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Uptake of Ni(II), Eu(III) and Pu(III/IV) by Hardened Cement Paste in the Presence of Proxy Ligands for the Degradation of Polyacrylonitrile

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The uptake of ^{63}Ni(II), ^{152}Eu(III) and ^{242}Pu(III/IV) by hardened cement paste (HCP, CEM I) in the degradation stage II (pH ≈ 12.5 [Ca] ≈ 0.02 M) was investigated in the absence and presence of α-hydroxyisobutyric, 3-hydroxybutyric and glutaric acids. These organic ligands were previously identified as proxies for the degradation products of UP2W (a polyacrylonitrile-based material used as filter aid in nuclear power plants) under repository conditions. Sorption experiments were conducted with various ligand concentrations (10^{-4} M ≤ $[L]_{tot}$ ≤ 0.1 M) and solid-to-liquid ratios (0.5 g·dm^{-3} ≤ S:L ≤ 20 g·dm^{-3}). Redox conditions in the Pu systems were buffered with either hydroquinone (HQ, pe + pH ≈ 10) or Sn(II) (pe + pH ≈ 2). Strong sorption is observed for ^{152}Eu(III) and ^{242}Pu(III/IV) in the absence of proxy ligands, with distribution coefficients (log R_d ≈ 2.2–4, with R_d in m^3·kg^{-1}) in line with data reported in the literature. No differences are observed for sorption experiments with Pu in HQ and Sn(II) systems. Lower R_d values are determined for ^{63}Ni(II) (log $R_{d,^{63}Ni}$ ≈ 0-1), consistently with previous studies. In combination with log $R_{d,Ni}$ determined on the basis of the concentration of stable Ni(II) in pristine HCP and in cement porewater, values of the partition coefficient (α) close to 1 are determined. This suggests that the uptake of ^{63}Ni is possibly driven by isotopic exchange with the complete species inventory of stable Ni present in pristine HCP, including Ni in solid phases and associated with surfaces, *e.g.,* of C-S-H phases. The presence of proxy ligands has a negligible effect on the uptake of ^{152}Eu(III) up to $[L]_{tot}$ = 0.1 M. A slight decrease in the distribution ratios for ^{63}Ni(II) and ^{242}Pu(III/IV) is observed at $[L]_{tot}$ > 10^{-2} M, although the effect is less evident in the case of plutonium due to the dispersion of the data and the increase of the detection limits with increasing ligand concentrations. Compared to strongly complexing ligands like isosaccharinic acid or gluconate, the investigated proxy ligands show a minor capacity for radionuclide mobilization in cementitious systems, even at high concentrations.

KEYWORDS

sorption, UP2W, polyacrylonitrile, α-hydroxyisobutyric acid, 3-hydroxybutyric acid, glutaric acid, cement, radionuclide

1 Introduction

UP2W is a polyacrylonitrile-based polymer (PAN) used as filter aid in nuclear power plants (Dario et al., 2004; Keith-Roach et al., 2021). Significant amounts of used UP2W are disposed of in SFR, the repository for short-lived low and intermediate level wastes (L/ILW) in Sweden (Dario et al., 2004; Duro et al., 2012; Keith-Roach et al., 2014; Keith-Roach et al., 2021).

Cement is extensively used in L/ILW repositories for the conditioning of the waste and for construction purposes. The porewater in cementitious materials is characterized by hyperalkaline pH conditions ($10 \leq \text{pH} \leq 13.3$) and Ca concentrations ranging from ~10^{-4} M to ~0.02 M (Taylor, 1997; Hewlett and Liska, 2019). Cementitious materials, in particular calcium silicate hydrate (C-S-H) phases, are known to sorb radionuclides strongly, primarily metal ions and cationic species (Wieland, 2014; Ochs et al., 2016).

In the context of an on-going collaboration between Karlsruhe Institute for Technology—Institute for Nuclear Waste Disposal (KIT-INE) and the Swedish Nuclear Fuel and Waste Management Co. (SKB), and within Work Package 3 CORI of the EURAD EU project (CORI-SOTA, 2021), the organic compounds glutaric acid (GTA), α-hydroxyisobutyric acid (HIBA) and 3-hydroxybutyric acid (HBA) were proposed as proxies for the degradation products of UP2W (Figure 1). The structure of these proxy ligands is consistent with ^{13}C-NMR data obtained for the degradation leachates of UP2W under hyperalkaline conditions (Tasi et al., 2021b). Considering the conversion of nitrile into carboxylate groups in the alkaline hydrolysis of PAN (Ermakov et al., 2000; Litmanovich and Plate, 2000), GTA represents the bulk chain of the PAN fragments, whereas HIBA and HBA correspond to the possible end-groups forming in the course of the degradation process.

