d.	n.d.	n.d.	n.d.

The results for Cs sorption onto tube walls with citric acid in LCPW, compared with reference case (no organics added), are shown in Table 5-27.

Table 5-27. Results for wall sorption L_d values (mL) of ^{134}Cs with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	0.3	0.2	1.1	0.5
1 week	0.6	n.d.	0.3	0.2	0.8	0.5
1 month	0.6	n.d.	0.3	0.4	n.d.	n.d.
3 months	0.6	n.d.	0.3	n.d.	0.6	0.2
6 months	0.2	0.2	1.0	n.d.	0.5	0.9

The results for Cs sorption onto cement with citric acid in LCPW, compared with reference case (no organics added) are shown in Table 5-28.

Table 5-28. Results for cement sorption R_d values (m^3/kg) of ^{134}Cs with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	n.d.	n.d.	2 ±0E–02	n.d.	n.d.	4 ±5E–04
1 week	7E–04	2 ±0E–03	1 ±0E–03	1 ±0E–03	n.d.	2 ±0E–03
1 month	(2E–04)	n.d.	1E–05	n.d.	3 ±2E–03	6 ±2E–04
3 months	1 ±1E–03	n.d.	(2E–6)	1 ±1E–03	5E–03	2 ±1E–03
6 months	2± 0E–03	n.d.	6E–04	1E–03	3 ±0E–03	n.d.

The results are also shown as Figures A2-7 and A2-8 in Appendix 2.

5.3.7 Sorption of ^{60}Co onto cement in the presence of UDP

The results for Co sorption onto tube walls with UDP in FCPW, compared with reference case (no organics added), are shown in Table 5-29.

Table 5-29. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of UP2 degradation products (UDP) in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	4.5	(0.1)	n.d.	(2.1)	(2.6)	4.4
1 week	8.2	n.d.	(1.0)	(2.9)	(1.0)	7.5
1 month	10.2	(2.0)	(1.0)	4.6	(2.4)	(0.6)
3 months	5.8	(0.7)	(1.3)	(2.9)	(1.9)	(1.8)
6 months	(2.6)	(0.3)	n.d.	5.6	(0.6)	(2.0)

The results for Co sorption onto cement with UDP in FCPW, compared with reference case (no organics added) are shown in Table 5-30.

Table 5-30. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of UP2 degradation products (UDP) in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	2 ±2E–02	(6E–03)	(5E–03)	(6E–03)	(4E–03)	8 ±5E–03
1 week	8 ±2E–03	(6E–03)	2 ±2E–02	2 ±0E–02	1 ±1E–02	2 ±1E–02
1 month	2 ±1E–02	5 ±5E–02	4 ±1E–02	3 ±2E–02	2 ±1E–02	4E–02
3 months	3 ±1E–02	9 ±1E–03	3 ±0E–02	4 ±4E–02	2 ±1E–02	5 ±1E–02
6 months	4 ±1E–02	5 ±1E–02	2 ±1E–02	3 ±1E–02	1 ±1E–02	6 ±5E–02

The results for Co sorption onto tube walls with UDP in LCPW, compared with reference case (no organics added), are shown in Table 5-31.

Table 5-31. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of UP2 degradation products (UDP) in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	14.4	n.d.	(2.0)	4.2	(0.1)	3.6
1 week	6.0	(0.8)	n.d.	7.0	(2.2)	3.2
1 month	5.5	3.0	(0.9)	3.1	(0.8)	(2.2)
3 months	8.3	(1.1)	(2.8)	(1.9)	n.d.	(2.3)
6 months	3.1	n.d.	(0.3)	3.1	(1.7)	3.0

The results for Co sorption onto cement with UDP in LCPW, compared with reference case (no organics added) are shown in Table 5-32.

Table 5-32. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of UP2 degradation products (UDP) in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3E–02	3 ±2E–02	1 ±1E–02	2E–02	2 ±1E–02	(4E–03)
1 week	4 ±4E–02	7E–02	3E–02	2 ±2E–02	9 ±0E–03	3 ±3E–02
1 month	5E–02	3 ±0E–02	7 ±3E–02	1 ±0E–01	3 ±0E–02	3 ±1E–02
3 months	6E–02	4 ±1E–02	7 ±2E–02	3 ±1E–02	3 ±1E–02	4 ±0E–02
6 months	2 ±2E–01*	4 ±1E–02	1 ±1E–01	6 ±3E–02	2 ±2E–02	4 ±2E–02

The results are also shown as Figures A2-9 and A2-10 in Appendix 2.

5.3.8 Sorption of ^{60}Co onto cement in the presence of EDTA

The results for Co sorption onto tube walls with EDTA in FCPW, compared with reference case (no organics added), are shown in Table 5-33.

Table 5-33. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	4.5	(2.0)	18	15	13	15
1 week	8.2	4.4	21	37	15	34
1 month	10	n.d.	27	12	18	20
3 months	5.8	(1.8)	16	36	10	11
6 months	(2.6)	3.4	13	7.6	17	10

The results for Co sorption onto cement with EDTA in FCPW, compared with reference case (no organics added) are shown in Table 5-34.

Table 5-34. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	2 ±2E–02	n.d.	3 ±1E–02	n.d.	4 ±4E–02	(6E–03)
1 week	8 ±2E–03	6 ±5E–02	1 ±0E–01	n.d.	3 ±0E–02	n.d.
1 month	2 ±1E–02	4 ±3E–02	4 ±3E–02	2E–02	1E–01	7E–02
3 months	3 ±1E–02	4 ±2E–02	2 ±1E–02	n.d.	5 ±6E–02	5E–02
6 months	4 ±1E–02	2E–02	2 ±2E–02	1E–02	3 ±2E–02	4 ±1E–02

The results for Co sorption onto tube walls with EDTA in LCPW, compared with reference case (no organics added), are shown in Table 5-35.

Table 5-35. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	14	n.d.	(1.0)	(0.1)	(0.8)	(2.6)
1 week	6.0	3.6	19	34	14	31
1 month	5.5	n.d.	4.0	3.1	9.2	8.8
3 months	8.3	(0.2)	(2.1)	(0.4)	4.7	3.3
6 months	3.1	n.d.	4.0	(1.3)	9.2	47

The results for Co sorption onto cement with EDTA in LCPW, compared with reference case (no organics added) are shown in Table 5-36.

Table 5-36. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3E–02	9E–03	n.d.	2 ±1E–01*	4 ±2E–02	8E–02
1 week	4 ±4E–02	6 ±4E–02	1 ±0E–01	n.d.	3 ±0E–02	n.d.
1 month	5E–02	4 ±3E–02	5 ±2E–02	1E–01	5 ±3E–02	8E–02
3 months	6E–02	3 ±0E–02	3 ±0E–02	7E–02	9 ±3E–02	8 ±4E–02
6 months	2 ±2E–01*	3E–02	n.d.	4 ±3E–02	5 ±7E–02	n.d.

The results are also shown as Figures A2-11 and A2-12 in Appendix 2.

5.3.9 Sorption of ^{60}Co onto cement in the presence of ISA

The results for Co sorption onto tube walls with ISA in FCPW, compared with reference case (no organics added), are shown in Table 5-37.

Table 5-37. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	4.5	7.6	16	25	33	51
1 week	8.2	13	17	37	36	53
1 month	10	6.4	16	30	58	21
3 months	5.8	11	13	28	24	23
6 months	(2.6)	12	14	30	19	33

The results for Co sorption onto cement with ISA in FCPW, compared with reference case (no organics added) are shown in Table 5-38.

Table 5-38. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	2 ±2E–02	4 ±0E–02	6 ±1E–02	6 ±2E–02	n.d.	n.d.
1 week	8 ±2E–03	5 ±0E–02	5 ±2E–02	6E–02	2E–01*	3 ±3E–02
1 month	2 ±1E–02	3 ±0E–02	4 ±0E–02	5 ±1E–02	2 E–02	5 ±3E–02
3 months	3 ±1E–02	7 ±4E–02	7 ±0E–02	2 ±0E–01*	2E–01*	6 ±2E–02
6 months	4 ±1E–02	4E–02	6 ±4E–02	1E–01	8 ±1E–02	3E–01*

The results for Co sorption onto tube walls with ISA in LCPW, compared with reference case (no organics added), are shown in Table 5-39.

Table 5-39. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	14	18	18	21	24	19
1 week	6.0	37	22	52	27	20
1 month	5.5	22	25	26	25	12
3 months	8.3	16	18	29	20	17
6 months	3.1	13	17	22	35	22

The results for Co sorption onto cement with ISA in LCPW, compared with reference case (no organics added) are shown in Table 5-40.

Table 5-40. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3E–02	3 ±2E–02	4 ±3E–02	1E–01	1E–01	8E–02
1 week	4 ±4E–02	3 ±1E–02	6 ±1E–02	2E–02	1E–01	1 ±0E–01
1 month	5E–02	5 ±3E–02	8E–02	1 ±0E–01	9 ±5E–02	8 ±1E–02
3 months	6E–02	1 ±1E–01	8 ±2E–02	4 ±0E–02	n.d.	2 ±0E–02
6 months	2 ±2E–01*	7E–02	1E–01	6 ±1E–02	4 ±1E–02	9E–02

The results are also shown as Figures A2-13 and A2-14 in Appendix 2.

5.3.10 Sorption of ^{60}Co onto cement in the presence of citric acid

The results for Co sorption onto tube walls with citric acid in FCPW, compared with reference case (no organics added), are shown in Table 5-41.

Table 5-41. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	4.5	4.0	38	25	40	31
1 week	8.2	8.3	48	26	37	30
1 month	10	(0.9)	23	21	45	21
3 months	5.8	3.8	16	28	24	19
6 months	(2.6)	3.7	13	26	27	21

The results for Co sorption onto cement with citric acid in FCPW, compared with reference case (no organics added) are shown in Table 5-42.

Table 5-42. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	2 ±2E–02	2 ±1E–02	2E–01*	n.d.	3E–02	4 ±0E–02
1 week	8 ±2E–03	2 ±2E–02	3E–02	1E–01	5 ±1E–02	n.d.
1 month	2 ±1E–02	n.d.	3E–02	3 ±2E–02	n.d.	2E–02
3 months	3 ±1E–02	4 ±1E–02	1 ±1E–01	1 ±1E–01	3 ±1E–02	(6E–03)
6 months	4 ±1E–02	3 ±1E–02	2 ±0E–02	6 ±0E–02	9 ±5E–02	2 ±1E–02

The results for Co sorption onto tube walls with citric acid in LCPW, compared with reference case (no organics added), are shown in Table 5-43.

Table 5-43. Results for wall sorption L_d values (mL) of ^{60}Co with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	14	(1.7)	31	n.d.	58	89
1 week	6.0	4.1	24	69	61	32
1 month	5.5	(1.5)	33	37	57	43
3 months	8.3	(2.7)	35	52	63	32
6 months	3.1	5.3	19	17	23	12

The results for Co sorption onto cement with citric acid in LCPW, compared with reference case (no organics added) are shown in Table 5-44.

Table 5-44. Results for cement sorption R_d values (m^3/kg) of ^{60}Co with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3E–02	3E–02	2 ±1 E–01*	1 ±0E–01	1E–02	1E–01
1 week	4 ±4E–02	2 ±2E–01*	n.d.	5E–02	1E–01	6E–02
1 month	5E–02	n.d.	1 ±1E–01	5 ±3E–02	n.d.	3E–02
3 months	6E–02	4 ±1E–02	3 ±1E–02	4E–02	2E–02	2 ±2E–02
6 months	2 ±2E–01*	5 ±1E–02	8 ±1E–02	8 ±3E–02	9 ±0E–02	4 ±2E–02

The results are also shown as Figures A2-15 and A2-16 in Appendix 2.

5.3.11 Sorption of ^{152}Eu onto cement in the presence of UDP

The results for Eu sorption onto tube walls with UDP in FCPW, compared with reference case (no organics added), are shown in Table 5-45.

Table 5-45. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of UP2 degradation products (UDP) in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	0.7	1.6	12	59	12	20
1 week	5.3	6.7	30	130	55	120
1 month	32	22	71	210	230	n.d.
3 months	29	43	130	540	300	n.d.
6 months	80	55	180	830	n.d.	n.d.

The few successful measurements of ^{152}Eu in solution contacted with cement are presented in Table 5-46.

Table 5-46. Results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of UP2 degradation products (UDP) in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3E–01	4 ±0E–02	1 ±0E–01	3 ±2E–01	2 ±0E–01	4E–01
1 week	n.d.	1 ±0E–01	6 ±3E–01	2 ±2E–00	n.d.	n.d.
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results for Eu sorption onto tube walls with UDP in LCPW, compared with reference case (no organics added), are shown in Table 5-47.

Table 5-47. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of UP2 degradation products (UDP) in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	6.4	7.2	140	520	n.d.	140
1 week	110	9.5	340	540	n.d.	n.d.
1 month	n.d.	16	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	33	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	43	n.d.	n.d.	n.d.	n.d.

No results for ^{152}Eu sorption onto cement with UDP in LCPW were obtained. However, for a consistent overview, this lack of results is nevertheless also shown in Table 5-48.

Table 5-48. No results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of UP2 degradation products (UDP) in synthetic leached cement pore-water (LCPW) were obtained, since no signals was detected.

	Reference	C1	C2	C3	C4	C5
1 day	3 ±0E–01	n.d.	n.d.	n.d.	n.d.	n.d.
1 week	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results are also shown as Figures A2-17 and A2-18 in Appendix 2.

5.3.12 Sorption of ^{152}Eu onto cement in the presence of EDTA

The results for Eu sorption onto tube walls with EDTA in FCPW, compared with reference case (no organics added), are shown in Table 5-49.

Table 5-49. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	0.7	2.3	11	15	24	34
1 week	5.3	7.1	44	45	92	70
1 month	32	20	130	140	390	170
3 months	29	400	n.d.	n.d.	n.d.	n.d.
6 months	80	n.d.	n.d.	380	n.d.	n.d.

The few results for ^{152}Eu sorption onto cement with EDTA in FCPW, compared with reference case (no organics added), that were obtained are shown in Table 5-50.

Table 5-50. Results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3E–01	8E–01	n.d.	n.d.	n.d.	n.d.
1 week	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results for Eu sorption onto tube walls with EDTA in LCPW, compared with reference case (no organics added), are shown in Table 5-51.

Table 5-51. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	6.4	12	4.0	4.3	8.5	15
1 week	110	6.8	40	43	90	66
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The few results for ^{152}Eu sorption onto cement with EDTA in LCPW, compared with reference case (no organics added), that were obtained are shown in Table 5-52.

Table 5-52. Results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3 ±0E–01	2E–01	7E–00*	2E–01	4 ±0E–01	6E–01
1 week	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results are also shown as Figures A2-19 and A2-20 in Appendix 2.

5.3.13 Sorption of ^{152}Eu onto cement in the presence of ISA

The results for Eu sorption onto tube walls with ISA in FCPW, compared with reference case (no organics added), are shown in Table 5-53.

Table 5-53. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	0.7	28	13	5.4	1.3	2.6
1 week	5.3	43	18	16	5.2	13
1 month	32	130	22	44	9.2	26
3 months	29	140	40	240	25	55
6 months	80	170	49	65	47	110

The very few obtainable results for ^{152}Eu sorption onto cement with ISA in FCPW, compared with reference case (no organics added) are shown in Table 5-54.

Table 5-54. Results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3E–01	n.d.	n.d.	3E–02	n.d.	n.d.
1 week	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results for Eu sorption onto tube walls with ISA in LCPW, compared with reference case (no organics added), are shown in Table 5-55.

Table 5-55. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	6.4	25	11	4.0	0.7	0.6
1 week	110	49	24	14	6.0	6.3
1 month	n.d.	240	140	78	33	39
3 months	n.d.	240	580	350	n.d.	200
6 months	n.d.	390	490	180	110	160

The few obtainable results for ^{152}Eu sorption onto cement with ISA in LCPW, compared with reference case (no organics added) are shown in Table 5-56.

Table 5-56. Results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3 ±0E–01	n.d.	n.d.	n.d.	3E–01	n.d.
1 week	n.d.	n.d.	n.d.	n.d.	n.d.	6E–01
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results are also shown as Figures A2-21 and A2-22 in Appendix 2.

5.3.14 Sorption of ^{152}Eu onto cement in the presence of citric acid

The results for Co sorption onto tube walls with citric acid in FCPW, compared with reference case (no organics added), are shown in Table 5-57.

Table 5-57. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	0.7	120	420	130	290	110
1 week	5.3	100	370	150	540	220
1 month	32	230	470	200	320	130
3 months	29	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	80	54	1,200	290	130	150

No results for Eu sorption onto cement with citric acid in FCPW were obtained, however, for a quick overview this lack of results is shown in Table 5-58.

Table 5-58. No results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW) were obtained, since no signal was detected.

	Reference	C1	C2	C3	C4	C5
1 day	3E–01	n.d.	n.d.	n.d.	n.d.	n.d.
1 week	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results for Eu sorption onto tube walls with citric acid in LCPW, compared with reference case (no organics added), are shown in Table 5-59.

Table 5-59. Results for wall sorption L_d values (mL) of ^{152}Eu with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	6.4	8.5	380	170	320	120
1 week	110	14	110	110	n.d.	230
1 month	n.d.	13	n.d.	1,300	770	130
3 months	n.d.	21	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	140	1,200	320	830	400

The very few results obtained for ^{152}Eu sorption onto cement with citric acid in LCPW, compared with reference case (no organics added) are shown in Table 5-60.

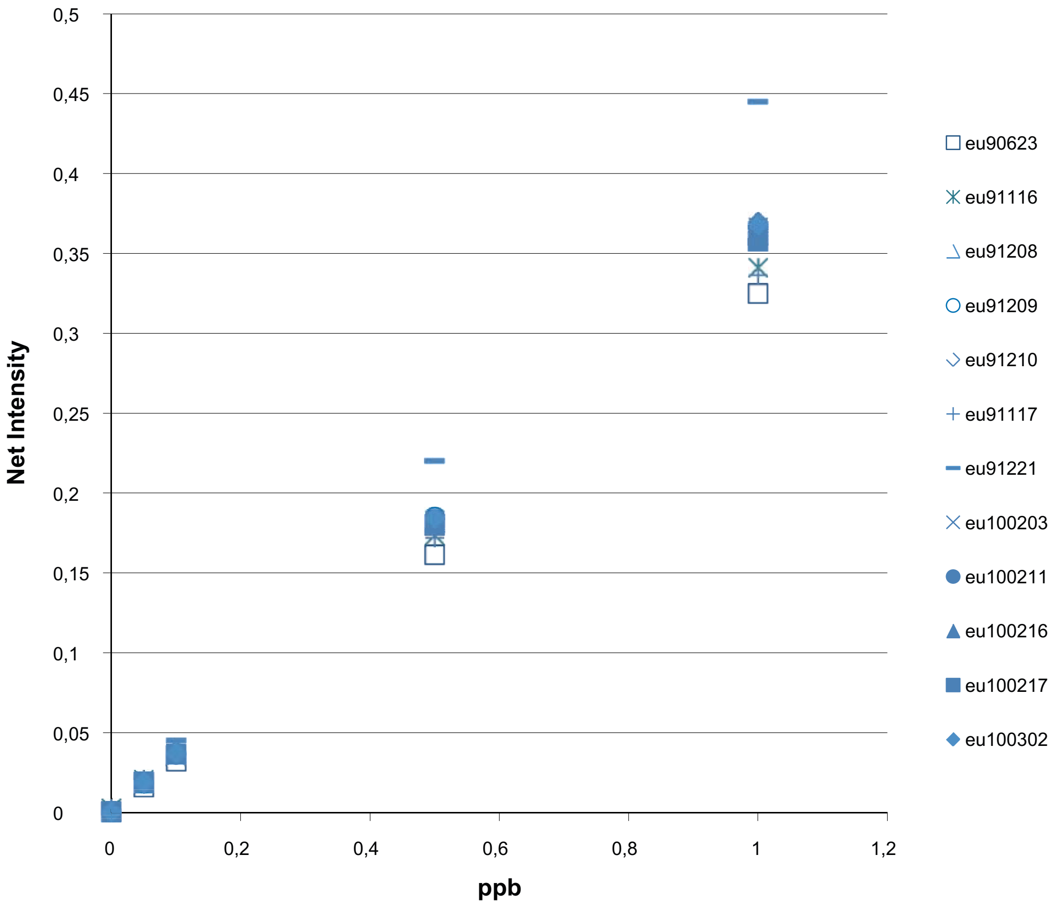
Table 5-60. Results for cement sorption R_d values (m^3/kg) of ^{152}Eu with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	3 ±0E–01	3 ±0E–01	n.d.	n.d.	n.d.	3* ±2E–00
1 week	n.d.	n.d.	2 E–00	n.d.	n.d.	n.d.
1 month	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
3 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6 months	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

The results are also shown as Figures A2-23 and A2-24 in Appendix 2.

5.3.15 Results of Eu total concentration measurements

Since the radiometric detection of ^{152}Eu in the batch sorption experiments gave few results, an attempt was made to also measure the total Eu concentration in the samples, using ICPMS. The calibration curves of the ICPMS measurements are shown in Figure 5-1.



Figur 5-1. *Calibration curves of ICPMS instrument of the 12 measurement sessions, using 0.05, 0.1, 0.5 and 1 ppb Eu standards.*

As can be seen in Table 5-61 below, the linearity of the calibration curves for the investigated concentration range 0–1 ppb was excellent. Evaluated detection levels are also presented. Considering also the dilution of samples (0.1 mL to 5 mL), the actual detection levels for the batch sorption experiments were 50 times higher than measured samples. In the following tables with results, values under the detection level are marked with ().

Table 5-61. Results for calibration of ICPMS instrument, using 0.05, 0.1, 0.5 and 1 ppb Eu standards.

Session	R2 goodness of fit	Detection limit, as measured (ppb)	Detection limit, in undiluted sample (M)
090623	0.999758	1.79E–03	5.89E–10
091116	0.999784	7.74E–03	2.54E–09
091117	0.999753	7.04E–03	2.32E–09
091208	0.99999	1.43E–03	4.70E–10
091209	0.999989	1.28E–03	4.21E–10
091210	0.999992	1.20E–03	3.95E–10
091221	0.99998	9.69E–04	3.19E–10
100203	0.999987	9.27E–04	3.16E–10
100211	0.999985	1.80E–03	5.92E–10
100216	0.999987	1.79E–03	5.89E–10
100217	0.999969	1.83E–03	6.02E–10
100302	0.999996	1.21E–03	3.98E–10

The results for the total Eu concentration measurements in the wall sorption experiments with UDP in FCPW conditions, compared with reference samples, are shown in Table 5-62.

Table 5-62. Results of $[Eu]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of UP2 degradation products in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	8.5E–10	9.1E–10	2.0E–09	1.0E–09	8.7E–10	1.0E–09
1 week	5.0E–09	(1.2E–09)	(1.1E–09)	(1.1E–09)	(1.0E–09)	(1.0E–09)
1 month	1.0E–09	1.5E–09	1.1E–09	7.8E–10	1.7E–09	1.1E–09
3 months	1.4E–09	n.m.*	8.0E–10	1.0E–09	8.7E–10	1.1E–09
6 months	6.9E–10	1.1E–09	6.3E–10	6.3E–10	1.1E–09	6.2E–10
acidic ref.	6.1E–09	5.5E–09	5.0E–09	8.2E–09	1.6E–08	8.7E–09

*not measured

The results for the total Eu concentration measurements in the cement sorption experiments with UDP in FCPW conditions, compared with reference samples, are shown in Table 5-63.

Table 5-63. Results of $[Eu]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of UP2 degradation products in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–09	1.3E–09	2.2E–09	2.2E–09	2.3E–09	3.0E–09
1 week	9.6E–09	(1.9E–09)	(1.1E–09)	(1.9E–09)	(2.2E–09)	(2.0E–09)
1 month	4.9E–09	5.6E–09	2.0E–09	3.3E–09	1.4E–09	4.6E–09
3 months	7.5E–09	9.2E–09	3.0E–09	4.9E–09	5.9E–09	5.2E–09
6 months	6.9E–09	9.8E–09	4.2E–09	6.6E–09	1.1E–08	7.1E–09
acidic ref.	4.8E–09	5.5E–09	5.0E–09	8.2E–09	1.6E–08	8.7E–09

The results are also shown as Figure A3-1 in Appendix 3.

The results for the total Eu concentration measurements in the wall sorption experiments with UDP in LCPW conditions, compared with reference samples, are shown in Table 5-64.

Table 5-64. Results of $[Eu]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of UP2 degradation products in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.5E–10)	(4.3E–10)	6.6E–10	1.0E–09	5.1E–10	8.8E–10
1 week	6.6E–10	(1.1E–09)	(8.7E–10)	(8.0E–10)	(1.2E–09)	(9.3E–10)
1 month	7.5E–10	8.6E–10	8.6E–10	1.1E–09	(3.4E–10)	(5.3E–10)
3 months	6.3E–10	1.9E–09	1.0E–09	6.2E–10	7.5E–10	7.4E–10
6 months	5.6E–10	8.1E–10	4.5E–10	4.8E–10	8.0E–10	5.5E–10
acidic ref.	4.8E–09	5.5E–09	5.0E–09	8.2E–09	1.6E–08	8.7E–09

The results for the total Eu concentration measurements in the cement sorption experiments with UDP in LCPW conditions, compared with reference samples, are shown in Table 5-65.

Table 5-65. Results of $[Eu]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of UP2 degradation products in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.1E–09	7.8E–10	1.6E–09	2.2E–09	8.3E–10	1.4E–09
1 week	6.9E–09	(1.5E–09)	(1.4E–09)	(1.4E–09)	(1.9E–09)	(1.2E–09)
1 month	2.6E–09	2.8E–09	1.7E–09	1.5E–09	1.1E–09	1.8E–09
3 months	3.0E–09	5.0E–09	2.6E–09	2.6E–09	2.9E–09	2.5E–09
6 months	3.6E–09	9.8E–09	3.3E–09	3.1E–09	4.4E–09	3.3E–09
acidic ref.	4.8E–09	5.5E–09	5.0E–09	8.2E–09	1.6E–08	8.7E–09

The results are also shown as Figure A3-2 in Appendix 3.

The results for the total Eu concentration measurements in the wall sorption experiments with EDTA in FCPW conditions, compared with reference samples, are shown in Table 5-66.

Table 5-66. Results of $[Eu]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	8.5E–10	(4.0E–10)	(2.1E–10)	4.4E–10	(3.5E–10)	(3.6E–10)
1 week	5.0E–09	(1.0E–09)	(1.0E–09)	(5.7E–10)	(6.6E–10)	(4.2E–10)
1 month	1.0E–09	9.2E–10	9.4E–10	(3.1E–10)	(4.1E–10)	6.4E–10
3 months	1.4E–09	6.5E–10	2.1E–09	1.1E–09	(4.0E–10)	(3.8E–10)
6 months	6.9E–10	(3.6E–10)	(5.0E–10)	(4.2E–10)	(3.9E–10)	(4.0E–10)
acidic ref.	4.8E–09	6.9E–09	6.1E–09	3.9E–09	3.4E–09	4.0E–09

The results for the total Eu concentration measurements in the cement sorption experiments with EDTA in FCPW conditions, compared with reference samples, are shown in Table 5-67.

Table 5-67. Results of $[Eu]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–09	1.6E–09	2.8E–09	1.6E–09	1.5E–09	1.3E–09
1 week	9.6E–09	(2.0E–09)	(1.6E–09)	(1.0E–09)	(1.3E–09)	(7.1E–10)
1 month	4.9E–09	3.0E–09	3.2E–09	1.9E–09	2.3E–09	2.7E–09
3 months	7.5E–09	7.0E–09	9.2E–09	6.0E–09	4.6E–09	5.4E–09
6 months	6.9E–09	4.0E–09	7.6E–09	4.6E–09	4.3E–09	4.6E–09
acidic ref.	4.8E–09	6.9E–09	6.1E–09	3.9E–09	3.4E–09	4.0E–09

The results are also shown as Figure A3-3 in Appendix 3.

The results for the total Eu concentration measurements in the wall sorption experiments with EDTA in LCPW conditions, compared with reference samples, are shown in Table 5-68.

Table 5-68. Results of $[Eu]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.5E–10)	4.8E–10	5.7E–10	1.1E–09	1.0E–09	8.7E–10
1 week	6.6E–10	(8.0E–10)	(1.0E–09)	(3.8E–10)	(6.6E–10)	(3.1E–10)
1 month	7.5E–10	9.1E–10	1.2E–09	(3.0E–10)	(5.1E–10)	(4.9E–10)
3 months	6.3E–10	5.7E–10	6.0E–10	9.3E–10	(4.4E–10)	(3.7E–10)
6 months	5.6E–10	(3.3E–10)	(4.9E–10)	(4.0E–10)	(3.5E–10)	2.2E–09
acidic ref.	4.8E–09	6.9E–09	6.1E–09	3.9E–09	3.4E–09	4.0E–09

The results for the total Eu concentration measurements in the cement sorption experiments with EDTA in LCPW conditions, compared with reference samples, are shown in Table 5-69.

Table 5-69. Results of $[Eu]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.1E–09	1.4E–09	6.5E–10	1.9E–09	1.2E–09	1.1E–09
1 week	6.9E–09	(1.3E–09)	(1.5E–09)	(5.6E–10)	(1.3E–09)	(4.6E–10)
1 month	2.6E–09	1.3E–09	2.1E–09	6.2E–10	1.1E–09	1.2E–09
3 months	3.0E–09	3.0E–09	3.4E–09	2.7E–09	2.0E–09	2.0E–09
6 months	3.6E–09	2.6E–09	2.8E–09	2.4E–09	2.0E–09	2.2E–09
acidic ref.	4.8E–09	6.9E–09	6.1E–09	3.9E–09	3.4E–09	4.0E–09

The results are also shown as Figure A3-4 in Appendix 3.

The results for the total Eu concentration measurements in the wall sorption experiments with ISA in FCPW conditions, compared with reference samples, are shown in Table 5-70.

Table 5-70. Results of $[Eu]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	8.5E–10	5.1E–10	1.1E–09	9.1E–10	4.7E–10	1.4E–09
1 week	5.0E–09	(6.5E–10)	(1.5E–09)	(5.9E–10)	(8.4E–10)	(6.1E–10)
1 month	1.0E–09	4.7E–10	1.4E–09	6.5E–10	7.0E–10	(5.2E–10)
3 months	1.4E–09	6.7E–10	1.2E–09	(5.5E–10)	6.0E–10	(5.1E–10)
6 months	6.9E–10	7.3E–10	(3.6E–10)	6.5E–10	9.8E–10	(5.5E–10)
acidic ref.	4.8E–09	7.5E–09	8.9E–09	5.0E–09	4.0E–09	4.4E–09

The results for the total Eu concentration measurements in the cement sorption experiments with ISA in FCPW conditions, compared with reference samples, are shown in Table 5-71.

Table 5-71. Results of $[Eu]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–09	1.8E–09	1.5E–09	1.2E–09	7.7E–10	2.3E–09
1 week	9.6E–09	(1.2E–09)	(2.2E–09)	(7.2E–10)	(1.3E–09)	(1.2E–09)
1 month	4.9E–09	2.3E–09	4.7E–09	2.6E–09	1.7E–09	1.9E–09
3 months	7.5E–09	6.8E–09	1.0E–08	6.4E–09	6.2E–09	6.3E–09
6 months	6.9E–09	7.7E–09	1.2E–08	6.7E–09	1.0E–08	6.2E–09
acidic ref.	4.8E–09	7.5E–09	8.9E–09	5.0E–09	4.0E–09	4.4E–09

The results are also shown as Figure A3-5 in Appendix 3.

The results for the total Eu concentration measurements in the wall sorption experiments with ISA in LCPW conditions, compared with reference samples, are shown in Table 5-72.

Table 5-72. Results of $[Eu]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.5E–10)	7.8E–10	5.0E–10	5.6E–10	4.7E–10	1.4E–09
1 week	6.6E–10	(7.2E–10)	(1.0E–09)	(5.9E–10)	(7.6E–10)	(6.3E–10)
1 month	7.5E–10	(3.0E–10)	(5.6E–10)	(5.6E–10)	(3.9E–10)	(4.5E–10)
3 months	6.3E–10	6.4E–10	6.2E–10	(4.8E–10)	(4.5E–10)	(4.5E–10)
6 months	5.6E–10	(5.7E–10)	(2.2E–10)	8.4E–10	7.6E–10	(5.0E–10)
acidic ref.	4.8E–09	7.5E–09	8.9E–09	5.0E–09	4.0E–09	4.4E–09

The results for the total Eu concentration measurements in the cement sorption experiments with ISA in LCPW conditions, compared with reference samples, are shown in Table 5-73.

Table 5-73. Results of $[Eu]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.1E–09	(4.0E–10)	1.2E–09	(3.8E–10)	7.7E–10	7.1E–10
1 week	6.9E–09	(7.2E–10)	(1.4E–09)	(7.2E–10)	(1.1E–09)	(8.1E–10)
1 month	2.6E–09	1.0E–09	1.8E–09	1.6E–09	8.9E–10	8.5E–10
3 months	3.0E–09	2.9E–09	3.2E–09	2.6E–09	2.6E–09	2.7E–09
6 months	3.6E–09	3.5E–09	1.7E–09	4.6E–09	4.8E–09	2.9E–09
acidic ref.	4.8E–09	7.5E–09	8.9E–09	5.0E–09	4.0E–09	4.4E–09

The results are also shown as Figure A3-6 in Appendix 3.

The results for the total Eu concentration measurements in the wall sorption experiments with citric acid in FCPW conditions, compared with reference samples, are shown in Table 5-74.

Table 5-74. Results of $[Eu]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	8.5E–10	6.4E–10	9.1E–10	5.5E–10	(2.9E–10)	1.5E–09
1 week	5.0E–09	(1.1E–09)	(1.1E–09)	(1.0E–09)	(1.2E–09)	(9.8E–10)
1 month	1.0E–09	(3.0E–10)	(1.4E–10)	(2.0E–10)	(1.6E–10)	(2.1E–10)
3 months	1.4E–09	6.1E–10	4.1E–10	7.2E–10	5.0E–10	5.1E–10
6 months	6.9E–10	6.3E–10	7.4E–10	7.5E–10	8.0E–10	4.9E–10
acidic ref.	4.8E–09	5.5E–09	6.3E–09	6.1E–09	6.2E–09	4.6E–09

*not measured

The results for the total Eu concentration measurements in the cement sorption experiments with citric acid in FCPW conditions, compared with reference samples, are shown in Table 5-75.

Table 5-75. Results of $[Eu]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–09	1.3E–09	1.3E–09	1.4E–09	1.7E–09	2.6E–09
1 week	9.6E–09	(1.8E–09)	(2.0E–09)	(2.2E–09)	(1.8E–09)	(1.7E–09)
1 month	4.9E–09	3.5E–09	2.9E–09	2.7E–09	2.3E–09	2.5E–09
3 months	7.5E–09	9.1E–09	9.9E–09	1.0E–08	7.6E–09	9.3E–09
6 months	6.9E–09	7.5E–09	1.1E–08	1.1E–08	9.9E–09	6.5E–09
acidic ref.	4.8E–09	5.5E–09	6.3E–09	6.1E–09	6.2E–09	4.6E–09

The results are also shown as Figure A3-7 in Appendix 3.

The results for the total Eu concentration measurements in the wall sorption experiments with citric acid in LCPW conditions, compared with reference samples, are shown in Table 5-76.

Table 5-76. Results of [Eu]$_{tot}$ (M) measurements in wall sorption experiments with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.5E–10)	4.6E–10	5.2E–10	(3.7E–10)	(2.9E–10)	1.6E–09
1 week	6.6E–10	(8.8E–10)	(1.2E–09)	(1.4E–09)	(8.6E–10)	(7.5E–10)
1 month	7.5E–10	4.4E–10	(1.3E–10)	(1.6E–10)	(1.7E–10)	(1.9E–10)
3 months	6.3E–10	8.4E–10	4.3E–10	6.4E–10	5.0E–10	5.3E–10
6 months	5.6E–10	4.3E–10	5.5E–10	6.5E–10	5.5E–10	4.7E–10
acidic ref.	4.8E–09	5.5E–09	6.3E–09	6.1E–09	6.2E–09	4.6E–09

The results for the total Eu concentration measurements in the cement sorption experiments with citric acid in LCPW conditions, compared with reference samples, are shown in Table 5-77.

Table 5-77. Results of [Eu]$_{tot}$ (M) measurements in cement sorption experiments with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.1E–09	8.2E–10	1.9E–09	5.3E–10	6.1E–10	1.7E–09
1 week	6.9E–09	(1.1E–09)	(1.4E–09)	(2.2E–09)	(1.1E–09)	(9.4E–10)
1 month	2.6E–09	1.6E–09	7.6E–10	1.1E–09	1.1E–09	2.5E–09
3 months	3.0E–09	3.9E–09	2.9E–09	4.4E–09	3.3E–09	3.5E–09
6 months	3.6E–09	3.3E–09	4.5E–09	4.8E–09	4.8E–09	6.5E–09
acidic ref.	4.8E–09	5.5E–09	6.3E–09	6.1E–09	6.2E–09	4.6E–09

The results are also shown as Figure A3-8 in Appendix 3.

5.3.16 Results of Th total concentration measurements

The calibration curves for total Th concentration in the batch sorption experiments are shown in Figure 5-2 below.

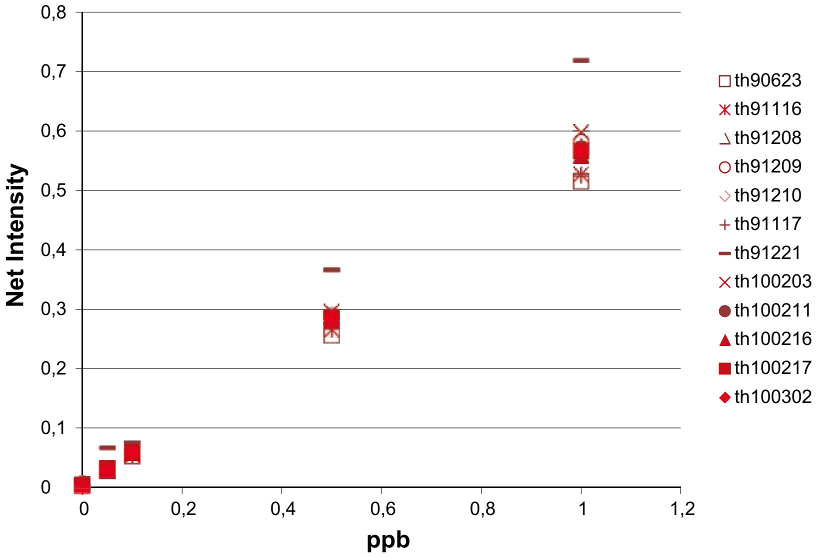


Figure 5-2. Calibration curves of ICPMS instrument of the 12 measurement sessions, using 0.05, 0.1, 0.5 and 1 ppb Th standards.

In Table 5-78 below, the goodness of fit and evaluated detection levels are also presented.

Considering also the dilution of samples (0.1 mL to 5 mL), the actual detection levels for the batch sorption experiments were 50 times higher than measured samples. In the following tables with results, values under the detection level are marked with ().

Table 5-78. Results for calibration of ICPMS instrument, using 0.05, 0.1, 0.5 and 1 ppb Th standards.

session	R2 goodness of fit	Detection limit, as measured (ppb)	Detection limit, in undiluted sample (M)
090623	0.999926	8.37E–03	1.80E–09
091116	0.999958	5.59E–03	1.20E–09
091117	0.999922	5.52E–03	1.19E–09
091208	0.99994	4.68E–03	1.01E–09
091209	0.9999	1.06E–02	2.28E–09
091210	0.999916	9.81E–03	2.11E–09
091221	0.998537	2.65E–03	5.71E–10
100203	0.999972	4.58E–03	9.87E–10
100211	0.999924	8.38E–03	1.81E–09
100216	0.999912	7.03E–03	1.52E–09
100217	0.999939	7.09E–03	1.53E–09
100302	0.999991	1.90E–03	4.09E–10

The results for the total Th concentration measurements in the wall sorption experiments with UDP in FCPW conditions, compared with reference samples, are shown in Table 5-79.

Table 5-79. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of UP2 degradation products in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.1E–10)	(8.8E–10)	1.3E–09	(4.9E–10)	1.2E–09	2.5E–09
1 week	2.0E–09	1.6E–09	1.8E–09	1.3E–09	2.0E–09	2.3E–09
1 month	(1.4E–09)	(1.4E–09)	(8.6E–10)	(8.9E–10)	(1.3E–09)	(3.3E–10)
3 months	(1.2E–09)	n.m.*	1.3E–09	7.8E–10	1.0E–09	(3.4E–10)
6 months	(1.1E–09)	1.5E–09	6.4E–10	7.6E–10	9.1E–10	(2.1E–10)
acidic ref.	6.7E–09	7.4E–09	9.3E–09	1.3E–08	2.8E–08	2.5E–08

*not measured

The results for the total Th concentration measurements in the cement sorption experiments with UDP in FCPW conditions, compared with reference samples, are shown in Table 5-80.

Table 5-80. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of UP2 degradation products in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(5.0E–10)	(9.9E–10)	1.1E–09	1.0E–09	1.3E–09	2.7E–09
1 week	1.4E–09	1.3E–09	(7.3E–10)	(9.8E–10)	1.5E–09	2.5E–09
1 month	(1.7E–09)	(7.1E–10)	(4.8E–10)	(3.8E–10)	(7.5E–10)	(2.9E–10)
3 months	1.5E–09	2.1E–09	4.4E–10	1.1E–09	2.3E–09	(3.5E–10)
6 months	(1.2E–09)	1.4E–09	6.1E–10	6.3E–10	2.8E–09	(2.5E–10)
acidic ref.	6.7E–09	7.4E–09	9.3E–09	1.3E–08	2.8E–08	2.5E–08

The results are also shown as Figure A3-9 in Appendix 3.

The results for the total Th concentration measurements in the wall sorption experiments with UDP in LCPW conditions, compared with reference samples, are shown in Table 5-81.

Table 5-81. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of UP2 degradation products in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(6.1E–10)	(4.9E–10)	(5.1E–10)	(4.9E–10)	(7.0E–10)	1.5E–09
1 week	(8.4E–10)	1.6E–09	1.3E–09	(9.8E–10)	1.5E–09	2.3E–09
1 month	(7.3E–10)	1.5E–09	(4.1E–10)	(4.1E–10)	(4.8E–10)	(2.1E–10)
3 months	(9.9E–10)	1.9E–09	8.2E–10	5.2E–10	1.0E–09	(2.0E–10)
6 months	(1.1E–09)	1.5E–09	4.1E–10	4.7E–10	7.6E–10	(1.9E–10)
acidic ref.	6.7E–09	7.4E–09	9.3E–09	1.3E–08	2.8E–08	2.5E–08

The results for the total Th concentration measurements in the cement sorption experiments with UDP in LCPW conditions, compared with reference samples, are shown in Table 5-82.

Table 5-82. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of UP2 degradation products in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(2.1E–10)	(9.1E–10)	(7.2E–10)	1.0E–09	(7.1E–10)	1.7E–09
1 week	2.1E–09	(1.1E–09)	(1.1E–09)	(8.8E–10)	2.3E–09	2.1E–09
1 month	2.7E–09	(1.2E–09)	(6.7E–10)	(1.1E–09)	(5.4E–10)	(3.5E–10)
3 months	(1.2E–09)	1.6E–09	5.1E–10	1.7E–09	1.7E–09	(3.5E–10)
6 months	(1.4E–09)	1.5E–09	1.9E–09	1.4E–09	1.4E–09	(2.7E–10)
acidic ref.	6.7E–09	7.4E–09	9.3E–09	1.3E–08	2.8E–08	2.5E–08

The results are also shown as Figure A3-10 in Appendix 3.

The results for the total Th concentration measurements in the wall sorption experiments with EDTA in FCPW conditions, compared with reference samples, are shown in Table 5-83.

Table 5-83. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.1E–10)	(5.5E–10)	(2.2E–10)	(3.0E–10)	(2.5E–10)	(3.0E–10)
1 week	2.0E–09	1.5E–09	1.6E–09	(1.1E–09)	1.2E–09	1.2E–09
1 month	(1.4E–09)	(1.4E–09)	(8.5E–10)	(1.1E–09)	(6.2E–10)	(6.7E–10)
3 months	(1.2E–09)	1.5E–09	1.5E–09	(8.7E–10)	(1.0E–09)	(1.0E–09)
6 months	(1.1E–09)	(1.3E–09)	(1.4E–09)	(7.5E–10)	(9.6E–10)	(9.3E–10)
acidic ref.	6.7E–09	1.4E–08	1.0E–08	6.3E–09	6.7E–09	7.7E–09

The results for the total Th concentration measurements in the cement sorption experiments with EDTA in FCPW conditions, compared with reference samples, are shown in Table 5-84.

Table 5-84. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(5.0E–10)	(1.1E–09)	(1.5E–09)	(3.5E–10)	(2.9E–10)	(3.1E–10)
1 week	1.4E–09	1.6E–09	2.7E–09	1.5E–09	1.6E–09	1.6E–09
1 month	(1.7E–09)	2.2E–09	3.8E–09	(1.2E–09)	(1.1E–09)	(1.7E–09)
3 months	1.5E–09	1.5E–09	2.3E–09	(9.1E–10)	(1.1E–09)	(1.0E–09)
6 months	(1.2E–09)	(1.4E–09)	(1.3E–09)	(7.7E–10)	(1.1E–09)	(1.0E–09)
acidic ref.	6.7E–09	1.4E–08	1.0E–08	6.3E–09	6.7E–09	7.7E–09

The results are also shown as Figure A3-11 in Appendix 3.

The results for the total Th concentration measurements in the wall sorption experiments with EDTA in LCPW conditions, compared with reference samples, are shown in Table 5-85.

Table 5-85. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(6.1E–10)	(5.1E–10)	(1.1E–09)	(1.9E–09)	(1.0E–09)	(9.3E–10)
1 week	(8.4E–10)	1.4E–09	1.8E–09	(1.1E–09)	1.2E–09	1.4E–09
1 month	(7.3E–10)	3.0E–09	(9.5E–10)	(6.0E–10)	(4.8E–10)	(5.7E–10)
3 months	(9.9E–10)	(1.3E–09)	(1.4E–09)	(8.2E–10)	(9.8E–10)	(9.4E–10)
6 months	(1.1E–09)	(1.2E–09)	(1.3E–09)	(7.0E–10)	(8.9E–10)	(1.2E–09)
acidic ref.	6.7E–09	1.4E–08	1.0E–08	6.3E–09	6.7E–09	7.7E–09

The results for the total Th concentration measurements in the cement sorption experiments with EDTA in LCPW conditions, compared with reference samples, are shown in Table 5-86.

Table 5-86. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(2.1E–10)	3.3E–09	(1.5E–09)	(2.0E–09)	(1.4E–09)	(1.4E–09)
1 week	2.1E–09	2.1E–09	1.8E–09	(1.1E–09)	1.6E–09	1.2E–09
1 month	2.7E–09	2.2E–09	(1.7E–09)	2.0E–09	(7.2E–10)	3.0E–09
3 months	(1.2E–09)	1.7E–09	1.8E–09	(1.0E–09)	(1.1E–09)	(1.2E–09)
6 months	(1.4E–09)	1.5E–09	1.7E–09	(9.1E–10)	(1.0E–09)	(1.0E–09)
acidic ref.	6.7E–09	1.4E–08	1.0E–08	6.3E–09	6.7E–09	7.7E–09

The results are also shown as Figure A3-12 in Appendix 3.

The results for the total Th concentration measurements in the wall sorption experiments with ISA in FCPW conditions, compared with reference samples, are shown in Table 5-87.

Table 5-87. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.1E–10)	(1.2E–09)	(7.1E–11)	(1.3E–09)	(7.6E–10)	(5.9E–10)
1 week	2.0E–09	1.2E–09	1.5E–09	1.3E–09	(1.1E–09)	1.2E–09
1 month	(1.4E–09)	(7.8E–10)	(1.2E–09)	(6.3E–10)	(1.0E–09)	2.2E–09
3 months	(1.2E–09)	(9.6E–10)	(1.0E–09)	(6.8E–10)	(8.5E–10)	(1.1E–09)
6 months	(1.1E–09)	(9.1E–10)	(1.1E–09)	(8.3E–10)	(1.2E–09)	(1.2E–09)
acidic ref.	6.7E–09	7.9E–09	9.0E–09	6.0E–09	4.9E–09	1.0E–08

The results for the total Th concentration measurements in the cement sorption experiments with ISA in FCPW conditions, compared with reference samples, are shown in Table 5-88.

Table 5-88. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(5.0E–10)	2.6E–09	(1.8E–09)	(1.9E–09)	(8.0E–10)	(6.4E–10)
1 week	1.4E–09	(9.6E–10)	1.7E–09	(1.0E–09)	(9.8E–10)	(1.1E–09)
1 month	(1.7E–09)	(7.6E–10)	(8.6E–10)	(7.1E–10)	(8.0E–10)	(1.0E–09)
3 months	1.5E–09	(9.7E–10)	(1.0E–09)	(8.3E–10)	(8.3E–10)	(1.1E–09)
6 months	(1.2E–09)	(1.0E–09)	(1.2E–09)	(8.7E–10)	(1.2E–09)	(1.1E–09)
acidic ref.	6.7E–09	7.9E–09	9.0E–09	6.0E–09	4.9E–09	1.0E–08

The results are also shown as Figure A3-13 in Appendix 3.

The results for the total Th concentration measurements in the wall sorption experiments with ISA in LCPW conditions, compared with reference samples, are shown in Table 5-89.

Table 5-89. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(6.1E–10)	(9.1E–10)	(4.2E–11)	(1.1E–09)	(7.6E–10)	(5.9E–10)
1 week	(8.4E–10)	(1.1E–09)	(9.6E–10)	1.3E–09	(1.0E–09)	1.2E–09
1 month	(7.3E–10)	(3.7E–10)	(2.5E–10)	(5.1E–10)	(8.4E–10)	(9.2E–10)
3 months	(9.9E–10)	(8.8E–10)	(6.7E–10)	(6.4E–10)	(7.7E–10)	(1.1E–09)
6 months	(1.1E–09)	(7.6E–10)	(7.5E–10)	(8.0E–10)	(9.7E–10)	(1.0E–09)
acidic ref.	6.7E–09	7.9E–09	9.0E–09	6.0E–09	4.9E–09	1.0E–08

The results for the total Th concentration measurements in the cement sorption experiments with ISA in LCPW conditions, compared with reference samples, are shown in Table 5-90.

Table 5-90. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(2.1E–10)	(9.5E–10)	(8.0E–11)	(8.2E–10)	(8.0E–10)	(5.8E–10)
1 week	2.1E–09	(1.0E–09)	(8.0E–10)	(1.0E–09)	1.5E–09	(1.0E–09)
1 month	2.7E–09	(1.7E–09)	(7.8E–10)	(6.1E–10)	(7.7E–10)	(8.2E–10)
3 months	(1.2E–09)	(1.0E–09)	(6.8E–10)	(7.5E–10)	(7.6E–10)	(1.6E–09)
6 months	(1.4E–09)	(9.7E–10)	(8.4E–10)	(7.7E–10)	(1.1E–09)	(1.5E–09)
acidic ref.	6.7E–09	7.9E–09	9.0E–09	6.0E–09	4.9E–09	1.0E–08

The results are also shown as Figure A3-14 in Appendix 3.