The presence of organic ligands disposed with the waste in L/ILW or generated through the degradation of more complex organic materials may result in the formation of stable complexes with radionuclides, eventually affecting the retention properties of the latter in repository systems. Previous studies have investigated the impact of the UP2W degradation products on the sorption of radionuclides in cementitious systems (Dario et al., 2004; Holgersson et al., 2011; Duro et al., 2012). These studies focused on the leachates resulting from the degradation of UP2W material, and did not attempt to assess the effect of individual degradation products on the uptake of radionuclides by cement. Isosaccharinic (ISA) and gluconic (GLU) acids are polyhydroxycarboxylic acids expected in L/ILW repositories as main degradation product of cellulose and cement additive, respectively. They share some structural similarities with HIBA and HBA, with alcohol groups in α- and β-positions with respect to the carboxylic group. Several studies in the literature highlight the strong complexes formed by ISA and GLU with radionuclides, including Ni(II), Ln(III) and An(III/IV/V/VI), among others (Vercammen et al., 2001; Tits et al., 2005; Gaona et al., 2008; Rojo et al., 2013; Rai and Kitamura, 2017; González-Siso et al., 2018; Tasi et al., 2018a; Tasi et al., 2018b; Rojo et al., 2021). The formation of these complexes can potentially affect the retention of radionuclides in cement-based repositories (Wieland and Van Loon, 2003; Wieland, 2014; Tasi et al., 2021a).

In this context, this study aims at investigating the uptake of ^{63}Ni(II), ^{152}Eu(III) and ^{242}Pu(III/IV) by HCP in the absence and presence of the proxy ligands HIBA, HBA and GTA. ^{59,63}Ni and ^{239}Pu are important contributors to the radiotoxicity of the wastes in SFR, whereas Eu(III) is often considered as inactive analogue of Am(III) and Pu(III). Experiments with plutonium are conducted under mildly and strongly reducing conditions ($\text{pe} + \text{pH} \approx 10$ and 2, respectively) to capture the possible interplay between Pu(IV) and Pu(III) oxidation states in the redox boundary conditions expected in SFR (Duro et al., 2014). The Pu(IV) system in HQ-buffered solutions provides also insight on the behaviour of other tetravalent actinides expected in SFR, *e.g.,* U(IV). The results obtained for the sorption of these radionuclides in the presence of proxy ligands are compared with analogous studies in the presence of ISA, which shares some structural similarities with HIBA and HBA. The present work complements and further expands the experimental studies by Szabo et al. dedicated to the proxy ligands of UP2W, *i.e.,* evaluating their effect on the solubility of selected radionuclides (Szabo et al., 2022b) and assessing their uptake by HCP (Szabo et al., 2022a).

2 Experimental

2.1 Chemicals and radiotracers

All experiments were conducted at $T = (22 \pm 2)$ °C in Ar gloveboxes with $O_2 < 2$ ppm. Solutions were prepared with purified water (Millipore Milli-Q Advantage A10 (18.2 MΩ·cm at 22°C, 4 ppb TOC) with Millipore Millipak® 40 0.22 µm), purged with Ar for >1 h to remove traces of O_2 and CO_2.

Glutaric acid ($C_5H_8O_4$, 99%, solid), α-hydroxyisobutyric acid ($C_4H_8O_3$, 99%, solid), 3-hydroxybutyric acid ($C_4H_8O_3$, 99%, liquid), portlandite ($Ca(OH)_2$ (cr)) and tin (II) chloride ($SnCl_2$, p.a) were purchased from Sigma-Aldrich. NaOH, HCl (both Titrisol), hydroquinone ($C_6H_6O_2$, HQ, p.a.), concentrated HNO_3 (Supra- and Ultrapure) were obtained from Merck.