The results for the total Th concentration measurements in the wall sorption experiments with citric acid in FCPW conditions, compared with reference samples, are shown in Table 5-91.

Table 5-91. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(3.1E–10)	(5.9E–10)	(5.7E–10)	(1.2E–09)	(9.1E–10)	(6.2E–10)
1 week	2.0E–09	(9.4E–10)	(1.0E–09)	1.3E–09	(1.1E–09)	(1.1E–09)
1 month	(1.4E–09)	(4.6E–10)	(2.3E–10)	(1.8E–10)	(2.1E–10)	(3.3E–10)
3 months	(1.2E–09)	8.0E–10	7.6E–10	8.1E–10	6.9E–10	7.0E–10
6 months	(1.1E–09)	(4.1E–10)	(9.5E–10)	1.4E–09	(9.4E–10)	(4.8E–10)
acidic ref.	6.7E–09	7.5E–09	1.1E–08	8.1E–09	6.8E–09	6.8E–09

The results for the total Th concentration measurements in the cement sorption experiments with citric acid in FCPW conditions, compared with reference samples, are shown in Table 5-92.

Table 5-92. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(5.0E–10)	(9.6E–10)	(1.8E–09)	(1.8E–09)	(6.3E–10)	(4.5E–10)
1 week	1.4E–09	(9.3E–10)	1.8E–09	1.4E–09	(1.1E–09)	1.5E–09
1 month	(1.7E–09)	(4.0E–10)	(3.7E–10)	(2.0E–10)	(2.1E–10)	(3.1E–10)
3 months	1.5E–09	9.1E–10	1.2E–09	1.0E–09	8.2E–10	1.0E–09
6 months	(1.2E–09)	(3.3E–10)	1.7E–09	1.7E–09	(8.4E–10)	(4.6E–10)
acidic ref.	6.7E–09	7.5E–09	1.1E–08	8.1E–09	6.8E–09	6.8E–09

The results are also shown as Figure A3-15 in Appendix 3.

The results for the total Th concentration measurements in the wall sorption experiments with citric acid in LCPW conditions, compared with reference samples, are shown in Table 5-93.

Table 5-93. Results of $[Th]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(6.1E–10)	2.8E–09	(9.3E–10)	(1.3E–09)	(9.1E–10)	(5.9E–10)
1 week	(8.4E–10)	(1.1E–09)	(9.3E–10)	(1.1E–09)	(8.0E–10)	(1.0E–09)
1 month	(7.3E–10)	(4.0E–10)	(2.0E–10)	(1.6E–10)	(2.0E–10)	(3.6E–10)
3 months	(9.9E–10)	7.8E–10	7.0E–10	7.6E–10	6.6E–10	6.9E–10
6 months	(1.1E–09)	(3.3E–10)	7.5E–10	1.1E–09	7.9E–10	(5.1E–10)
acidic ref.	6.7E–09	7.5E–09	1.1E–08	8.1E–09	6.8E–09	6.8E–09

The results for the total Th concentration measurements in the cement sorption experiments with citric acid in LCPW conditions, compared with reference samples, are shown in Table 5-94.

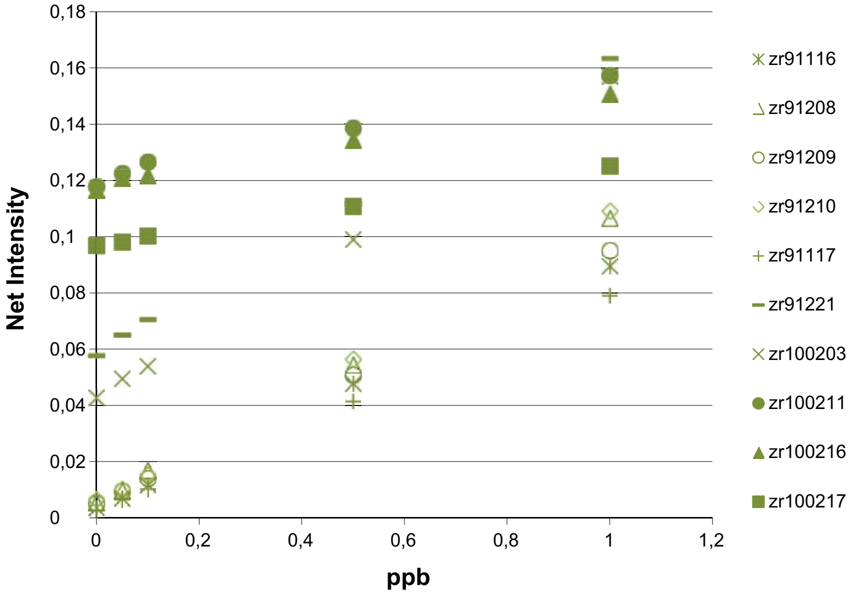
Table 5-94. Results of $[Th]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	(2.1E–10)	(1.4E–09)	(1.4E–09)	2.7E–09	(1.1E–09)	(1.5E–09)
1 week	2.1E–09	2.4E–09	1.5E–09	1.4E–09	(9.4E–10)	(1.1E–09)
1 month	2.7E–09	7.9E–10	(3.0E–10)	(2.6E–10)	8.3E–10	(3.1E–10)
3 months	(1.2E–09)	1.3E–09	1.5E–09	1.1E–09	1.3E–09	1.2E–09
6 months	(1.4E–09)	(5.0E–10)	3.0E–09	1.3E–09	1.0E–09	(4.6E–10)
acidic ref.	6.7E–09	7.5E–09	1.1E–08	8.1E–09	6.8E–09	6.8E–09

The results are also shown as Figure A3-16 in Appendix 3.

5.3.17 Results of Zr total concentration measurements

The calibration curves for total Zr concentration in the batch sorption experiments are shown in Figure 5-3 below.



Figur 5-3. *Calibration curves of ICPMS instrument of the 12 measurement sessions, using 0.05, 0.1, 0.5 and 1 ppb Zr standards.*

The calibration curves illustrate a progressively worsening contamination problem in the measurements. The source of Zr contamination is unknown, but different batches of sample tubes for storing the ICPMS samples can be suspected. However, it is interesting that a clear increasing trend is displayed, which may instead point towards a build-up problem of high Zr background in the ICPMS instrument itself.

Only the five first measurement sessions were evaluated for Zr concentrations in the batch experiments, corresponding to results for 1 day and 1 week samplings.

Table 5-95. Results for calibration of ICPMS instrument, using 0.05, 0.1, 0.5 and 1 ppb Zr standards.

session	R2 goodness of fit	Detection limit, as measured (ppb)	Detection limit, in undiluted sample (M)
091116	0.997066	4.94E–02	2.60E–08
091117	0.997529	5.17E–02	2.72E–08
091208	0.994411	4.98E–02	2.70E–08
091209	0.9933	6.12E–02	3.22E–08
091210	0.994403	6.30E–02	3.32E–08

The results for the total Zr concentration measurements in the wall sorption experiments with UDP in FCPW conditions, compared with reference samples, are shown in Table 5-96.

Table 5-96. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of UP2 degradation products in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	3.4E–08	6.9E–08	6.2E–08	1.1E–07	1.1E–07
1 week	1.2E–07	8.7E–08	1.1E–07	6.4E–08	7.7E–08	1.0E–07
acidic ref.	6.9E–07	2.5E–07	2.7E–07	2.8E–07	6.2E–07	4.5E–07

The results for the total Zr concentration measurements in the cement sorption experiments with UDP in FCPW conditions, compared with reference samples, are shown in Table 5-97.

Table 5-97. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of UP2 degradation products in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.4E–07	7.4E–08	9.6E–08	8.2E–08	1.2E–07	1.3E–07
1 week	1.7E–07	9.5E–08	6.6E–08	6.2E–08	1.1E–07	1.4E–07
acidic ref.	6.9E–07	2.5E–07	2.7E–07	2.8E–07	6.2E–07	4.5E–07

The results for the total Zr concentration measurements in the wall sorption experiments with UDP in LCPW conditions, compared with reference samples, are shown in Table 5-98.

Table 5-98. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of UP2 degradation products in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.2E–07	3.8E–08	6.4E–08	6.2E–08	6.5E–08	7.3E–08
1 week	1.2E–07	1.0E–07	1.0E–07	7.5E–08	7.5E–08	1.3E–07
acidic ref.	6.9E–07	2.5E–07	2.7E–07	2.8E–07	6.2E–07	4.5E–07

The results for the total Zr concentration measurements in the cement sorption experiments with UDP in LCPW conditions, compared with reference samples, are shown in Table 5-99.

Table 5-99. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of UP2 degradation products in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	8.2E–08	6.4E–08	8.2E–08	7.7E–08	7.8E–08
1 week	1.5E–07	9.7E–08	1.0E–07	6.9E–08	1.2E–07	1.1E–07
acidic ref.	6.9E–07	2.5E–07	2.7E–07	2.8E–07	6.2E–07	4.5E–07

The results for the total Zr concentration measurements in the wall sorption experiments with EDTA in FCPW conditions, compared with reference samples, are shown in Table 5-100.

Table 5-100. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	2.9E–08	1.8E–08	1.7E–08	1.7E–08	1.9E–08
1 week	1.2E–07	1.5E–08	1.4E–08	1.6E–08	2.0E–08	1.4E–08
acidic ref.	6.9E–07	1.3E–07	1.0E–07	9.7E–08	1.0E–07	9.7E–08

The results for the total Zr concentration measurements in the cement sorption experiments with EDTA in FCPW conditions, compared with reference samples, are shown in Table 5-101.

Table 5-101. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of EDTA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.4E–07	3.9E–08	4.1E–08	1.8E–08	1.9E–08	2.2E–08
1 week	1.7E–07	2.9E–08	3.9E–08	3.6E–08	3.6E–08	2.6E–08
acidic ref.	6.9E–07	1.3E–07	1.0E–07	9.7E–08	1.0E–07	9.7E–08

The results for the total Zr concentration measurements in the wall sorption experiments with EDTA in LCPW conditions, compared with reference samples, are shown in Table 5-102.

Table 5-102. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.2E–07	2.1E–08	2.1E–08	2.1E–08	2.2E–08	2.6E–08
1 week	1.2E–07	1.6E–08	1.3E–08	1.4E–08	2.0E–08	1.5E–08
acidic ref.	6.9E–07	1.3E–07	1.0E–07	9.7E–08	1.0E–07	9.7E–08

The results for the total Zr concentration measurements in the cement sorption experiments with EDTA in LCPW conditions, compared with reference samples, are shown in Table 5-103.

Table 5-103. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of EDTA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	3.8E–08	2.8E–08	3.5E–08	3.7E–08	3.8E–08
1 week	1.5E–07	2.5E–08	2.1E–08	2.4E–08	3.6E–08	1.8E–08
acidic ref.	6.9E–07	1.3E–07	1.0E–07	9.7E–08	1.0E–07	9.7E–08

The results for the total Zr concentration measurements in the wall sorption experiments with ISA in FCPW conditions, compared with reference samples, are shown in Table 5-104.

Table 5-104. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	2.4E–08	2.4E–08	2.7E–08	2.0E–08	2.5E–08
1 week	1.2E–07	3.1E–08	2.8E–08	2.9E–08	2.4E–08	3.6E–08
acidic ref.	6.9E–07	2.4E–07	2.3E–07	1.5E–07	1.3E–07	1.5E–07

The results for the total Zr concentration measurements in the cement sorption experiments with ISA in FCPW conditions, compared with reference samples, are shown in Table 5-105.

Table 5-105. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of ISA in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.4E–07	3.9E–08	4.0E–08	3.7E–08	2.4E–08	3.0E–08
1 week	1.7E–07	4.3E–08	5.2E–08	3.0E–08	3.7E–08	4.5E–08
acidic ref.	6.9E–07	2.4E–07	2.3E–07	1.5E–07	1.3E–07	1.5E–07

The results for the total Zr concentration measurements in the wall sorption experiments with ISA in LCPW conditions, compared with reference samples, are shown in Table 5-106.

Table 5-106. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.2E–07	1.7E–08	1.8E–08	2.4E–08	2.0E–08	2.5E–08
1 week	1.2E–07	2.9E–08	2.8E–08	2.9E–08	2.7E–08	2.5E–08
acidic ref.	6.9E–07	2.4E–07	2.3E–07	1.5E–07	1.3E–07	1.5E–07

The results for the total Zr concentration measurements in the cement sorption experiments with ISA in LCPW conditions, compared with reference samples, are shown in Table 5-107.

Table 5-107. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of ISA in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	1.9E–08	2.9E–08	2.1E–08	2.4E–08	2.4E–08
1 week	1.5E–07	4.1E–08	4.2E–08	3.0E–08	6.6E–08	3.8E–08
acidic ref.	6.9E–07	2.4E–07	2.3E–07	1.5E–07	1.3E–07	1.5E–07

The results for the total Zr concentration measurements in the wall sorption experiments with citric acid in FCPW conditions, compared with reference samples, are shown in Table 5-108.

Table 5-108. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	1.5E–08	1.9E–08	1.7E–08	1.9E–08	1.6E–08
1 week	1.2E–07	1.6E–08	1.1E–08	1.8E–08	1.8E–08	1.6E–08
acidic ref.	6.9E–07	1.3E–07	2.3E–07	1.2E–07	7.0E–08	1.0E–07

The results for the total Zr concentration measurements in the cement sorption experiments with citric acid in FCPW conditions, compared with reference samples, are shown in Table 5-109.

Table 5-109. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of citric acid in synthetic fresh cement pore-water (FCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.4E–07	1.6E–08	3.9E–08	2.0E–08	1.9E–08	1.6E–08
1 week	1.7E–07	1.8E–08	3.7E–08	2.0E–08	2.0E–08	1.9E–08
acidic ref.	6.9E–07	1.3E–07	2.3E–07	1.2E–07	7.0E–08	1.0E–07

The results for the total Zr concentration measurements in the wall sorption experiments with citric acid in LCPW conditions, compared with reference samples, are shown in Table 5-110.

Table 5-110. Results of $[Zr]_{tot}$ (M) measurements in wall sorption experiments with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.2E–07	1.7E–08	2.1E–08	1.8E–08	1.9E–08	4.5E–08
1 week	1.2E–07	1.7E–08	1.4E–08	1.8E–08	1.3E–08	2.1E–08
acidic ref.	6.9E–07	1.3E–07	2.3E–07	1.2E–07	7.0E–08	1.0E–07

The results for the total Zr concentration measurements in the cement sorption experiments with citric acid in LCPW conditions, compared with reference samples, are shown in Table 5-111.

Table 5-111. Results of $[Zr]_{tot}$ (M) measurements in cement sorption experiments with five dilutions of citric acid in synthetic leached cement pore-water (LCPW).

	Reference	C1	C2	C3	C4	C5
1 day	1.3E–07	1.8E–08	2.3E–08	2.2E–08	2.0E–08	2.0E–08
1 week	1.5E–07	4.0E–08	2.3E–08	2.0E–08	1.5E–08	2.3E–08
acidic ref.	6.9E–07	1.3E–07	2.3E–07	1.2E–07	7.0E–08	1.0E–07

5.4 Discussion of results

The results from experiments with leaching of cement show that degraded conditions, corresponding to what can be described as the first stage of cement degradation, when alkali hydroxides have been leached away and instead portlandite controls the pH of the pore water, can be accomplished within 6 months with a crushed material.

Since these particular conditions are expected to be valid for most of the period where a repository for LILW is designed to function, it is important to use a solid phase in laboratory experiments, which simulates these conditions as close as possible.

The experiments show that such material can be fairly quickly produced, at least when a crushed material is used.

The results from experiments with alkaline degradation of the fibre mass UP2 at room temperature at pH 12.5 and 13.3, gave NPOC concentrations of 28±1 and 33±0 ppm, respectively, (mean values for the duplicate experiments wih standard deviation, *cf.* Table 5-6) after 300 days of leaching. These values can be compared with 7 and 13 ppm DOC, respectively, for the similar experiments and similar leaching period (276 days) reported in the work by Duro et al. (2005)[4]. The difference may be due to experimental factors such as water composition, stirring method etc. Also, Duro et al. made a washing step of the UP2 fibre with distilled water before the alkaline leaching was started. Such a washing step was not used in this work.

Long-term measurements of up to 1,200 days were also made and gave 44±6 and 156±15 ppm NPOC, for pH 12.5 and pH 13.3 conditions, respectively (Table 5-6). Corresponding results for the longest leaching time in Duro et al. (2005), 700 days, gave 8 ppm and 30 ppm DOC, respectively. The results confirm the findings by Duro et al. that the DOC level is steadily increasing in FCPW conditions, while, on the other hand, a limiting value seems to be approached for LCPW conditions.

Results for **Cs** sorption in the **reference** cases show final wall sorption L_d values of 0.2–0.3 mL (corresponding to 2–3% of added tracer) for both FCPW and LCPW conditions, while final cement sorption R_d values are about $3 \cdot 10^{-3}$ m^3/kg for FCPW and $2 \cdot 10^{-3}$ m^3/kg for LCPW conditions (corresponding to 15% and 9% of added tracer, respectively). The difference is small and not significant. It should be noted, however, that wall sorption removes nearly the same amount of tracer from solution as cement does.

Results of Cs sorption onto tube walls in the presence of **UDP** show final L_d values of 0.1–0.6 mL, when detectable. Final R_d values are in the range of $4 \cdot 10^{-4}$–$2 \cdot 10^{-3}$ m^3/kg, when detectable.

Both wall and cement sorption are close to what can be detected with the method and many measurements gave, in fact, no detection of sorption. Most of the long time measurements with high concentrations of UDP (C1–C2, see Table 4-2) give no detection of L_d or R_d values and this may indicate reduced sorption due to UDP and not just effects of error fluctuations.

Results of Cs sorption onto tube walls in the presence of **EDTA** show final L_d values of 0.5–1 mL, when detectable. Final R_d values are in the range of $9 \cdot 10^{-4}$–$2 \cdot 10^{-3}$ m^3/kg, when detectable.

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[4] **Duro L, Grivé M, Gaona X, Bruno J, Andersson T, Borén H, Dario M, Allard B, Hagberg J, 2005.** Study of the effect of the fibre mass UP2 degradation products on radionuclide mobilisation. Unpublished report.

The predicament of measurement close to detection limits is repeated with the EDTA experiments. The non-detectable wall sorption in the long-term with the higher concentrations of EDTA may give an indication that reduced sorption on tube walls have taken place. A corresponding effect on the sorption onto cement, a reduction below detection limit, is seen for FCPW conditions only.

Results of Cs sorption onto tube walls in the presence of **ISA** give final L_d values of 0.1–0.8 mL, when detectable. For cement the final R_d values are in the range of $2 \cdot 10^{-4}$–$3 \cdot 10^{-3}$ m^3/kg, when detectable. ISA seems not to affect wall sorption of Cs, but a possible reduction of cement R_d values below detection limits for high concentrations of ligand (C1–C3, see Table 4-2) and for FCPW conditions is seen, as was also found for UDP and EDTA.

Results of Cs sorption onto tube walls in the presence of **citric acid** (CA) give final L_d values of 0.1–2 mL, when detectable. For cement the final R_d values are in the range of 1–$3 \cdot 10^{-3}$ m^3/kg, when detectable. Like ISA, citric acid does not affect wall sorption of Cs. However, the same effect of non-detectable cement sorption for FCPW conditions and high concentration of CA, as was seen with the other ligands, is observed for citric acid too.

To summarize the results for Cs sorption, it can first of all be concluded that Cs sorption onto cement is very weak, even without organic ligands, particularly at pH 13.3 (FCPW conditions). Although the results are generally rather scattered, partly due to the proximity to the detection limit of the method used here and partly due to a wall sorption of Cs that is of the same strength as Cs sorption onto cement. FCPW results generally seems to give R_d values closer to 10^{-4} m^3/kg, while LCPW results give R_d values closer to 10^{-3} m^3/kg. At the final measurement at 6 months, however, there was no significant difference.

The latter result is consistent with results from a previous work where batch sorption experiments with Cs and cement in FCPW conditions gave a R_d value of $3 \cdot 10^{-3}$ m^3/kg (Holgersson et al. 1998).

The Cs^+ ion is expected to adsorb with electrostatic interactions only and the effect of high ionic strength should suppress such a sorption mechanism, as the results here also confirm. Also according to theory, the results indicate (but do not actually confirm) that the further increase in ionic strength, by going from LCPW to FCPW conditions, weakens Cs sorption even further.

The organic ligands do not form metal complexes with Cs and should not reduce Cs sorption by such a mechanism. However, there may be a possibility for an effect from ligand sorption onto the solid phases that in turn may modify the surfaces and make them more or less attractive for an electrostatic interaction. The effect may be similar to cement superplasticizer compounds, surface-active organic polymers that are commonly added to the cement-water mixture when casting. The surface-active compound sorbs on the cement grains, reduces the electrostatic attraction between the grains and prevents them from sticking together. The result is a more workable mixture.

Such an effect may explain the observed results here for UDP and EDTA, since particularly these two ligands seems to reduce the wall sorption of Cs, and generally for all ligands, since all of them seems to reduce Cs sorption onto cement below detection limits. The effect is notable at high alkalinity FCPW conditions only. UDP contain polymeric compounds that may work as surface active agents. It is therefore somewhat surprising that short-chained C_6, C_{10} ligands, such as EDTA, ISA and citric acid, should show a similar surface-active effect of reducing Cs sorption onto cement.

The detection problem again makes it difficult to draw any definitive conclusions of effects of the added organics on Cs sorption onto cement, the results merely indicates that something is happening. Increased experimental resolution by a more sensitive detection method (for example Liquid or Solid state Scintillation Counting) is necessary to give an answer to the question. However, as discussed in the Introduction, Cs sorption is likely to be considerably enhanced when aggregate and cement is used together, that is, in the form of concrete. If the organics will affect Cs sorption onto concrete is therefore of more interest.

Results for **Co** sorption in the **reference** cases show final wall sorption L_d values of about 3 mL (corresponding to 2–10% of added tracer) for both FCPW and LCPW conditions, while final cement sorption R_d values differ somewhat with $4 \cdot 10^{-2}$ m^3/kg (corresponding to sorption of 70% of added tracer) for FCPW and $1 \cdot 10^{-1}$ m^3/kg (corresponding to 80% of added tracer) for LCPW conditions.

Results of Co sorption onto tube walls in the presence of **UDP** show final L_d values of 0.3–6 mL, when detectable. Final R_d values are in the range of $1\cdot10^{-2}$–$1\cdot10^{-1}$ m^3/kg.

Any effects of UDP on Co sorption onto cement cannot be discerned, however, there may be an effect of reduced wall sorption with concentrations C1 and C2.

Results of Co sorption onto tube walls in the presence of **EDTA** show final L_d values of 1–47 mL, when detectable. Final R_d values are in the range of 1–$5\cdot10^{-2}$ m^3/kg, when detectable.

There is a significant effect of stronger wall sorption, compared to the reference case, with the lower concentrations of EDTA. This may at first seem confusing, but may be explained by the assumption that EDTA sorbs on the tube walls. The Co^{2+} ion readily forms complexes with EDTA and it is possible that the complexes sorb onto tube walls too. However, when the ligand concentration is increased, the wall surface becomes saturated with EDTA and Co-EDTA in solution will increase. This would explain decreasing wall sorption for the highest EDTA concentration.

Any significant effect of EDTA in the investigated concentration range, either increase or decrease, on Co sorption onto cement is not found.

Results of Co sorption onto tube walls in the presence of **ISA** show final L_d values of 12–35 mL. Final R_d values are in the range of $4\cdot10^{-2}$–$3\cdot10^{-1}$ m^3/kg.

As with EDTA, also the results with ISA show increased wall sorption, particularly for the experiments with low concentration of ISA. A similar mechanism with Co-ISA complex sorption onto tube walls may be the explanation.

Any significant effect of ISA in the investigated concentration range, either increase or decrease, on Co sorption onto cement is not found.

Results of Co sorption onto tube walls in the presence of **citric acid** show final L_d values of 4–27 mL. Final R_d values are in the range of $2\cdot10^{-2}$–$1\cdot10^{-1}$ m^3/kg.

As with EDTA and ISA, also the results with citric acid show increased wall sorption, particularly for the experiments with low concentration of citric acid. A similar mechanism with Co-citric acid complex sorption onto tube walls may be the explanation.

Any significant effect of citric acid in the investigated concentration range, either increase or decrease, on Co sorption onto cement is not found.

Co sorption is stronger than Cs sorption, as can be expected with a metal that binds preferentially by covalent bonding to oxygen on surfaces. Such sorption sites are abundant on cement, but should be less common on tube walls. Compared with Cs it is also the cement phase that show increased attraction for Co, with R_d values in the range of $3\cdot10^{-2}$ to $1\cdot10^{-1}$ m^3/kg. LCPW results generally seems to give R_d values close to 10^{-1} m^3/kg, while FCPW results give R_d values somewhat below this.

A previous investigation with Ni sorption onto cement in FCPW conditions show final R_d values of 0.04 m^3/kg (Holgersson et al. 1998), which is consistent with the results for Co in the present work, if Ni is considered as a close analogue element to Co.

No effects of the organic ligands in the investigated concentration ranges can be seen for Co sorption onto cement, despite the fact that Co complex formation is documented in the literature for the ISA analogue compound THPA (Bourbon and Toulhoat 1996) and EDTA (Duewer and Freiser 1977). At least for ISA, the results are nevertheless consistent with previous findings where no effect of ISA, in similar or higher concentrations as used here, on Ni sorption onto cement was found (Holgersson et al. 1998).

However, an effect was found on Co wall sorption, where decreasing concentrations of EDTA, ISA and citric acid increased Co wall sorption, compared with reference experiments. For the moment, the only explanation that can be given is a simultaneous sorption on the tube walls by free ligands and Co-ligands complexes. An increasing ligand concentration would then cause desorption of Co-ligand complexes. It is interesting that UDP, in contrast, show the expected behavior, with reduced wall sorption compared with references and not, as with the other ligands, increased wall sorption.

Results for **Eu** sorption, using radioactive tracer ^{152}Eu, in the **reference** cases show final wall sorption L_d values of 80 mL (corresponding to 90% of added tracer) after 6 months for FCPW, while LCPW conditions gave 110 mL already after 1 week and thereafter a too strong wall sorption to be detected.

^{152}Eu sorption onto cement was even stronger, since nothing at all can be detected after the first sampling at 1 day. At that time R_d values were both 0.3 m^3/kg (corresponding to sorption of 90% of added tracer) for FCPW and LCPW conditions.

Results of Eu sorption onto tube walls in the presence of **UDP** show final L_d values of 43–830 mL, when detectable. R_d values could only be measured up to 1 week in FCPW conditions and were in the range of 0.1–2 m^3/kg before they went above upper detection level.

Any effects of UDP on ^{152}Eu sorption onto cement cannot be established due to the few data that could be collected. Final R_d values should at least be larger than 2–3 m^3/kg, which was the upper detection level of the experimental configuration.

The peculiar effect of stronger wall sorption of ^{152}Eu, when compared with references, for the lower concentrations of UDP was observed. Such "anomalies" were observed also for Co wall sorption in the presence of EDTA, ISA and CA, as described above.

Results of Eu sorption onto tube walls in the presence of **EDTA** show one final L_d value of 380 mL, the other were not detectable. R_d values for Eu sorption onto cement in the presence of EDTA could be measured only at the one day sampling and values are in the range of 0.2–7 m^3/kg.

Just as in the case with the UDP experiments, far too few data for ^{152}Eu sorption onto cement in the presence of EDTA could be collected in order to establish any effect from the organic ligand on metal sorption. The data do not deviate significantly from the likewise few reference data. Final R_d values should at least be larger than 2–3 m^3/kg, which was the upper detection level of the experimental configuration.

Results of Eu sorption onto tube walls in the presence of **ISA** show final L_d values of 47–390 mL. Very few R_d values for Eu sorption onto cement in the presence of ISA could be collected and then only at one day or one week, values are in the range of $2 \cdot 10^{-2}$–0.6 m^3/kg.

Any significant effect of ISA in the investigated concentration range, either increase or decrease, on Eu sorption onto cement is not found. The few data do not deviate significantly from the likewise few reference data. Final R_d values should at least be larger than 2–3 m^3/kg, which was the upper detection level of the experimental configuration.

Results of Eu sorption onto tube walls in the presence of **citric acid** show final L_d values of 54–1,200 mL. Very few R_d values for Eu sorption onto cement in the presence of CA could be collected and then only at one day or one week for LCPW conditions, values are in the range of 0.3–3 m^3/kg.

Any significant effect of citric acid in the investigated concentration range, either increase or decrease, on Eu sorption onto cement is not found. The few data do not deviate significantly from the likewise few reference data. Final R_d values should at least be larger than 2–3 m^3/kg, which was the upper detection level of the experimental configuration.

The batch sorption experiments with ^{152}Eu were generally not successful since too few results below the upper detection limit of 2–3 m^3/kg could be collected. The problem may be alleviated by changing the experimental configuration to a lower S:L ratio, but also by utilizing a more sensitive detection method, such as Liquid or Solid Scintillation Counting, both have efficiencies above 50% (compared with HPGe detection efficiency of under 1%). Strong wall sorption will, however, continue to be a problem.

An attempt to increase detection level by increased radionuclide loading is not recommended, since this may provoke hydroxide precipitations and/or Eu colloid formation. This method should only be considered when a radionuclide of better specific radioactivity is available, thus exchanging excess of carrier Eu for radioactive Eu.

The few data that could be collected nevertheless show the expected strong sorption of Eu onto cement. In the literature, final R_d values of no less than 10^3–10^4 m^3/kg (Wieland et al. 1998) are reported.

More of immediate concern is that the adverse effect of UP2 degradation products on Eu sorption onto cement previously reported (Dario et al. 2004a, b, Duro et al. 2005) was not even indicated in the present investigation.

As already mentioned in the introduction, similar experiments have shown that UDP in the concentration range from 0.3 to 3mM DOC (corresponding to 3.6 to 36 ppm DOC) gives a reduction of final R_d values for Eu sorption onto cement from 3,000 down to 5 m^3/kg (Dario et al. 2004a, b).

Apart from the impressive upper detection level achieved in those experiments (no doubt by using a S:L ratio of 1:1000 compared with 1:20 used here), the reduction of R_d, with a factor of almost three orders of magnitude, takes place in a domain of R_d values that is entirely above the detection level of the present investigation. Not even when using the UDP additive of 33 ppm DOC (concentration C1) in the present work an increased detection is achieved. It does not, however, contradict the previous results, which show R_d values in the range 3–5 m^3/kg for the whole period, when using UDP addition of 36 ppm DOC.

The results for EDTA, ISA and CA additions are similar to results for UDP, giving R_d values above detection limits for the entire ligand concentration ranges investigated.

Results for the addition of $10^{-2.5}$ M ISA, corresponding to 20 mM or 228 ppm DOC, to Eu sorption experiments with cement have been reported (Dario et al. 2004a, b). They show R_d values in the range of 30–300 m^3/kg.

Results for Eu sorption onto cement with "equilibrium concentrations" of ISA in the range of 10^{-5}–10^{-2} M of ISA, show that a slight reduction of Eu sorption, from $2 \cdot 10^3$ m^3/kg down to $7 \cdot 10^2$ m^3/kg takes place at the highest ISA concentration 10^{-2} M only (Wieland et al. 1998). It should be noted that the "equilibrium concentration" of ISA that were given is not the total added concentration, but is ISA remaining in solution, presumably after cement sorption of ISA itself, so it may not be straightforward for comparison with other results.

Results are also reported for Pm sorption onto cement and concrete in the presence of 5 mM ISA (corresponding to 30 mM or 360 ppm DOC), where an effect of reduced sorption, from 20 m^3/kg down to about 5 m^3/kg was noted at the 1 day and 1 week sampling but not at the later samplings. However, by using an alkaline leachate of cellulose, reported to contain 27 mM ISA (corresponding to 162 mM or 1,944 ppm DOC) a sustained effect on Pm sorption was observed for the whole 6 months of duration of the experiments, with a final R_d value of 0.05 m^3/kg (Holgersson et al. 1998).

The highest ISA concentration investigated here was 300 ppm DOC (concentration C1), corresponding to 25 mM DOC, however, no effects of a reduced Eu sorption could be detected, not even on wall sorption. This is consistent with the slight and temporary effect observed in the cited previous works, when ISA total concentrations in the range of 20–30 mM DOC were used (Dario et al. 2004a, b, Holgersson et al. 1998), if Pm in the last reference can be considered as an analogue for Eu.

Results for the addition of 10^{-2} M EDTA, corresponding to 100 mM or 1,200 ppm DOC, to Eu sorption experiments with cement have been reported (Dario et al. 2004a, b). They show R_d values in the range of 0.1–0.5 m^3/kg. The highest concentrations investigated here was 500 ppm DOC and results were above upper detection level of 2–3 m^3/kg.

Results for the addition of 10^{-2} M citric acid, corresponding to 60 mM or 720 ppm DOC, to Eu sorption experiments with cement have been reported (Dario et al. 2004a, b). They show R_d values in the range of 10–100 m^3/kg. The highest concentrations investigated here was 500 ppm DOC and results were above upper detection level of 2–3 m^3/kg.

To conclude, the few results for ^{152}Eu sorption onto cement that could be measured here, with or without organic ligands present, are at least fully consistent with other results, taken from the literature.

The measurements of **total Eu concentration** were generally successful since most results were over detection levels. The expected $[Eu]_{tot}$ in the acidified reference samples was about 4 nM, a value deducted from the dilution of the stock solution. Variations are expected of the actual amount added to each batch.

The expected concentration was confirmed with measurements, were $[Eu]_{tot}$ in the acidified samples were: 4.8 nM for the reference series (no organic ligand), in the range 5.0–16 nM for the UDP series, in the range 3.9–6.9 nM for the EDTA series, in the range 4.0–8.9 nM for the ISA series and finally in the range 3.5–5.3 nM for the CA series.

For the wall sorption experiments, lower total Eu concentrations were expected due to wall sorption and this was also confirmed. Concentrations were in the range of 0.5–1 nM, irrespective of any additions of organic ligands. This corresponds to wall sorption L_d values of about 60–30 mL, which is in fairly good agreement with the values measured for ^{152}Eu.

The total Eu concentrations measured in the batch experiments with cement are, however, nothing less than surprising since all measurements clearly show values of $[Eu]_{tot}$ that *increase* with time, whether organic ligands were present or not. Final concentrations were about 5–10 nM. If the source of Eu is the cement itself or a progressive mobilization of the added Eu tracer is not known.

Radiometric measurements points to the former explanation since no ^{152}Eu were detected at all in the later sampling occasions, only at the first at one day and one week, as described above.

On the other hand, the concentrations in all the batch experiments with cement do converge in a suspicious way to final concentrations with values expected from the addition of tracer and this points to the latter explanation.

Due to the increasing Eu concentrations with time in the batches with cement, compared to wall sorption experiments, evaluation of R_d values from the $[Eu]_{tot}$ measurements will give zero values, because concentrations approach those in the acidic references. Under these circumstances the wall references are not useable for correction of wall sorption, since obviously, the factor that mobilizes Eu in the cement experiments is not present in the wall sorption experiments.

If this apparent Eu mobilization is a persistent and non-artificial problem in cement systems and then if it will influence measurements of R_d values also for Eu tracer are important but unfortunately still to be answered questions here.

No effects of the addition of organic ligands on Eu total concentrations were established.

The measurements of **total Th concentration** were problematic because they were close to detection levels and most of the measurements in the non-acidic experiments were in fact under the formal detection level. It was noted that the detection levels with ICPMS were slightly higher for Th than for Eu, due to a more noisy background at mass 232 compared with mass 153.

The contribution to $[Th]_{tot}$ in the acidified reference samples from tracer addition is expected to be about 0.8 nM, a value deducted from the dilution of the stock solution. However, higher concentrations can be expected because of additional contribution from background concentrations in LCPW/FCPW (see Table 5-8), which should give an additional 0.5–1.5 nM and total concentrations in the range of 1.3–2.3 nM.

The actual measured $[Th]_{tot}$ in the acidified samples were, however, slightly higher than expected: 6.7 nM for the reference series (no organic ligand), in the range 7.4–28 nM for the UDP series, in the range 6.3–14 nM for the EDTA series, in the range 4.9–10 nM for the ISA series and finally in the range 6.8–11 nM for the CA series.

The reason for the higher concentration than expected, as measured in the acidified references, is not clear. It may be a contribution from the 1 M HCl used for the acidification or acidic leaching of containing vessels.

For the wall sorption and cement sorption experiments, the measured total Th concentrations were about the same, in the range 0.1–2 nM and this is only slightly lower than what can be expected from the addition of Th from tracer and background in LCPW/FCPW. However, since most measurements are close or below detection level, it would be to go too far to say that there is weak sorption of Th. The question of the concentration of acidified references also makes any evaluations of R_d values from total Th concentrations dubious.

As with Eu, very high R_d values, in the range of 10^3–10^4 kg/m^3, are previously reported for Th sorption onto cement (Wieland et al. 1998).

It is interesting to note that there seem to be no major difference in results for measurements of $[\mathrm{Th}]_{\mathrm{tot}}$ between experiments with or without cement. This indicates that $[\mathrm{Th}]_{\mathrm{tot}}$ may be controlled by a solubility constant, for example, the K_s for $\mathrm{Th(OH)_4}$ (am), despite the effort to keep the total concentration of Th low enough to prevent solid phases to precipitate.

The measurements of **total Zr concentration** were only partly successful due to rising contamination levels in the later measurements. Only data for 1 day and 1 week of sampling in the batch sorption experiments could be measured.

The contribution to $[\mathrm{Zr}]_{\mathrm{tot}}$ in the acidified reference samples from tracer addition is expected to be about 0.8 nM, a value deducted from the dilution of the stock solution. However, higher concentrations can be expected because of additional contribution from background concentrations in LCPW/FCPW (see Table 5-9), which should give an additional 6–40 nM and total concentrations in the range of 7–40 nM.

The actual measured $[\mathrm{Zr}]_{\mathrm{tot}}$ in the acidified samples were *much* higher than expected: 690 nM for the reference series (no organic ligand), in the range 250–620 nM for the UDP series, in the range 100–130 nM for the EDTA series, in the range 130–240 nM for the ISA series and finally in the range 70–230 nM for the CA series.

Just as for Th , the reason for the higher concentration of Zr than expected, as measured in the acidified references, is not clear. It may be a contribution from the 1M HCl used for the acidification or from acidic leaching of containing vessels. Relatively high levels of $[\mathrm{Zr}]_{\mathrm{tot}}$ were, however, also measured in the washings of cement and centrifugation tubes (Table 5-9). It is therefore not unlikely that Zr is continuously leached from the centrifugation tubes used for the batch experiments, also under alkaline conditions.

There are no major difference in $[\mathrm{Zr}]_{\mathrm{tot}}$ between reference batches (no organic ligand) with or without cement, which are about 130 nM. However, the batches with organic ligands are, curiously, lower in $[\mathrm{Zr}]_{\mathrm{tot}}$, about 10–140 nM.

6 Conclusions

In this work, to investigate the alkaline degradation products of UP2 and their possible effects on Cs, Co, Eu and Th/Zr sorption onto fresh and degraded cement, three different tasks were adressed.

Firstly, it has been shown that degraded cement for subsequent batch sorption experiments, can be prepared relatively quickly, within 6 months, when starting with a crushed fresh material.

Secondly, it has been shown that the alkaline degradation of UP2 yields DOC concentrations of about 30 ppm after 300 days of leaching, while continued leaching to about 1,200 days gave about 45 and 150 ppm DOC when using leached and fresh artificial cement pore-water, respectively.

Thirdly, batch sorption experiments with ^{134}Cs and ^{60}Co in the presence of alkaline degradation products of UP2 of up to 30 ppm DOC show no effects on metal sorption either on fresh or leached cement. R_d values for Cs were measured to about 10^{-3} kg/m^3 and for Co the values were in the range of 0.03–0.1 kg/m^3. Other ligands investigated were EDTA, ISA and citric acid of concentrations up to 500, 300 and 300 ppm DOC, respectively. However, no effects on Cs and Co sorption of these ligands were established either.

Batch sorption experiments with ^{152}Eu were not successful because most results were above the upper detection levels of 2–3 m^3/kg. Initial R_d values of 0.3 m^3/kg were measured at the first day only. The addition of the aforementioned organic ligands in the concentrations stated did not improve detection.

Measurements of total concentrations of Eu, Th and Zr were also made and gave valuable insight in background concentrations in the batch sorption experiments. For different reasons the concentrations could not be utilized for establishing R_d values. In the case of Eu it was found that total Eu concentration appeared to increase with time in the batch experiments with cement. Final concentrations after 6 months were in the range 5–10 nM, or about the same as was added with tracer.

If the Eu is leached from cement, a mobilisation of added tracer or purely an artefact is not yet established.

In the case of Th, concentrations were close to detection limits and gave no significant difference between blank and cement experiments. Final concentrations after 6 months were about 1 nM, which is also close to what was added with tracer and from background in the artificial pore-waters.

In the case of Zr, an unidentified contamination source was present. Also here the concentrations in blank and cement experiments were very similar in the few measurements without contamination problems. Concentrations were about 100–700 nM, which were much higher than expected from added tracer. A leaching of tube walls may be the answer, particularly in the acidic reference samples.

To improve methods in the future it is suggested that different S:L ratios are used, depending on what tracer are measured. Detection can also be improved by utilising separate experiments and optimal radiometric detectors for each tracer. Use of tracers with improved and high specific activity are recommended.

ICPMS measurements give important information of background total concentrations of added tracer elements. It also have the potential to measure low tracer concentrations (meaning high R_d values), especially for elements with atomic masses above 100.

However, ICPMS measurements of background total concentrations also point to the potential problem when the tracer element in question is also leached out from a solid phase and is then “interfering” with added tracer. Such conditions make an evaluation of R_d values from added total concentration of tracer meaningless, since 1) the total tracer concentration is unknown (requiring a total digestion of solid phase and subsequent analyses) and 2) the tracer concentration in solution may be controlled by a potentially complex process, which can include diffusion (in and out), sorption/desorption and dissolution.

In such a case any potential tracer element solubility-controlling solid-phases have to be identified. If such a phase is not present, there is still hope that the tracer element can be leached out completely from solid phase before commencing batch sorption experiments with tracer additions. Using a lower S:L ratio may alleviate also this problem, but the potential problem of leaching tracer element from container walls remains.

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8 List of abbreviations

CA	Citric Acid
DIC	Dissolved Inorganic Carbon
DL	Detection Limit
DOC	Dissolved Organic Carbon, DOC is TOC minus POC
EDTA	Ethylene Diamine Tetraacetic Acid
FCPW	Fresh Cement Pore-Water, artificial alkaline water of pH 13.3
HPGe	High Purity Germanium detector, for γ radiation
ICPMS	Ion Coupled Plasma with Mass Spectrometry
ISA	IsoSaccharinic Acid
LCPW	Leached Cement Pore-Water, artificial alkaline water of pH 12.5
LILW	Low to Intermediate Level (radioactive) Waste
NPOC	Non-Purgeable Organic Carbon, NPOC is TOC minus VOC
OPC	Ordinary Portland Cement
POC	Particular Organic Carbon
TC	Total Carbon, dissolved and suspended in solution
THPA	Tetra Hydroxy Pentanoic Acid
TOC	Total Organic Carbon, TOC is TC minus DIC
UDP	UP2 fibre mass alkaline Degradation Products
VOC	Volatile Organic Carbon

Appendix 1

Diagrams of cement degradation experiments

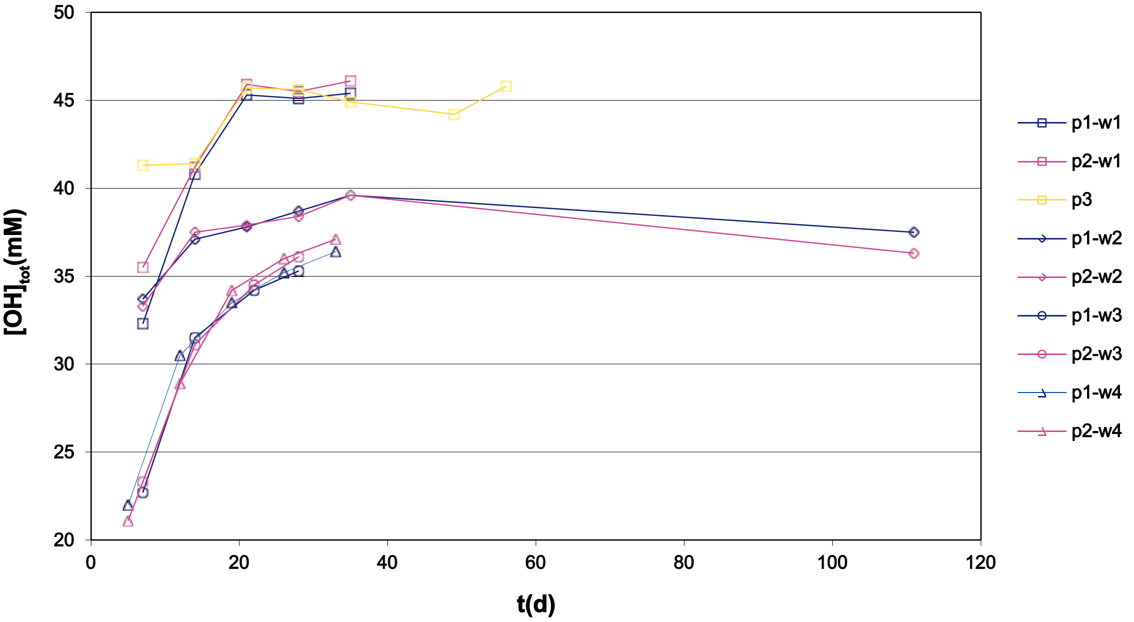

Figure A1-1. The development of total alkalinity in the initial water and three subsequent water exchanges of cement leaching solutions (p1 and p2). An additional sample (p3) was monitored with initial water only

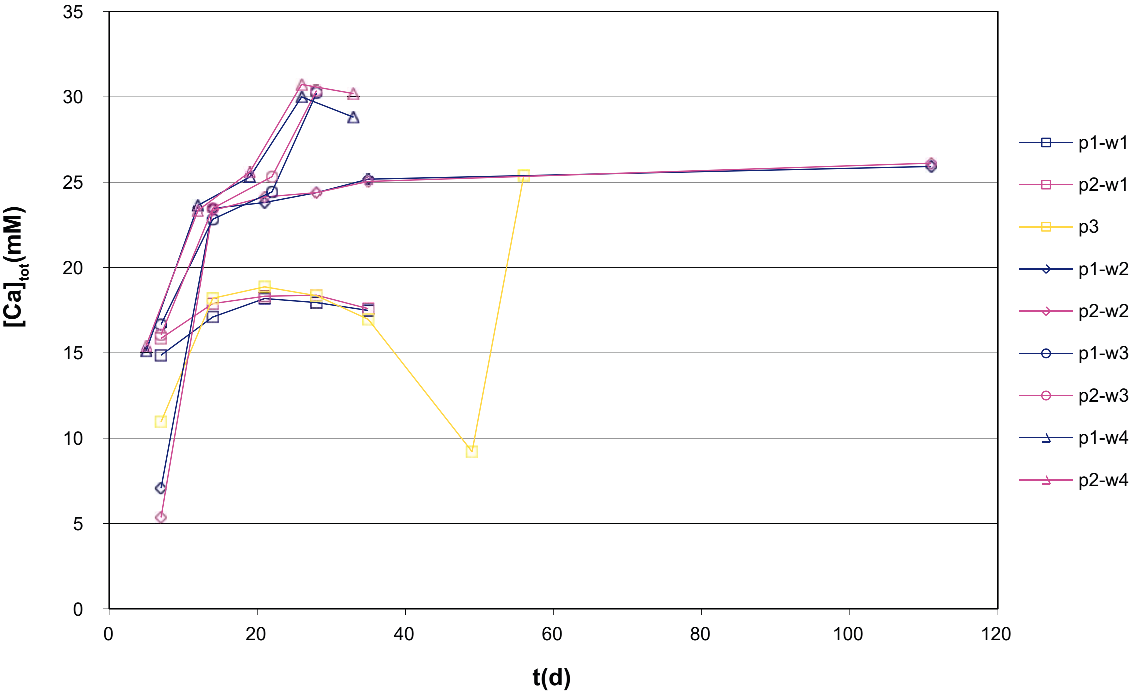

Figure A1-2. The development of total calcium in the initial water and in three subsequent water exchanges of cement leaching solutions (p1 and p2). An additional sample (p3) was monitored with initial water only.

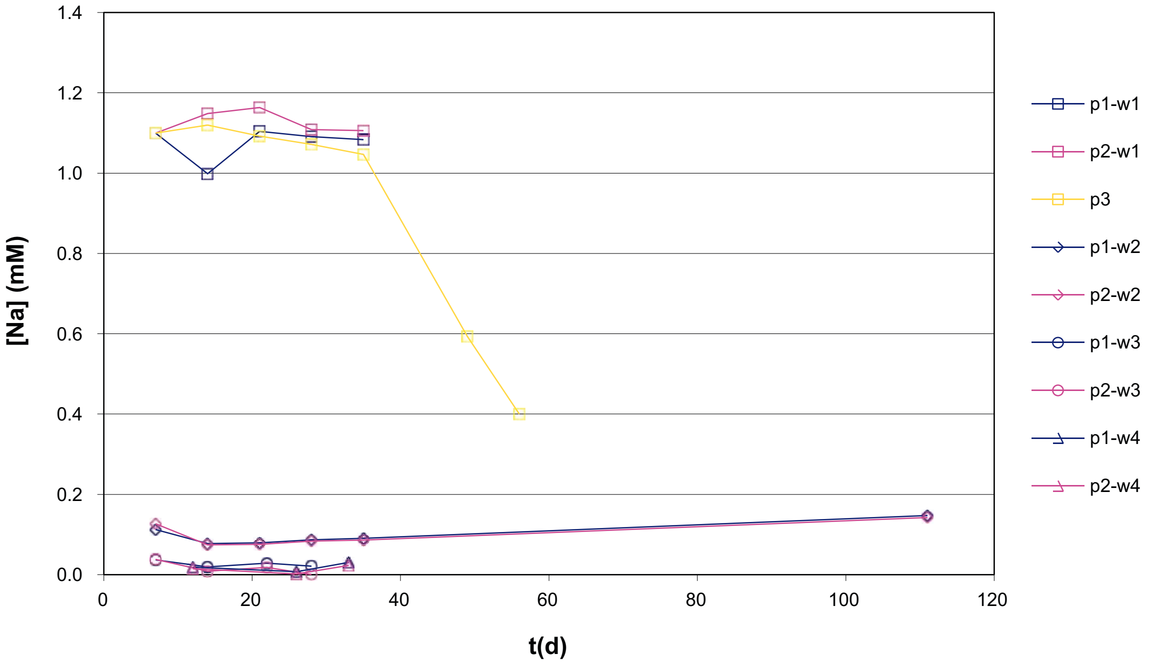

Figure A1-3. *The development of sodium in the initial water and in three subsequent water exchanges of cement leaching solutions (p1 and p2). An additional sample (p3) was monitored with initial water only.*

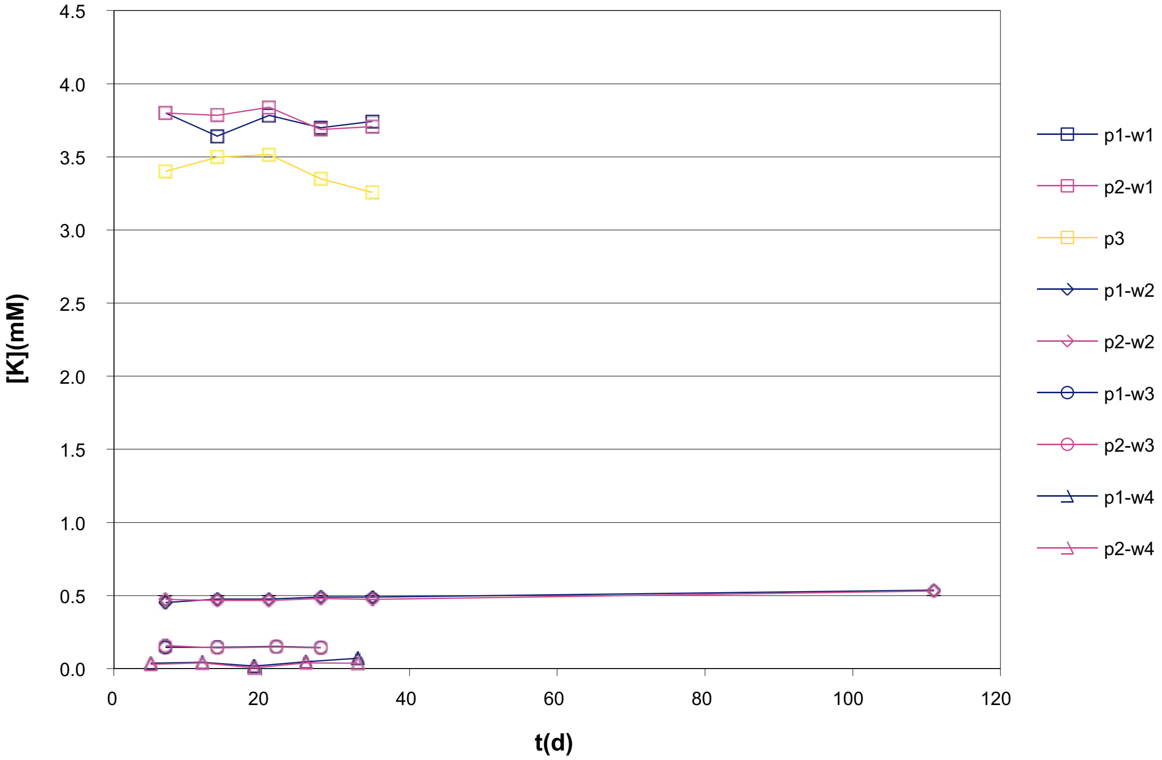

Figure A1-4. *The development of potassium in the initial water and in three subsequent water exchanges of cement leaching solutions (p1 and p2). An additional sample (p3) was monitored with initial water only.*

Appendix 2

Diagrams of cement sorption experiments

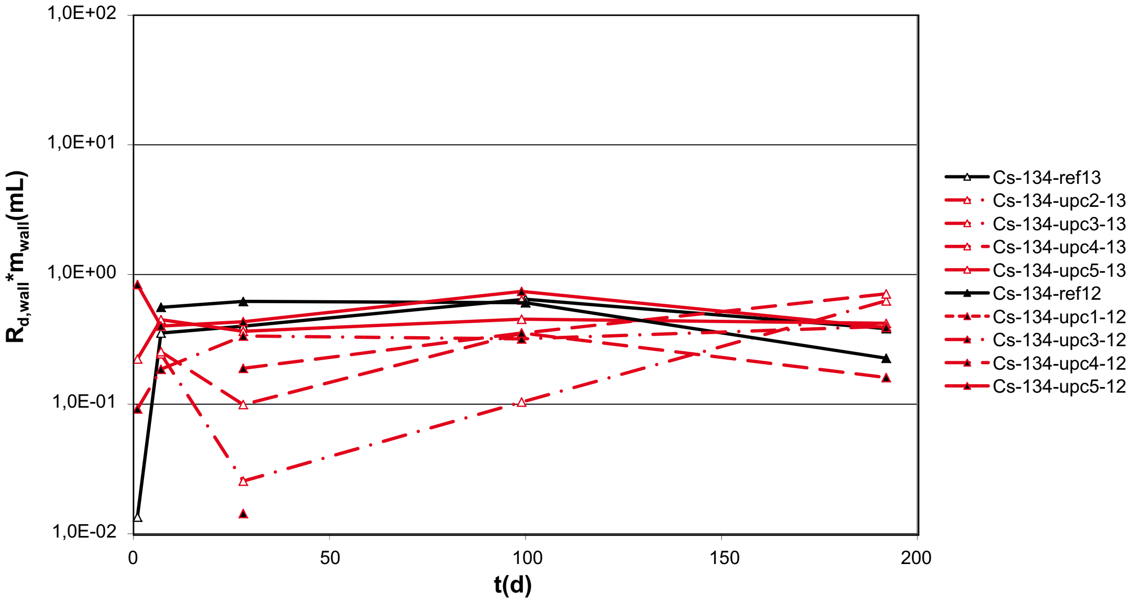

Figure A2-1. Results of ^{134}Cs wall sorption with five dilutions of UP2 degradation products. Legend: 13=fresh cement pore-water, 12=leached cement pore water.

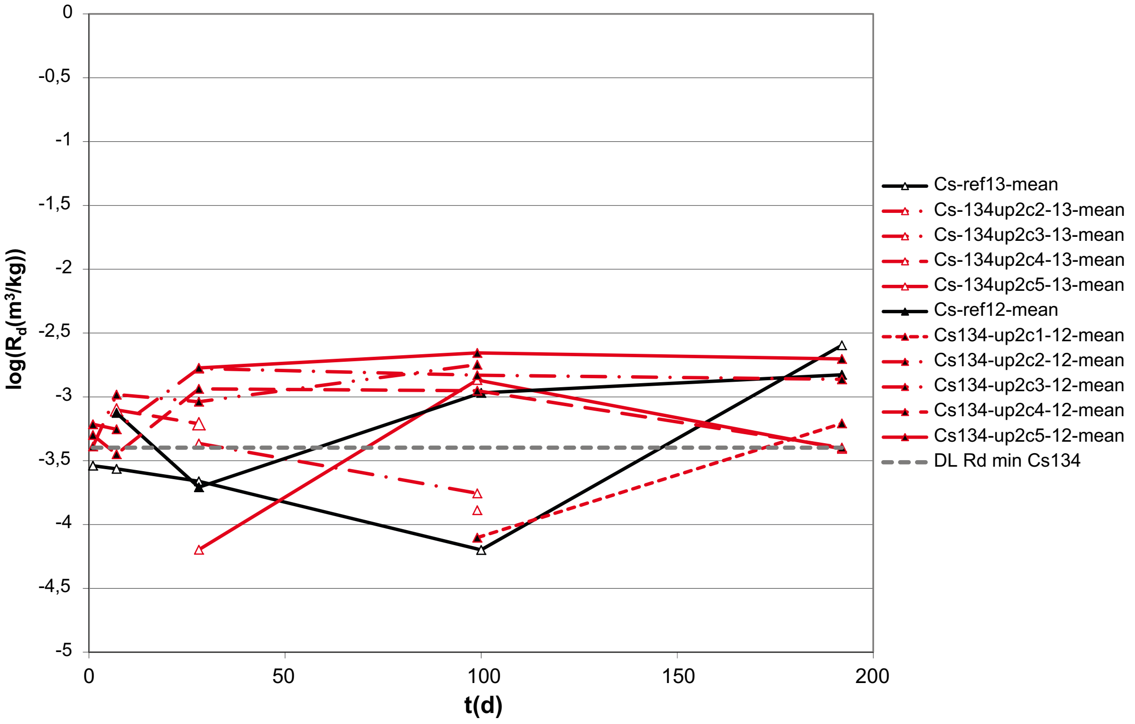

Figure A2-2. Results of ^{134}Cs cement sorption with five dilutions of UP2 degradation products. Legend: 13=fresh cement pore-water, 12=leached cement pore water.

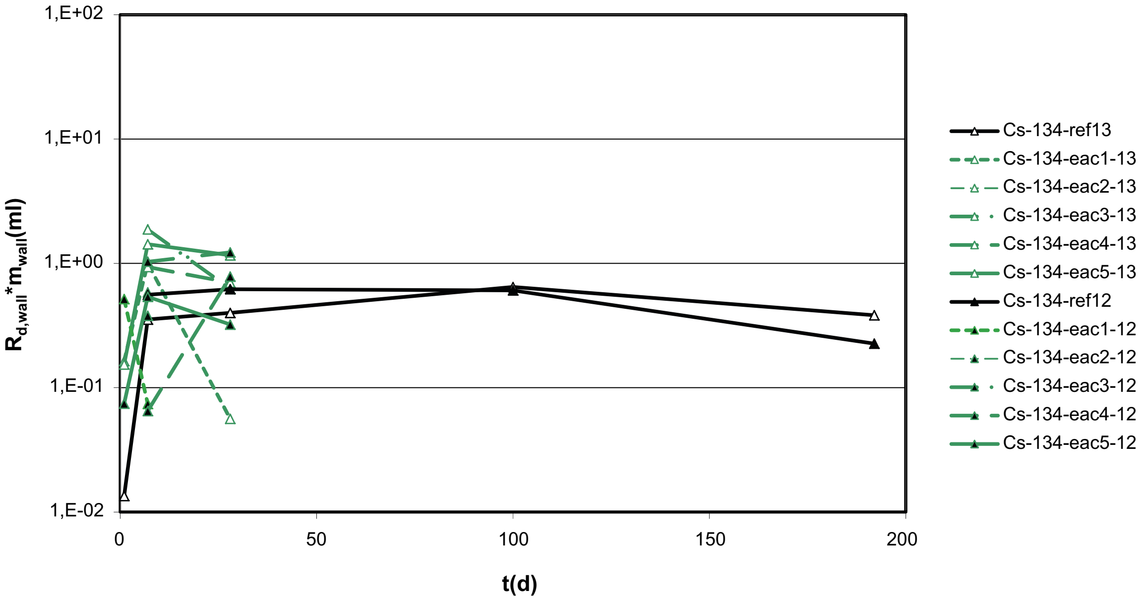

Figure A2-3. *Results of ^{134}Cs wall sorption with five dilutions of EDTA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

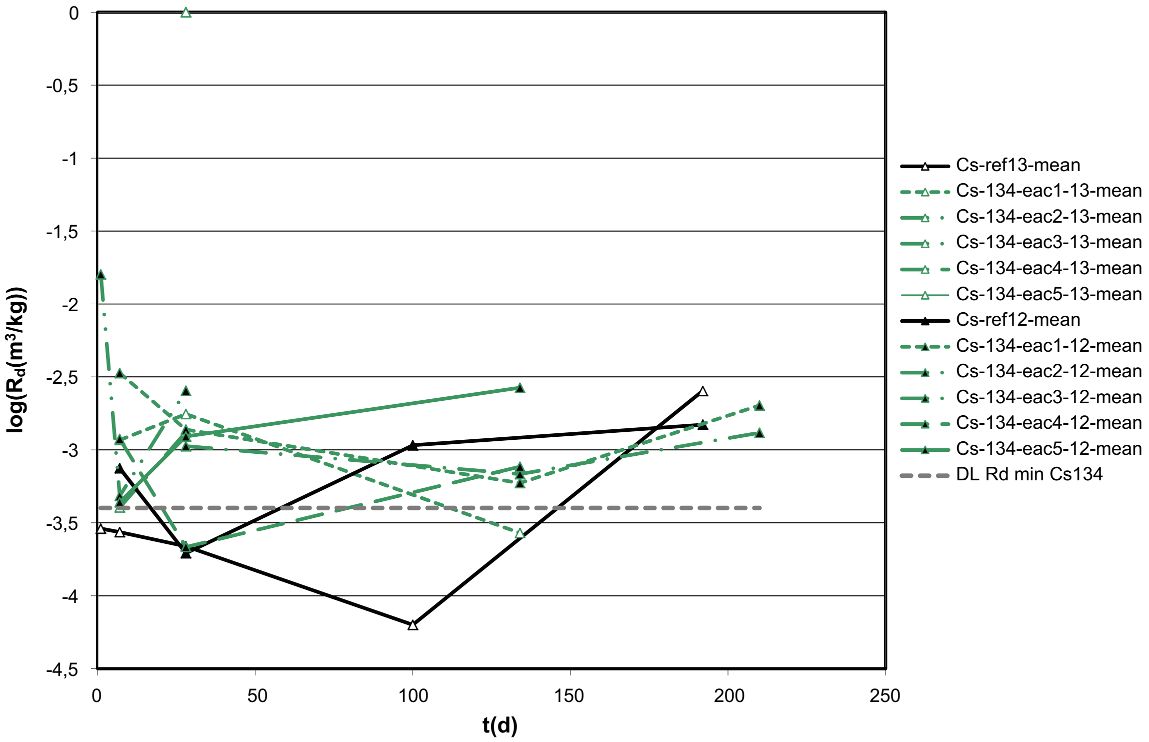

Figure A2-4. *Results of ^{134}Cs cement sorption with five dilutions of EDTA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

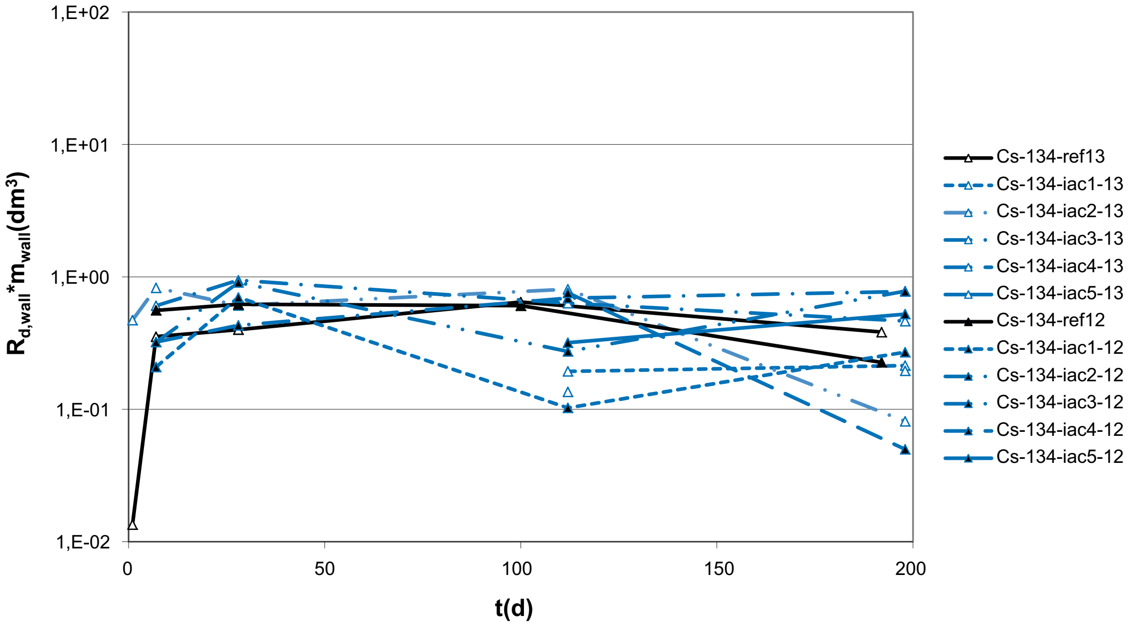

Figure A2-5. *Results of* ^{134}*Cs wall sorption with five dilutions of ISA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

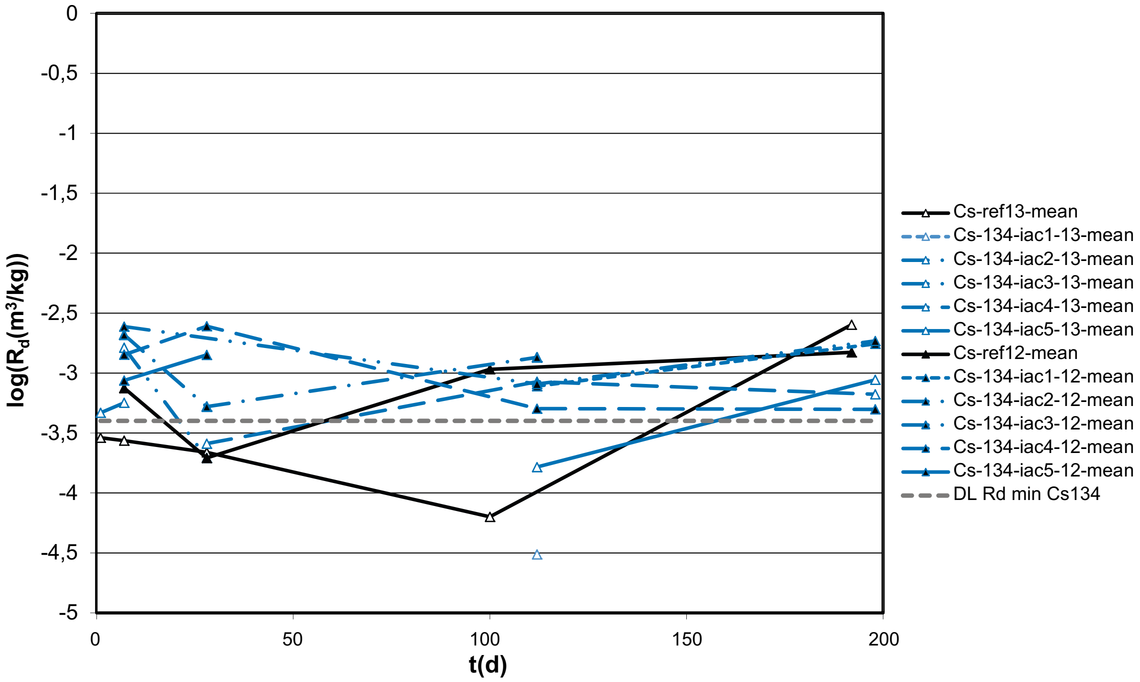

Figure A2-6. *Results of* ^{134}*Cs cement sorption with five dilutions of ISA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

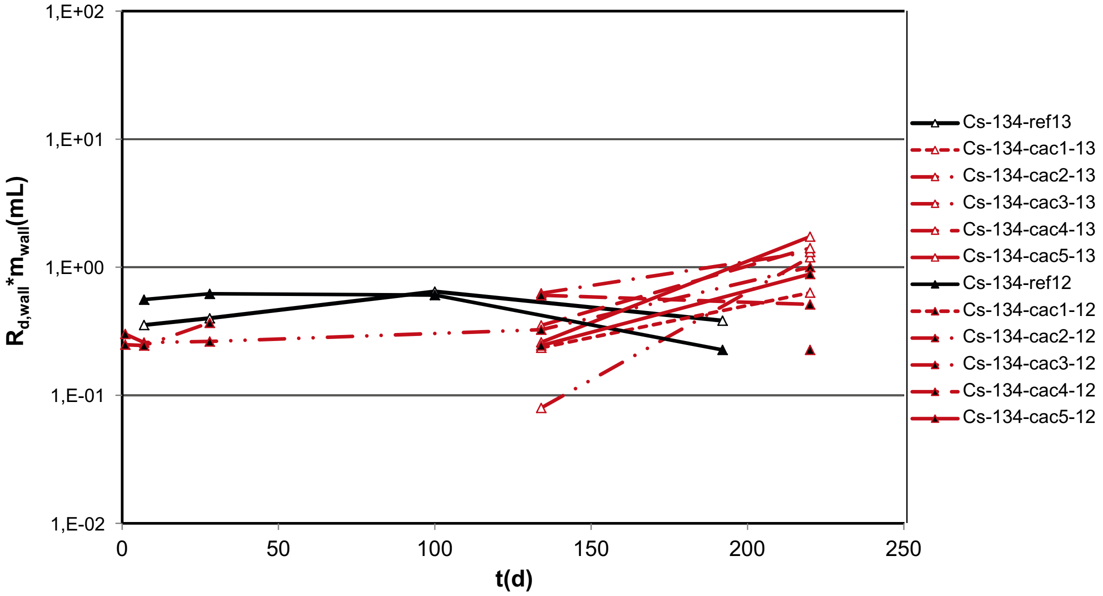

Figure A2-7. *Results of* ^{134}*Cs wall sorption with five dilutions of citric acid. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

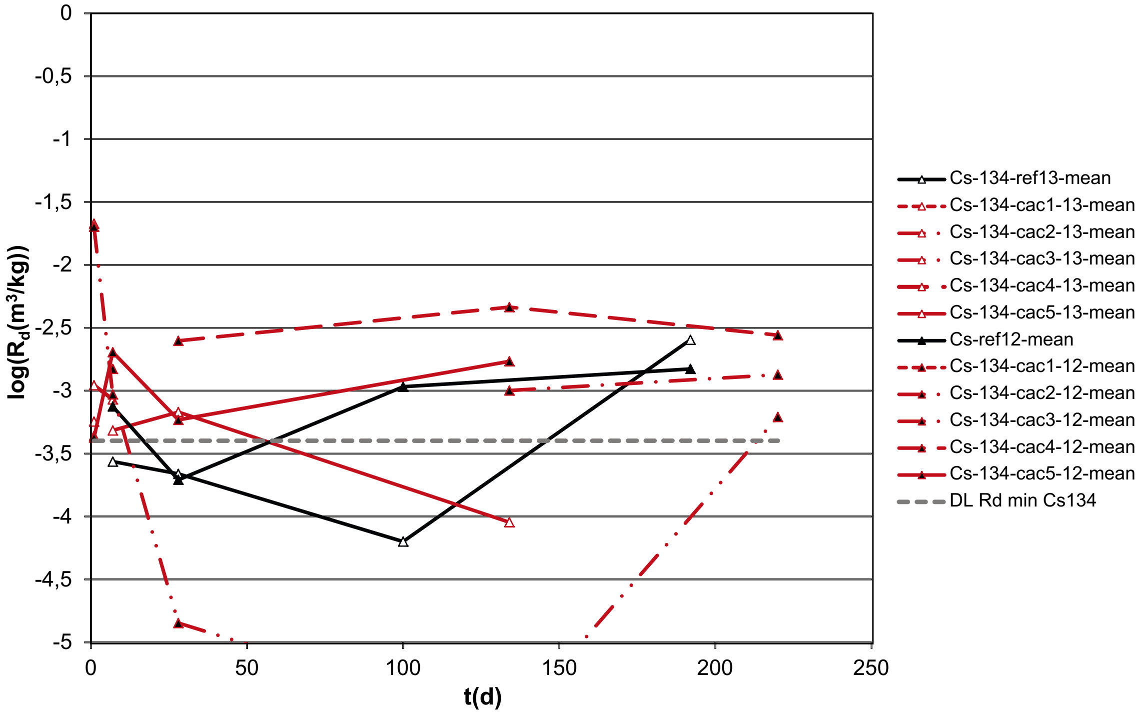

Figure A2-8. *Results of* ^{134}*Cs cement sorption with five dilutions of citric acid. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

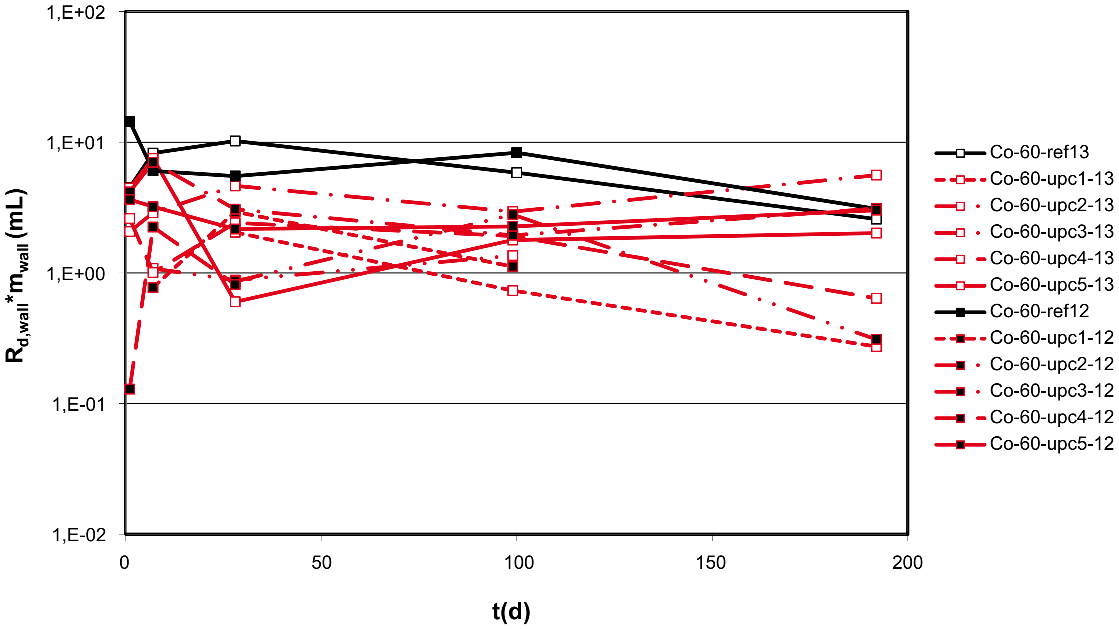

Figure A2-9. *Results of* ^{60}*Co wall sorption with five dilutions of UP2 degradation products. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

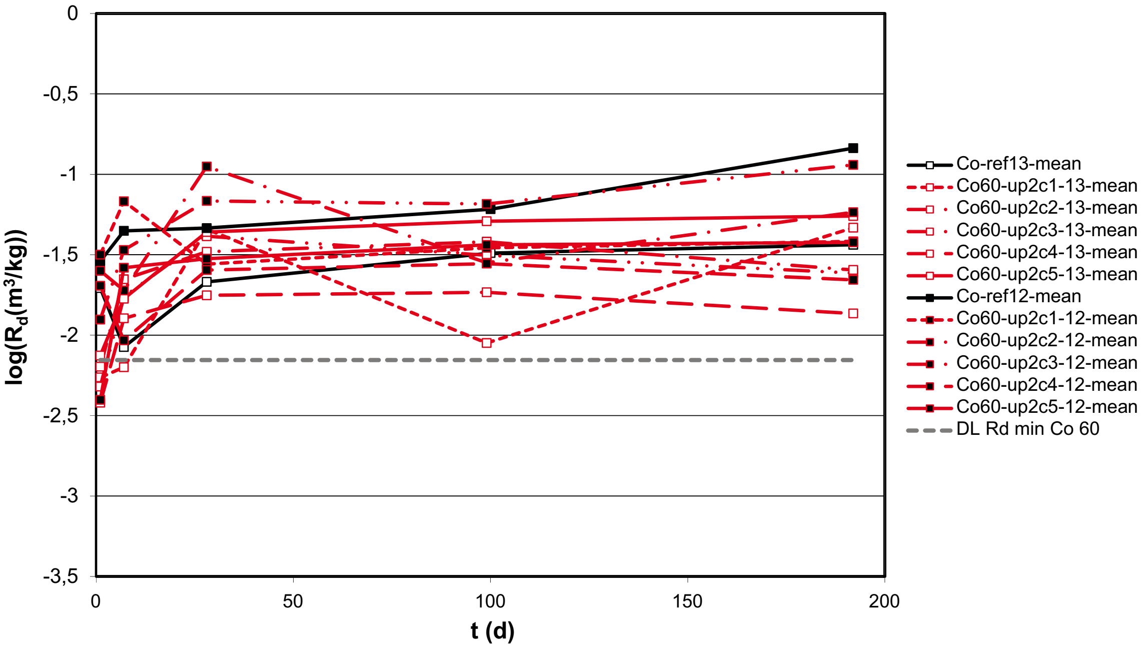

Figure A2-10. *Results of* ^{60}*Co cement sorption with five dilutions of UP2 degradation products. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

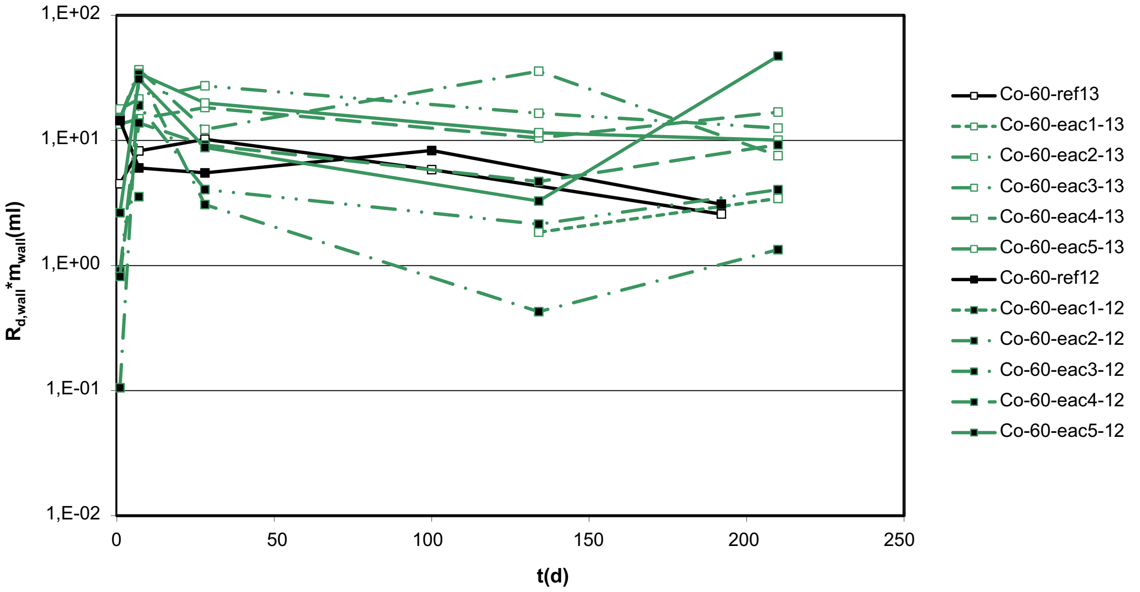

Figure A2-11. *Results of* ^{60}*Co wall sorption with five dilutions of EDTA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

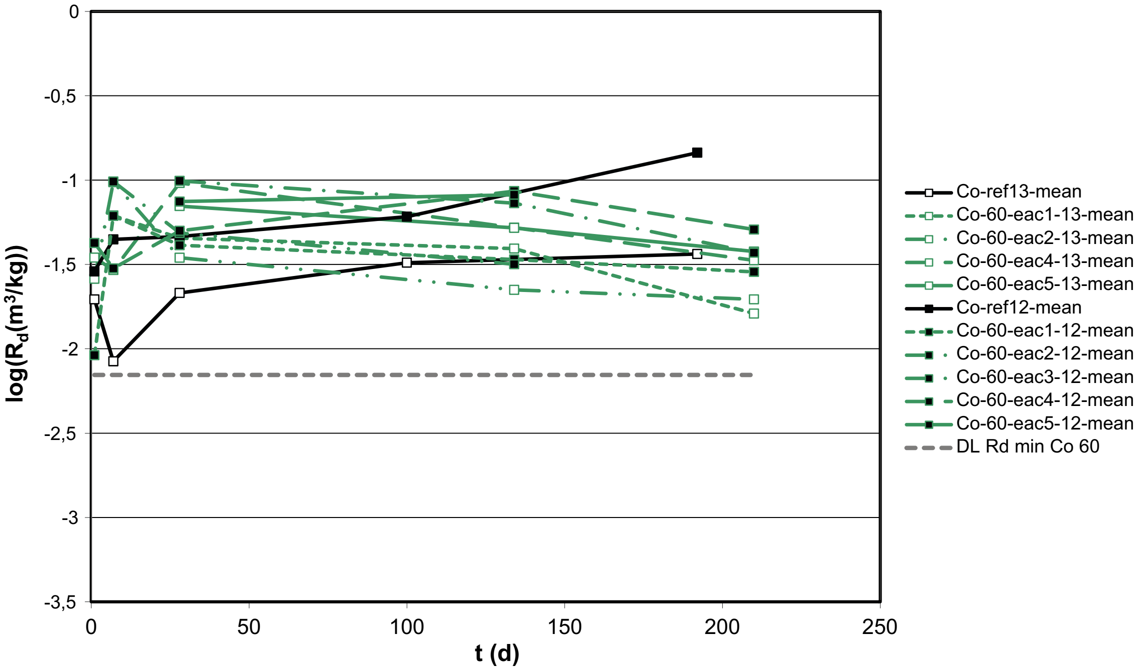

Figure A2-12. *Results of* ^{60}*Co cement sorption with five dilutions of EDTA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

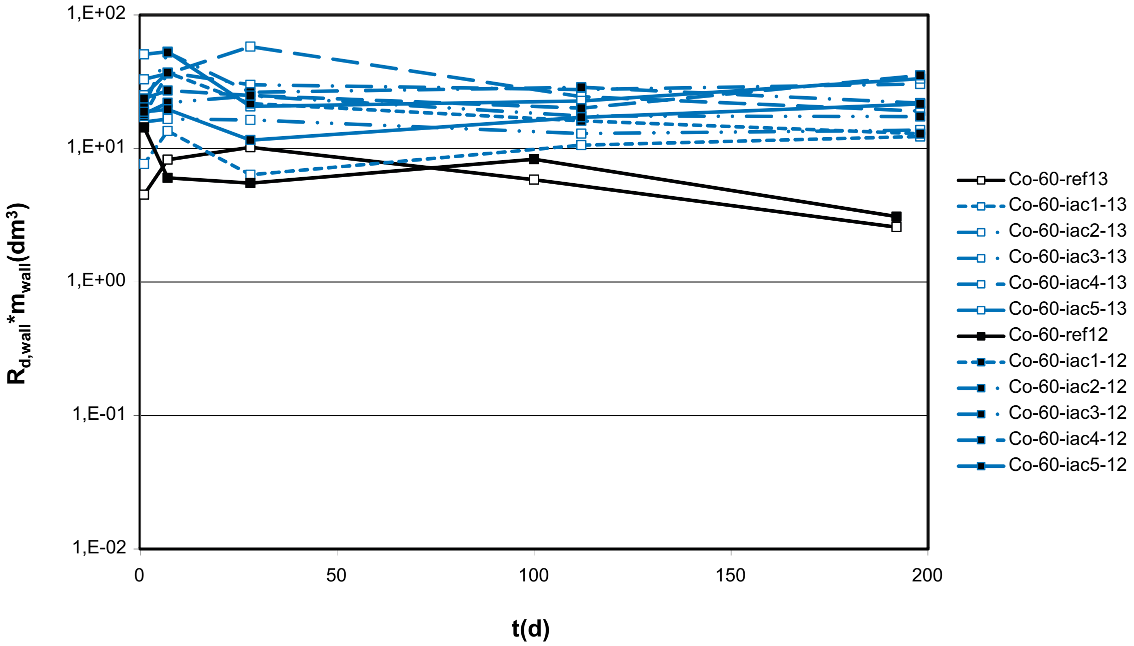

Figure A2-13. *Results of ^{60}Co wall sorption with five dilutions of ISA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

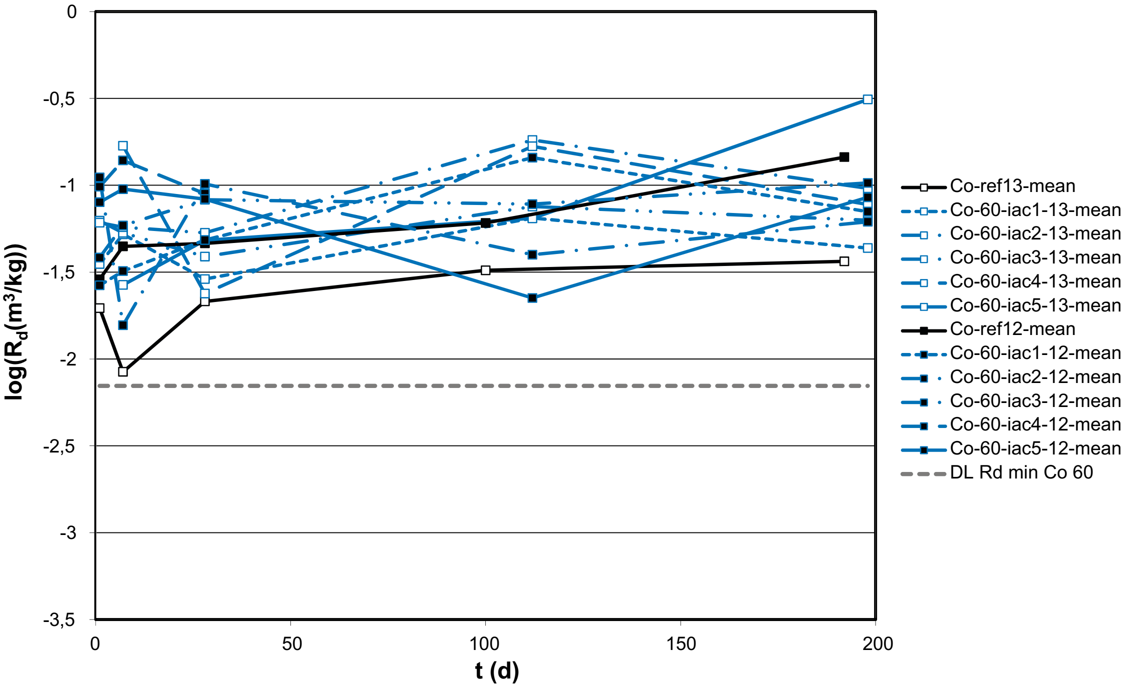

Figure A2-14 Results of ^{60}Co cement sorption with five dilutions of ISA. *Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

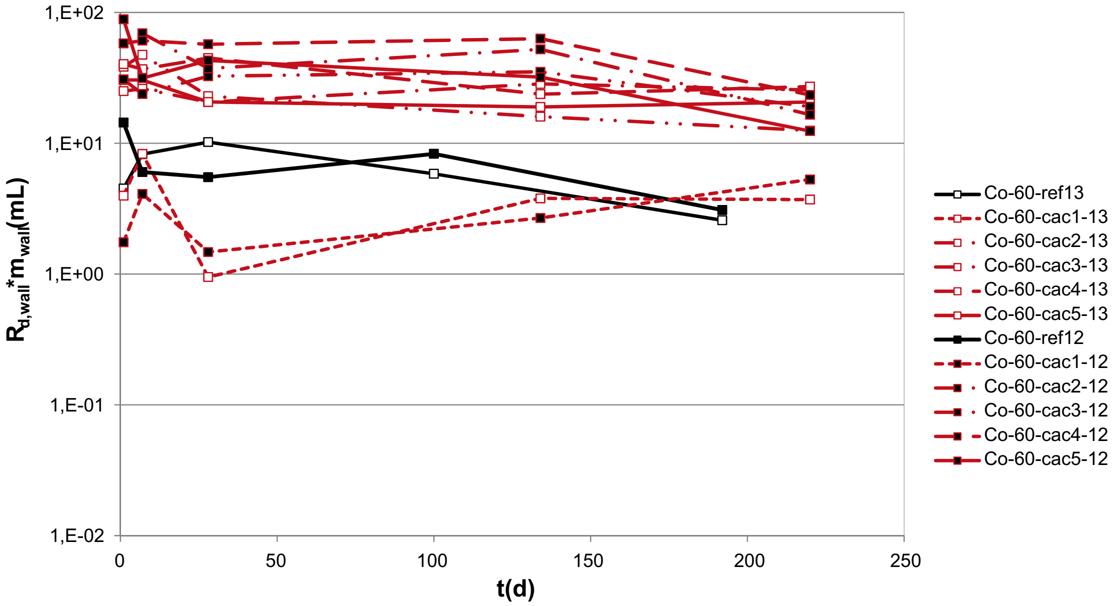

Figure A2-15. Results of ^{60}Co wall sorption with five dilutions of citric acid. Legend: 13=fresh cement pore-water, 12=leached cement pore water.

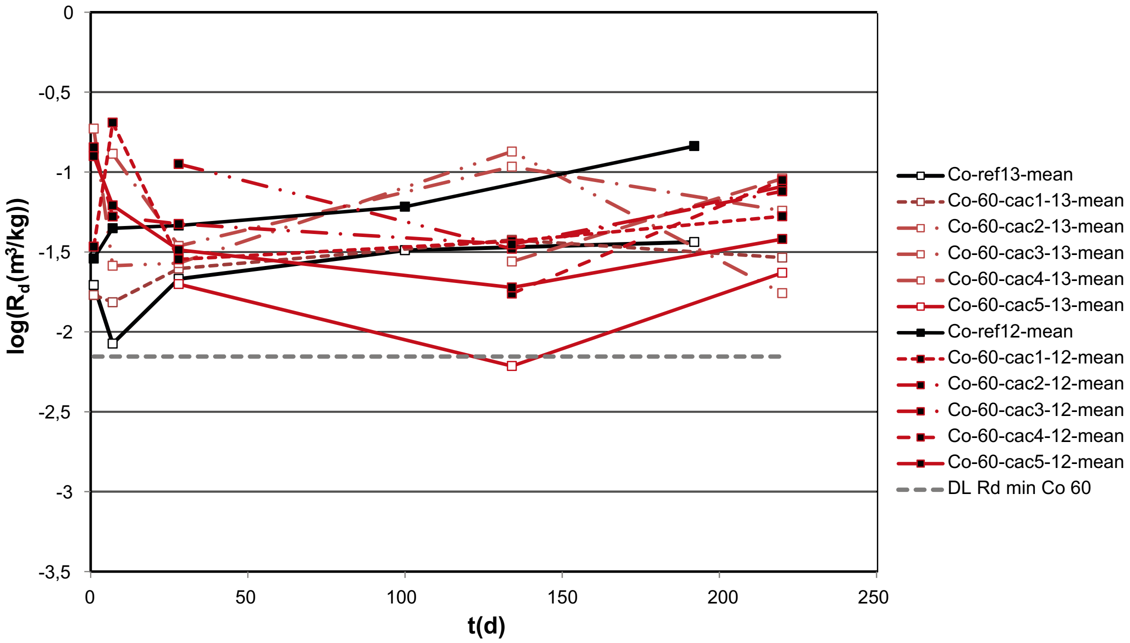

Figure A2-16. Results of ^{60}Co cement sorption with five dilutions of citric acid. Legend: 13=fresh cement pore-water, 12=leached cement pore water.

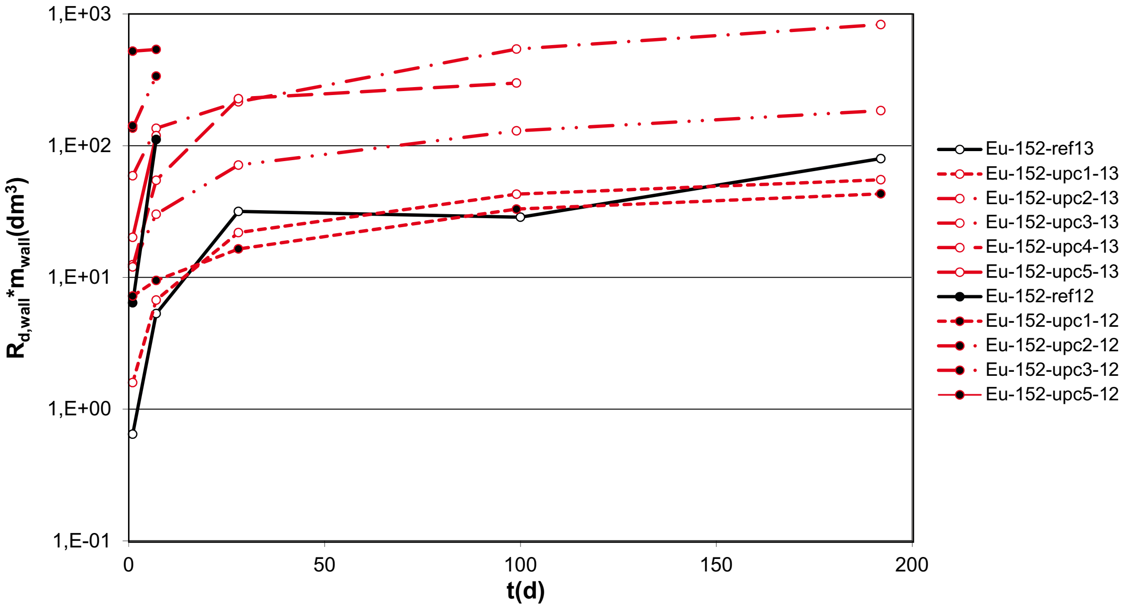

Figure A2-17. *Results of ^{152}Eu wall sorption with five dilutions of UP2 degradation products. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

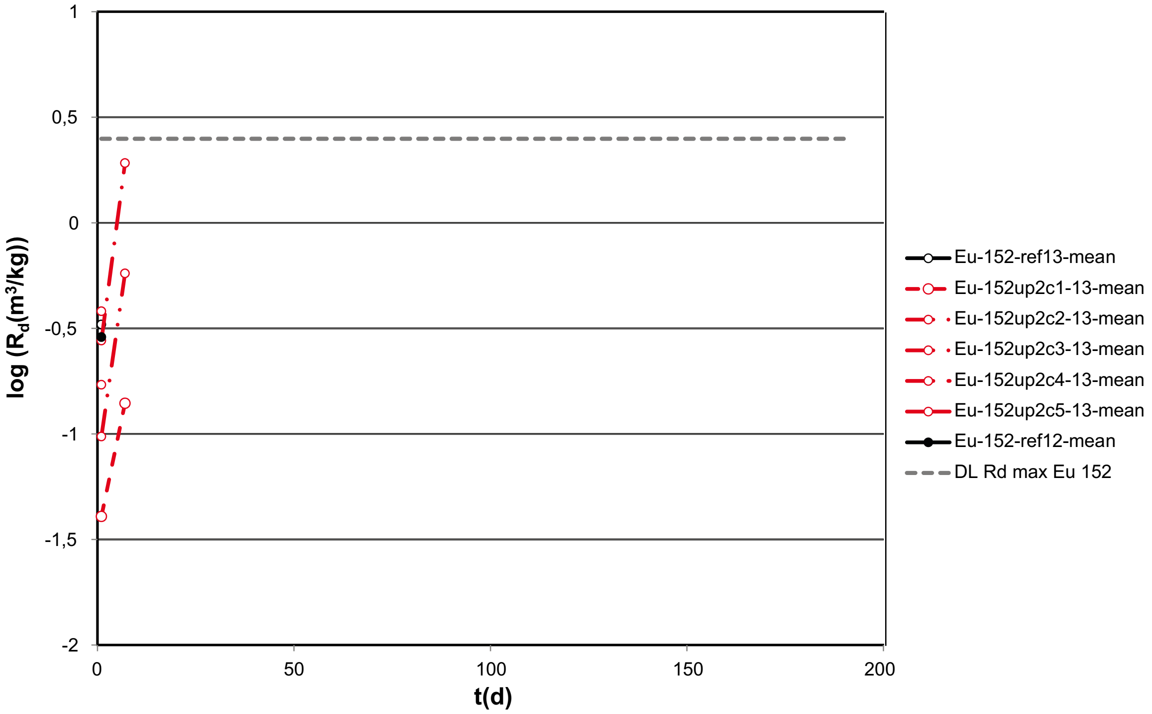

Figure A2-18. *Results of ^{152}Eu cement sorption with five dilutions of UP2 degradation products. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

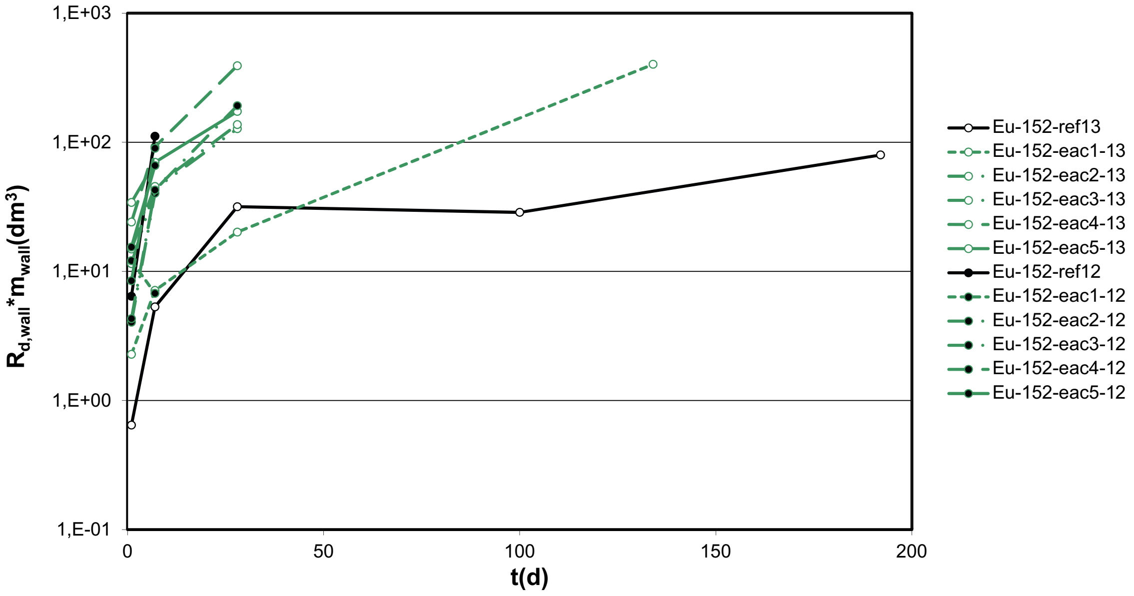

Figure A2-19. *Results of ^{152}Eu wall sorption with five dilutions of EDTA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

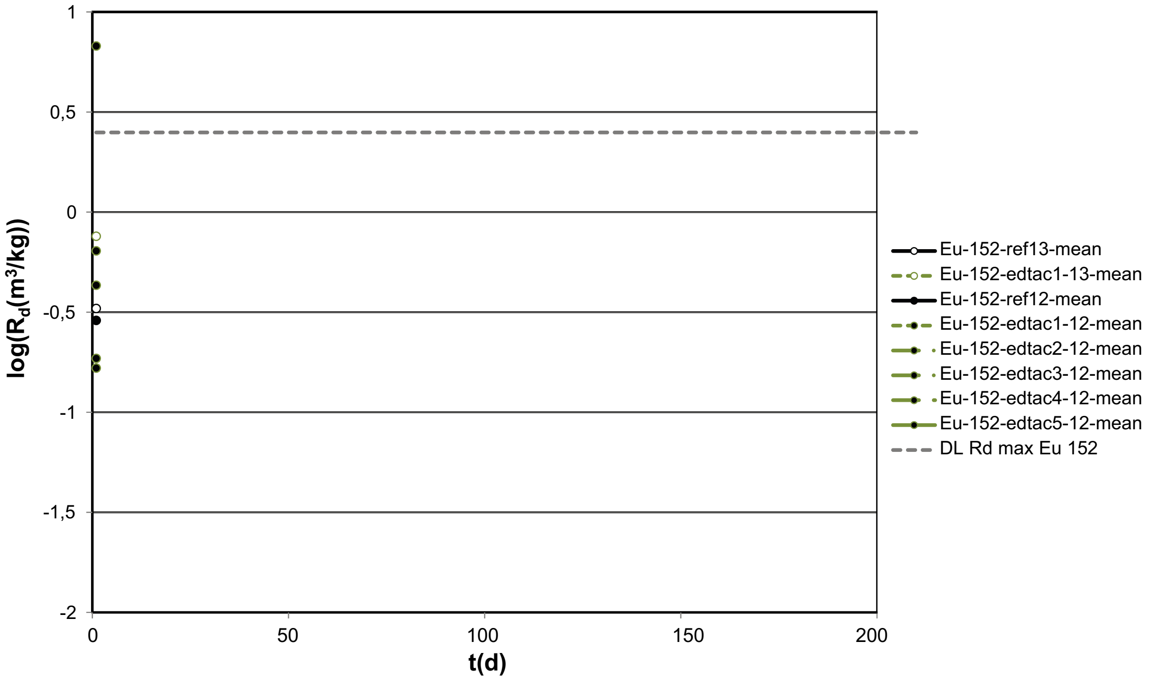

Figure A2-20. *Results of ^{152}Eu cement sorption with five dilutions of EDTA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

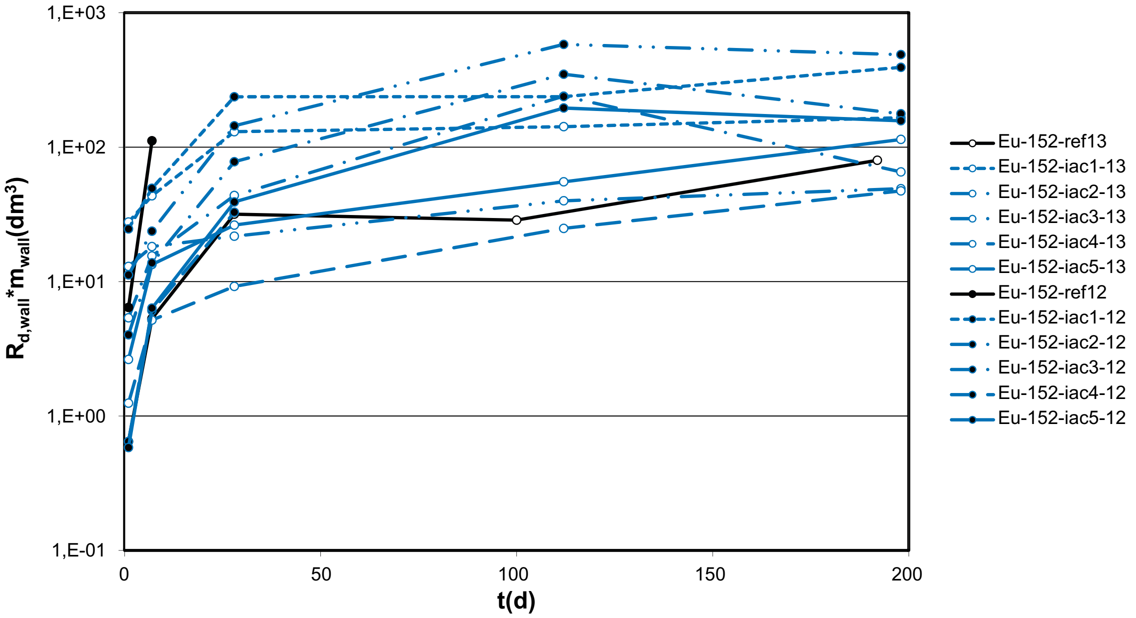

Figure A2-21. *Results of* ^{152}*Eu wall sorption with five dilutions of ISA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

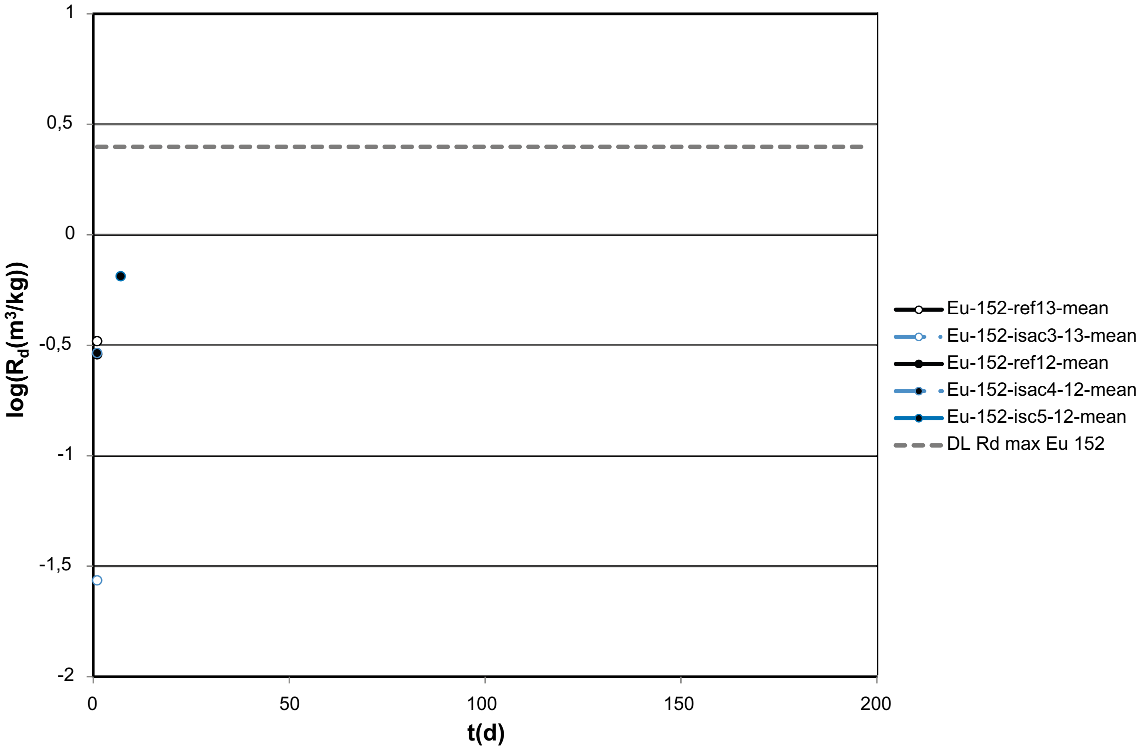

Figure A2-22. *Results of* ^{152}*Eu cement sorption with five dilutions of ISA. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

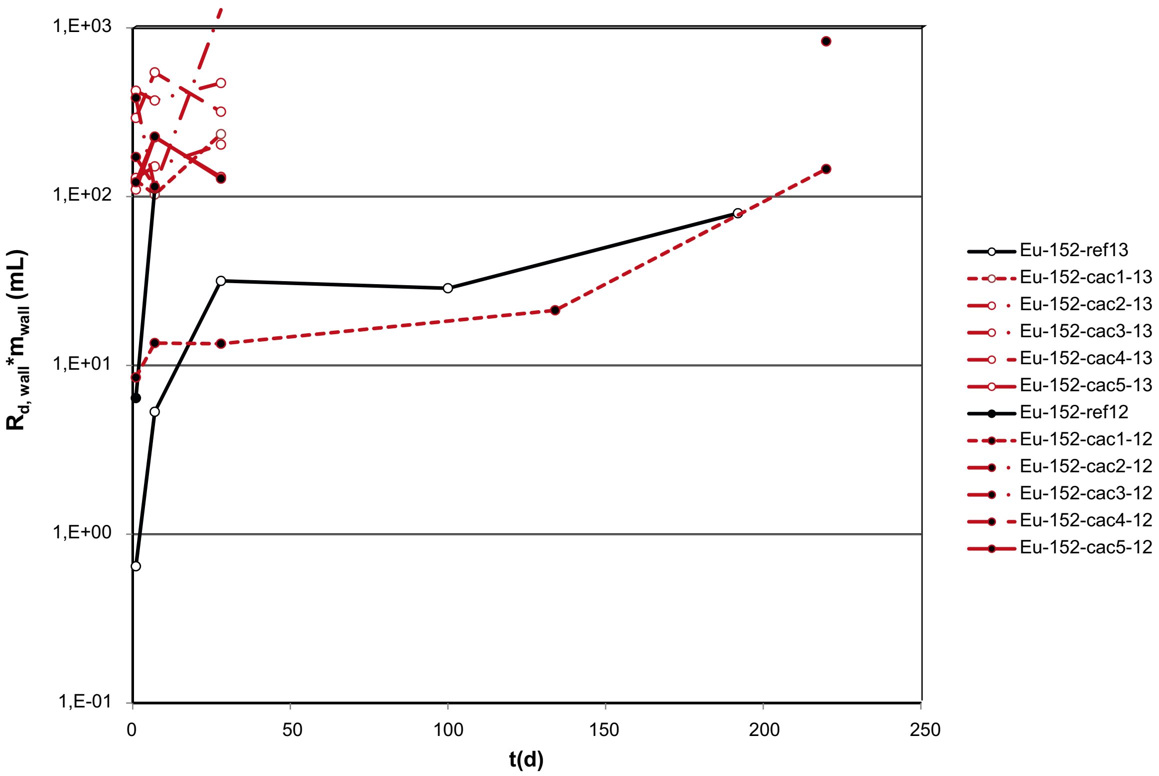

Figure A2-23. *Results of ^{152}Eu wall sorption with five dilutions of citric acid. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

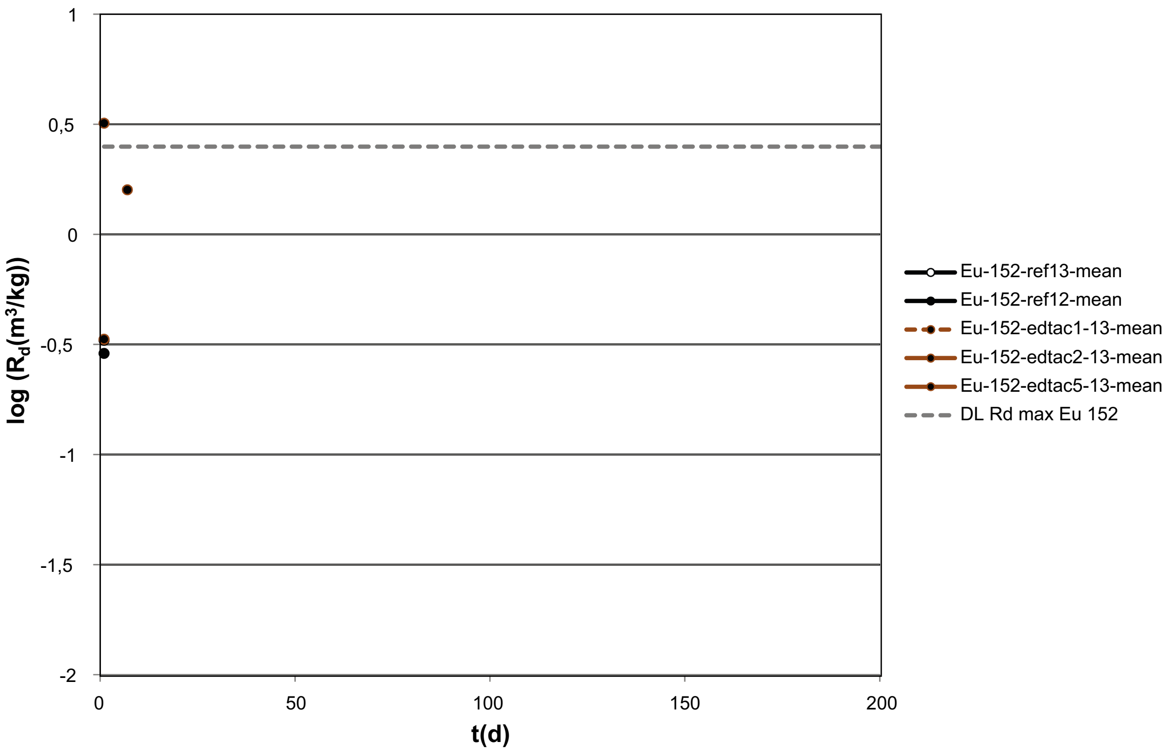

Figure A2-24. *Results of ^{152}Eu cement sorption with five dilutions of citric acid. Legend: 13=fresh cement pore-water, 12=leached cement pore water.*

Appendix 3

Diagrams of $[Eu]_{tot}$ and $[Th]_{tot}$ measurements in the batch sorption experiments

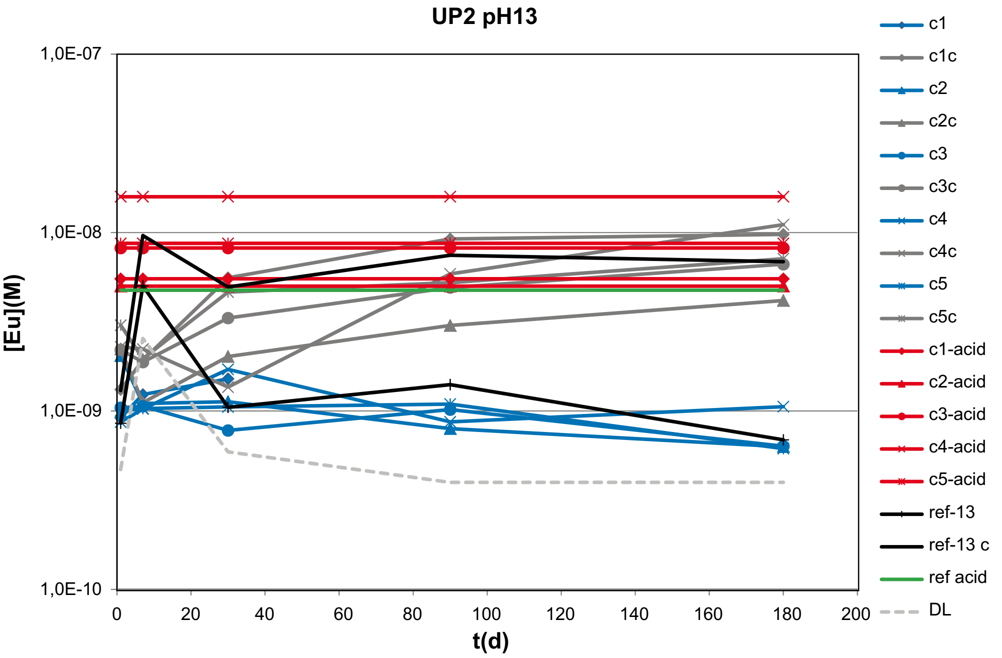

Figure A3-1. *Total Eu concentration in batch sorption experiments with five dilutions of UP2 degradation products in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

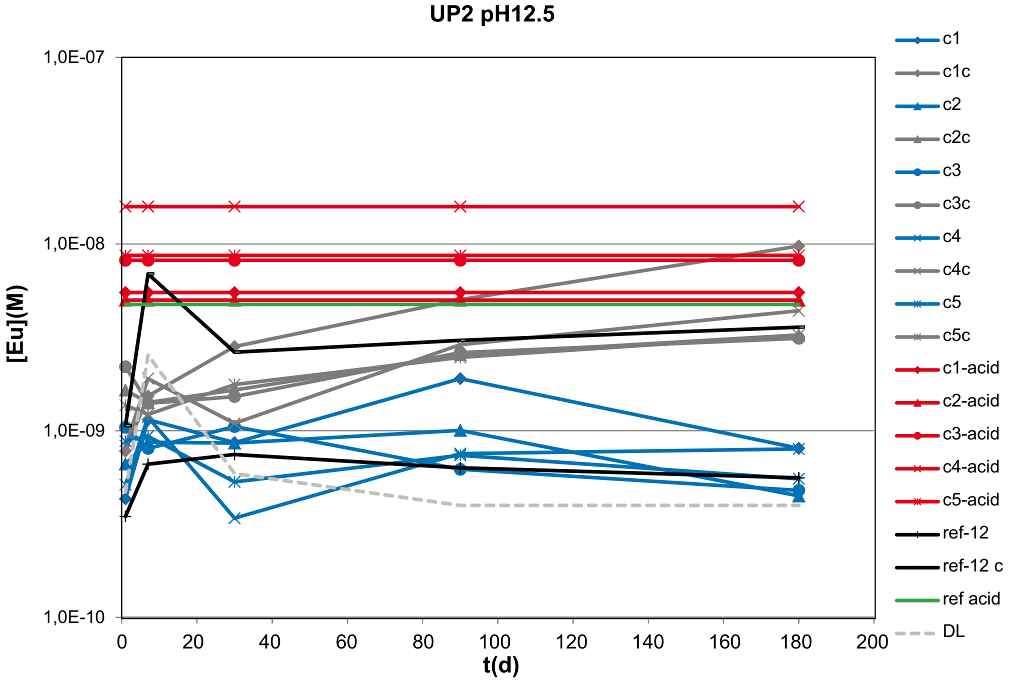

Figure A3-2. *Total Eu concentration in batch sorption experiments with five dilutions of UP2 degradation products in LCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

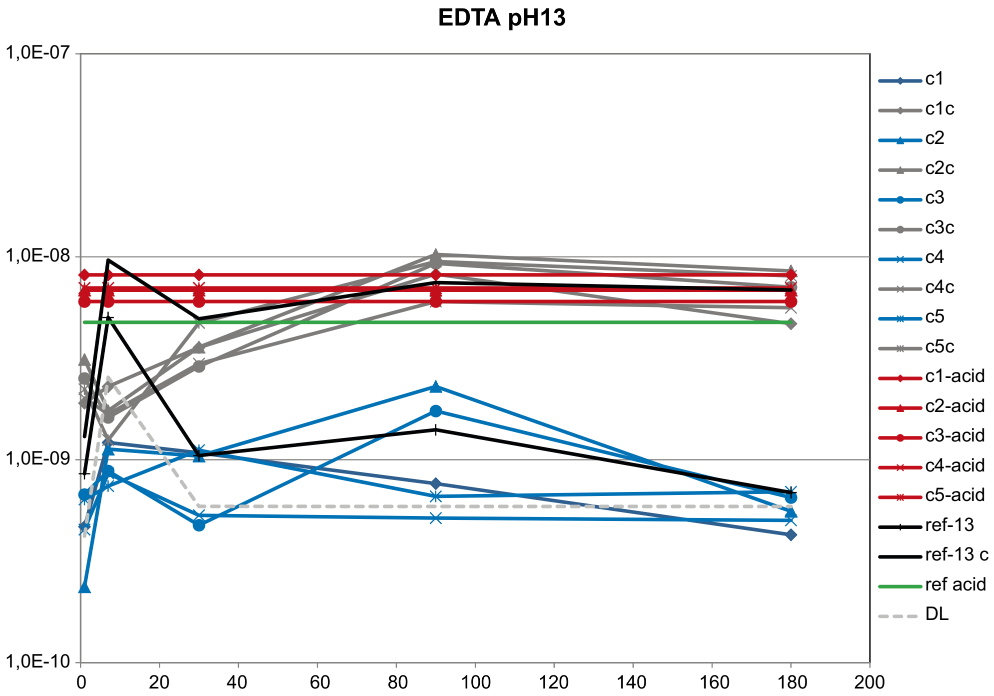

Figure A3-3. *Total Eu concentration in batch sorption experiments with five dilutions of EDTA in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

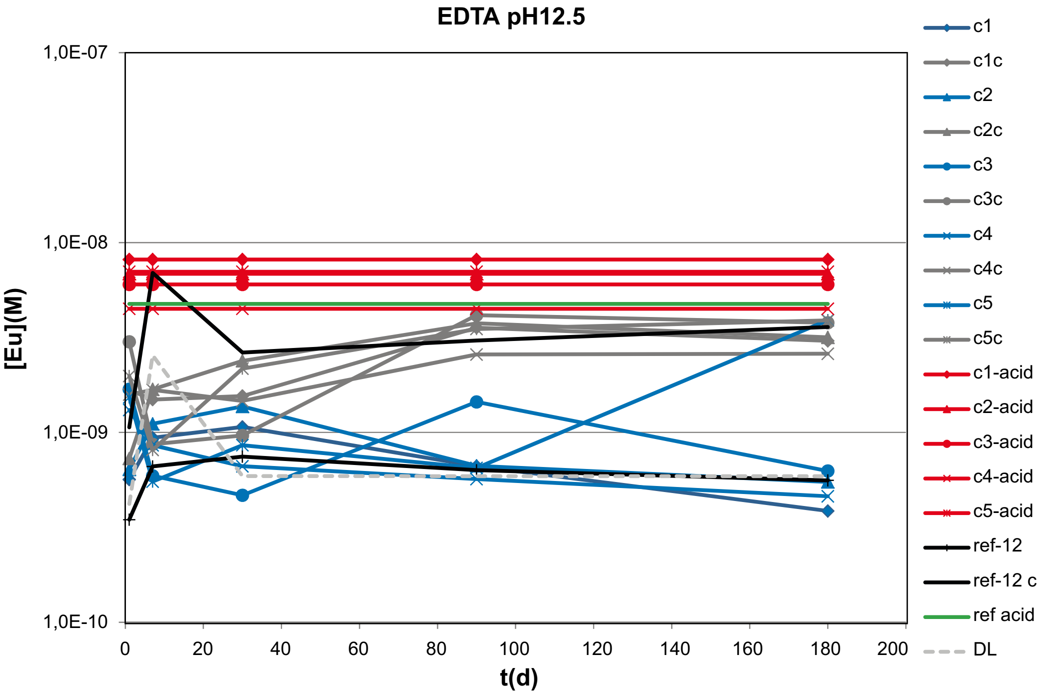

Figure A3-4. *Total Eu concentration in batch sorption experiments with five dilutions of EDTA in LCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

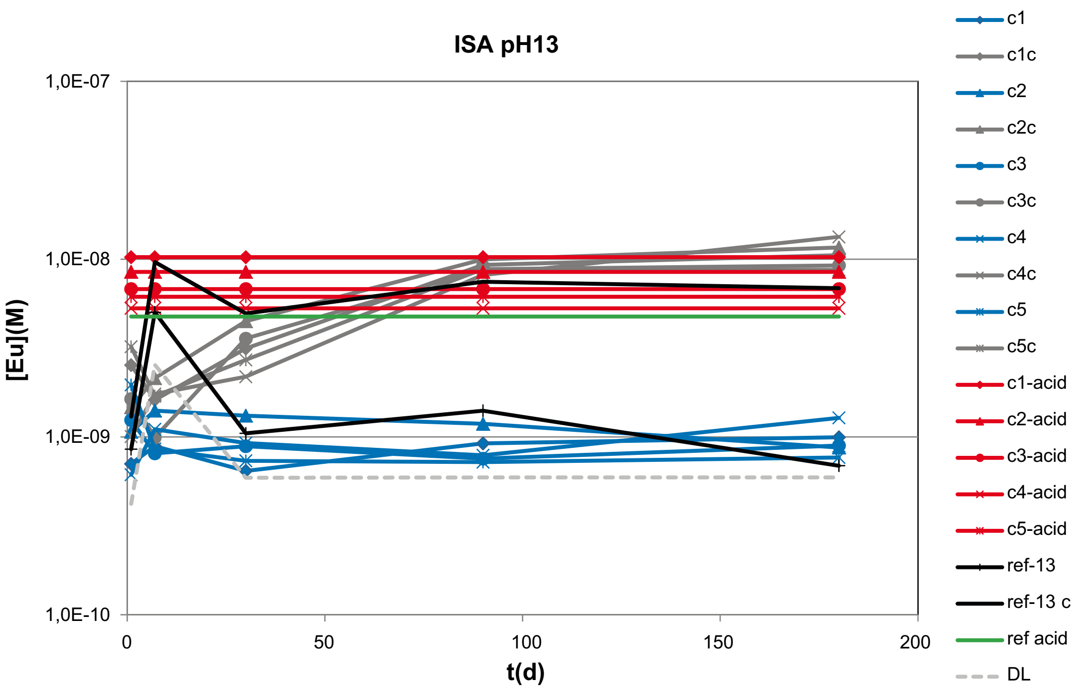

Figure A3-5. *Total Eu concentration in batch sorption experiments with five dilutions of ISA in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

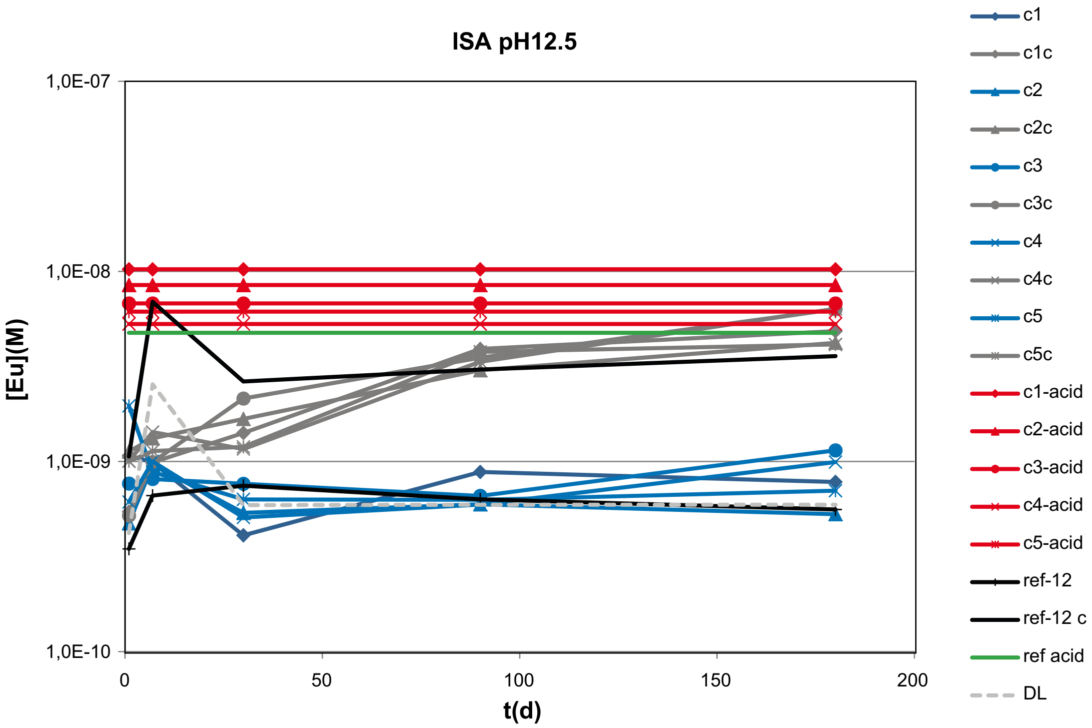

Figure A3-6. *Total Eu concentration in batch sorption experiments with five dilutions of ISA in LCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

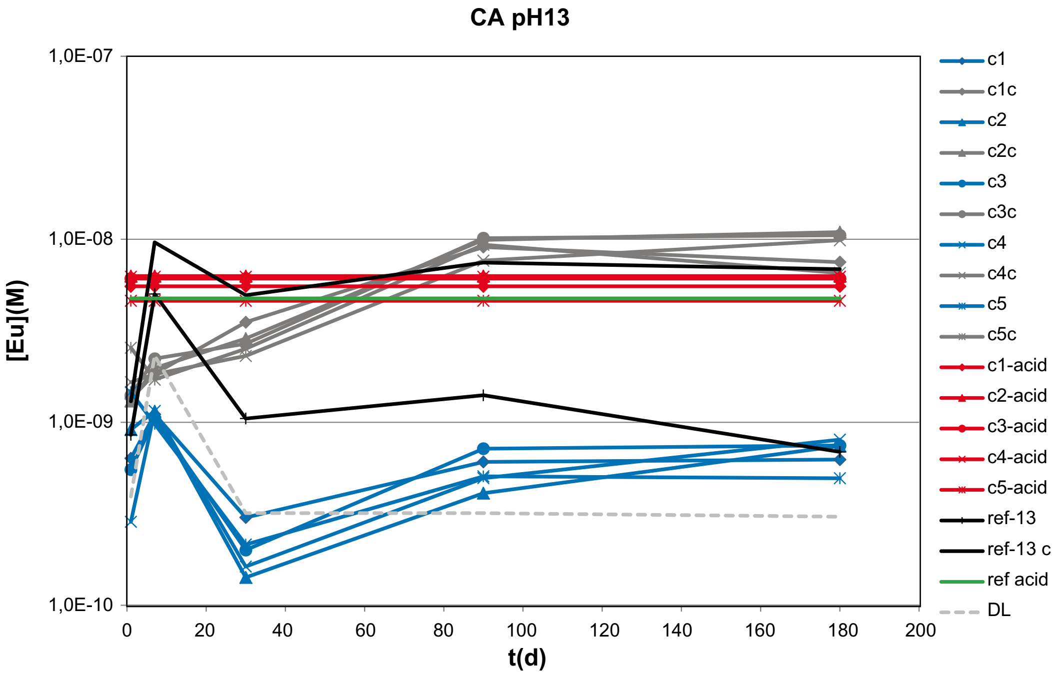

***Figure A3-7.** Total Eu concentration in batch sorption experiments with five dilutions of citric acid in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

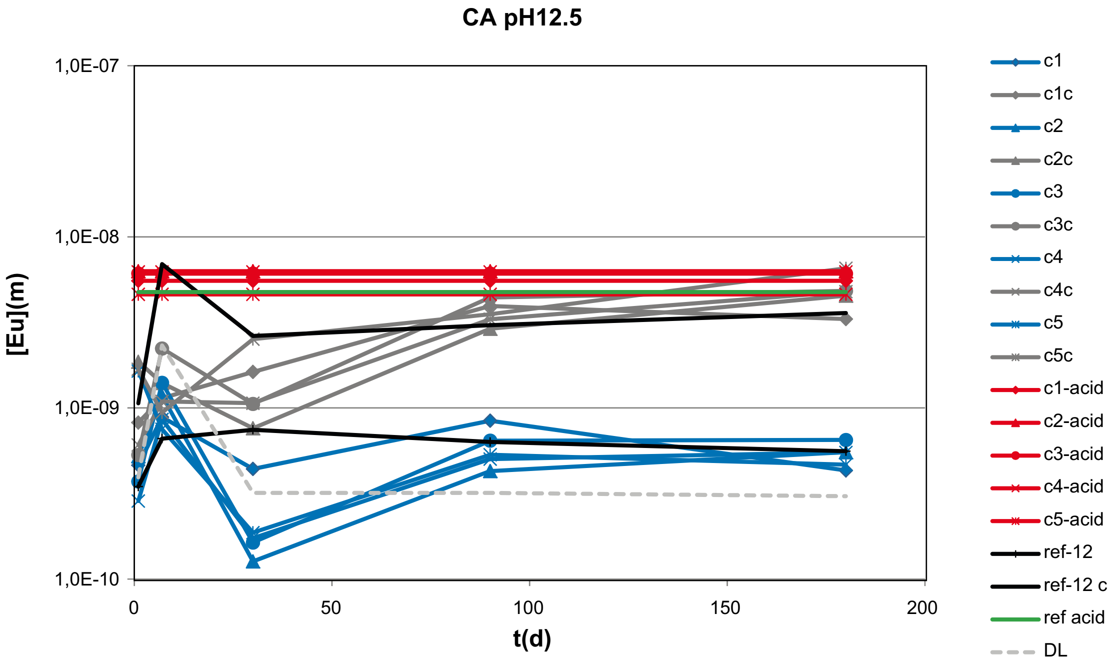

***Figure A3-8.** Total Eu concentration in batch sorption experiments with five dilutions of citric acid in LCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

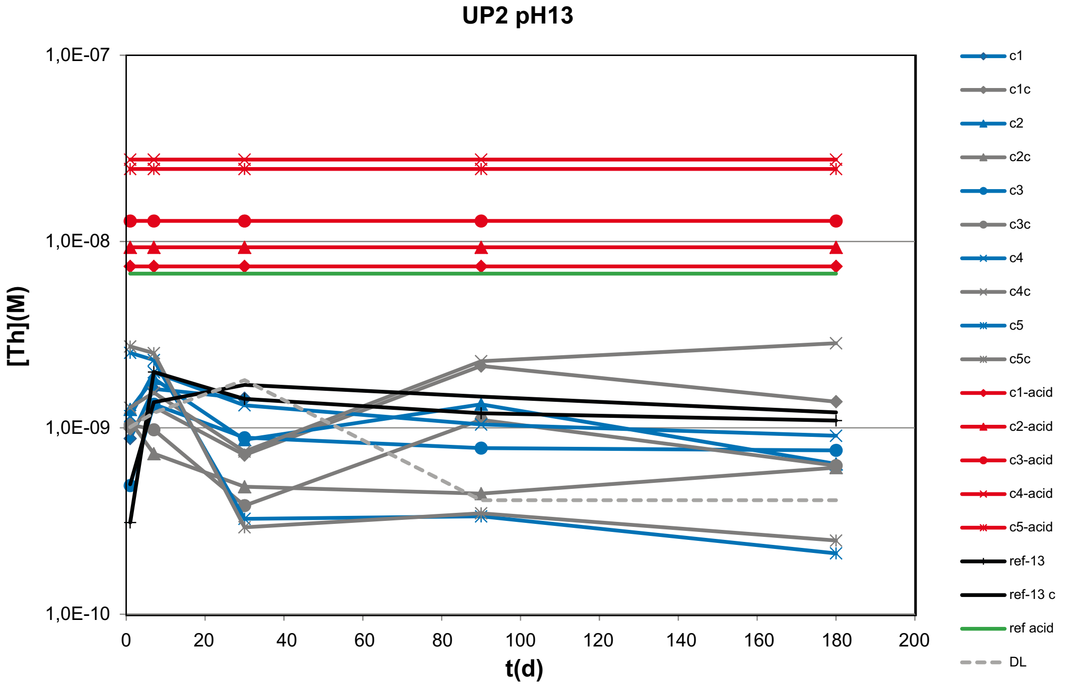

Figure A3-9. *Total Th concentration in batch sorption experiments with five dilutions of UP2 degradation products in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

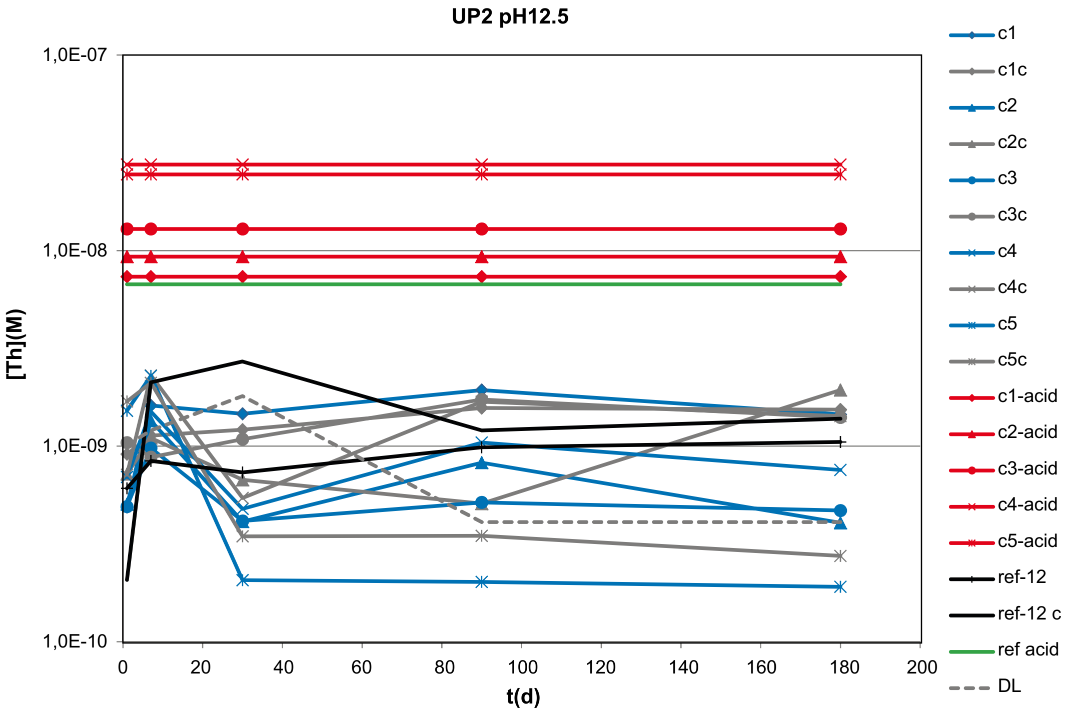

Figure A3-10. *Total Th concentration in batch sorption experiments with five dilutions of UP2 degradation products in LCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

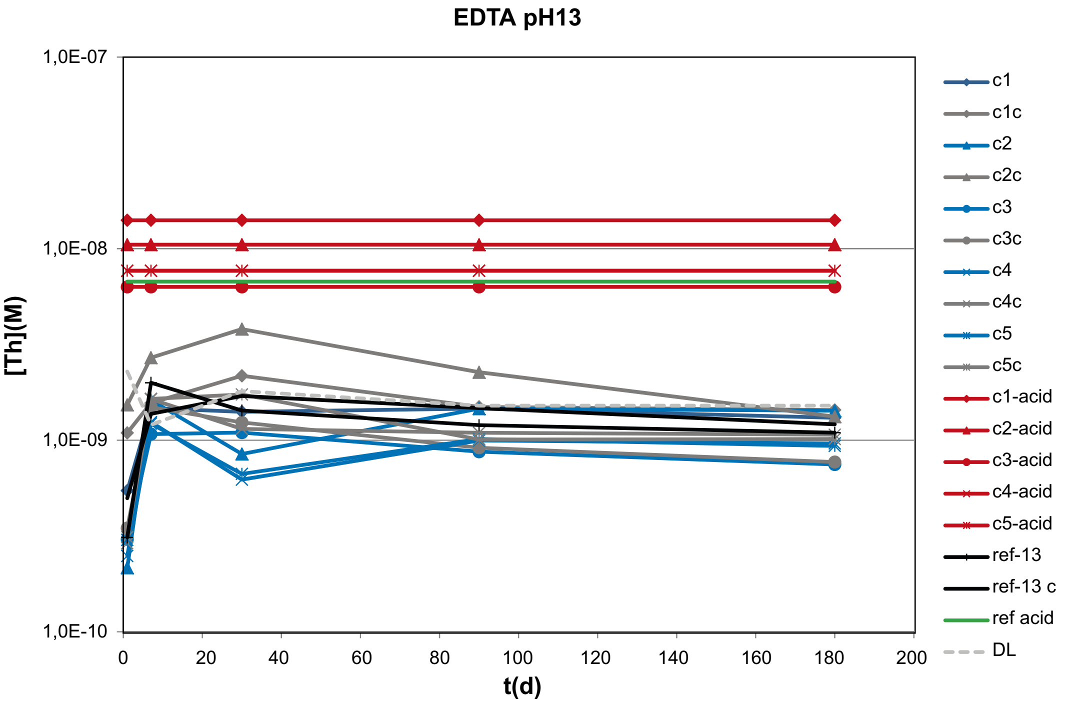

Figure A3-11. Total Th concentration in batch sorption experiments with five dilutions of EDTA in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.

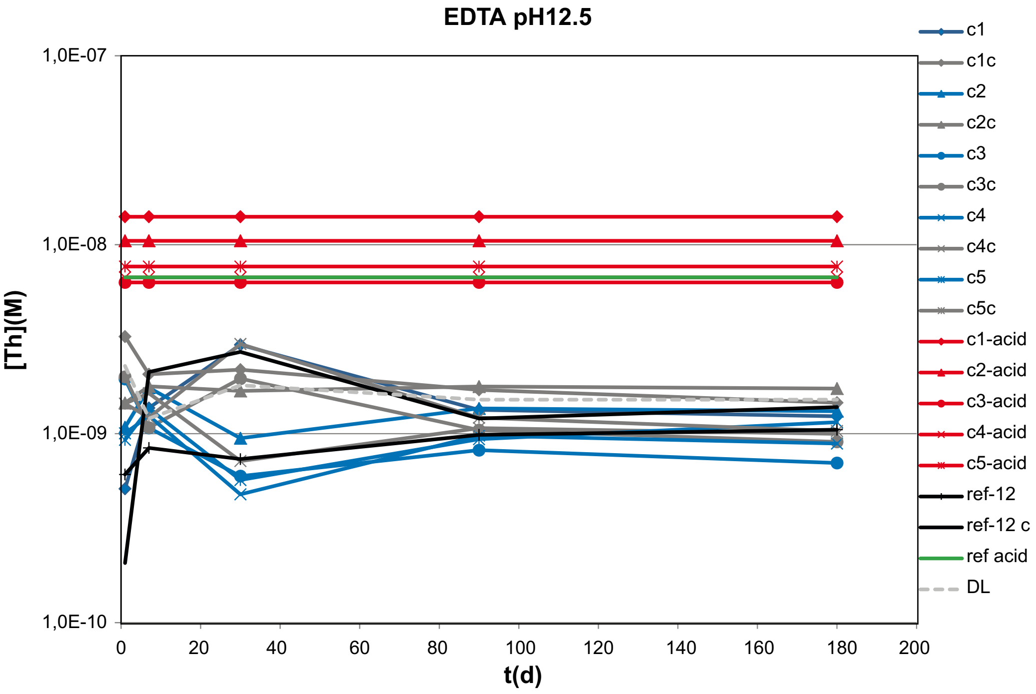

Figure A3-12. Total Th concentration in batch sorption experiments with five dilutions of EDTA in LCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.

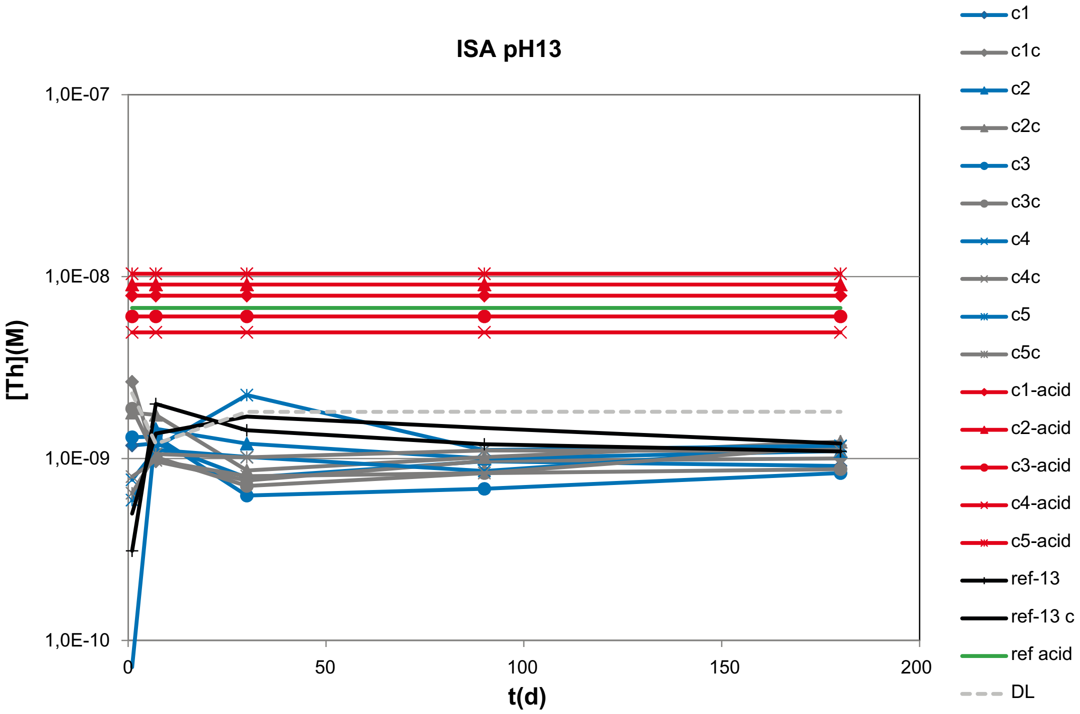

Figure A3-13. Total Th concentration in batch sorption experiments with five dilutions of ISA in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.

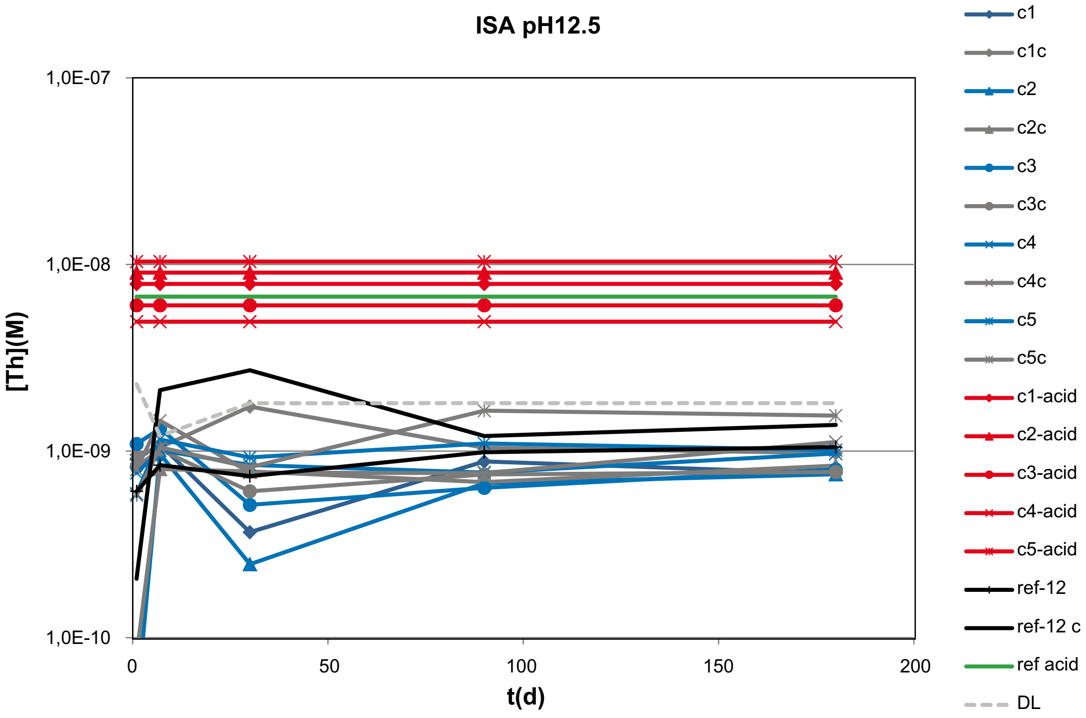

Figure A3-14 .Total Th concentration in batch sorption experiments with five dilutions of ISA in LCPW and references (no organic ligand). *Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

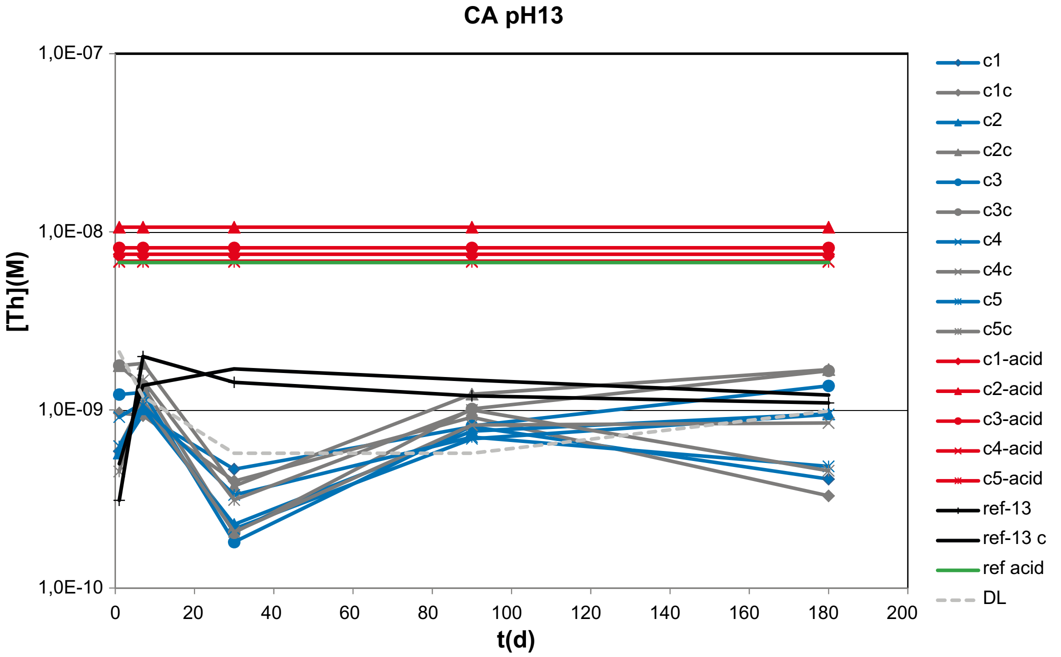

Figure A3-15. *Total Th concentration in batch sorption experiments with five dilutions of citric acid in FCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*

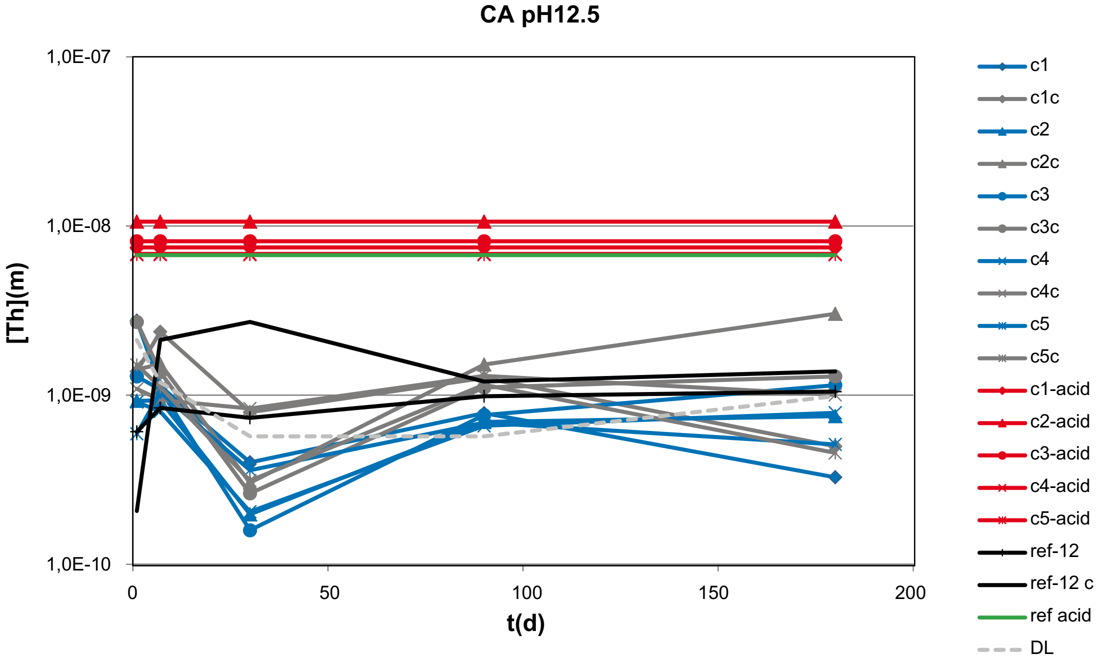

Figure A3-16. *Total Th concentration in batch sorption experiments with five dilutions of citric acid in LCPW and references (no organic ligand). Legend: last "c" indicates an experiment with cement, "acid" indicates acidified experiment without cement and no terminal label indicates wall sorption experiment without cement.*