^{63}Ni and ^{152}Eu radiotracers were purchased from Eckert and Ziegler, with total activities of 100 µCi/3.7 MBq in 1 mL of 0.5 and 0.1 M HCl, respectively. Although both radiotracers were commercialized as "carrier-free", the concentrations of stable Ni in the ^{63}Ni stock solution and stable Eu in the ^{152}Eu stock solutions were quantified as $(3.0 \pm 0.3)\cdot 10^{-5}$ M and $(1.1 \pm 0.1)\cdot 10^{-5}$ M. The isotopic composition of the Pu(VI) stock used in this work was 99.4 wt% ^{242}Pu, 0.58 wt% ^{239}Pu, 0.005 wt% ^{238}Pu and 0.005 wt% ^{241}Pu, as characterized

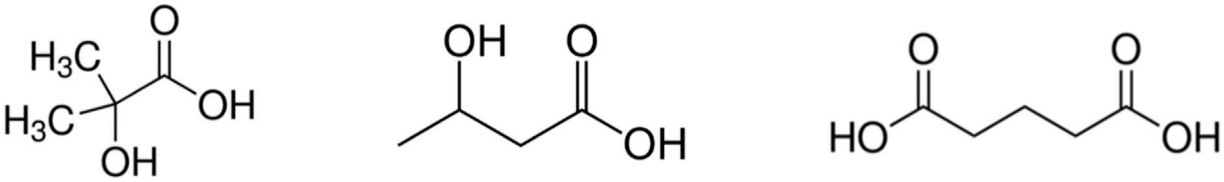

FIGURE 1
Structural formulae of the proxy ligands investigated in this work: α-hydroxyisobutyric acid (HIBA, left), 3-hydroxybutyric acid (HBA, centre) and glutaric acid (GTA, right).

in a previous study (Altmaier et al., 2008). The original Pu(VI) stock solution ($[Pu]_{tot} = 5.63 \cdot 10^{-2}$ M) in 3 M $HClO_4$ was diluted to $[Pu]_{tot} = 2.64 \cdot 10^{-6}$ M in 0.2 M HCl. The latter solution was used for the preparation of the sorption samples containing plutonium. Pu(IV) and eventually Pu(III) are expected to prevail in the reducing conditions of the experiments (see Tasi et al., 2018a), but the choice of the +VI oxidation state for the spike of Pu aimed at avoiding high initial oversaturation conditions that may result in the formation of Pu(IV) colloids (see Tasi et al., 2021a).

2.2 Cement and cement porewater

The hardened cement paste used in this work was provided by SKB as a monolith, which was prepared from a mixture of Swedish structural Portland cement for civil engineering (CEM I 42.5N BV/SR/LA) and deionized water at a water-to-cement weight ratio of 0.5. In a previous study (Tasi et al., 2021a), the HCP monolith was milled, sieved to a particle size of <100 µm, extensively characterized and stored under Ar atmosphere until use in the sorption experiments. Tasi and co-workers reported a (Brunauer–Emmett–Teller, BET) surface area of 79.2 $m^2 \cdot g^{-1}$ for the HCP powder material used in the present study.

The cement porewater was prepared using the protocol described in Tasi et al. (2021a). The HCP was weighted in a 2 L Kautex flask and contacted with Milli-Q water to reach a solid-to-liquid ratio (S:L) of 25 $g \cdot dm^{-3}$. After a contact time of 1 week, the initial leachate was separated by decantation from the HCP, and the solid material was equilibrated again with fresh Milli-Q water during one additional week. The same HCP material and cement pore water were used in the solubility and sorption studies with proxy ligands for UP2W degradation products (Szabo et al., 2022a; Szabo et al., 2022b). The composition of the cement porewater is buffered by portlandite at pH ≈ 12.5 and [Ca] ≈ 0.02 M, and is characterized by a low content of Na and K ($\leq 3 \cdot 10^{-4}$ M). A detailed description of the impact of the proxy ligands investigated in this work on the HCP is provided in our previous study dedicated to this binary system (Szabo et al., 2022a).

2.3 pH and E_h measurements

The pH was measured using a ROSS combination pH electrode (Thermo Scientific, OrionTM) calibrated against standard buffer solutions (pH = 2 to 12, Merck).

Redox potentials of plutonium systems containing either HQ or Sn(II) were measured using Pt combination electrodes (Metrohm) with Ag/AgCl as a reference system. Measurements were performed following the protocol described in the literature (Altmaier et al., 2010). The measured potentials were converted to E_h values (referred to the standard hydrogen electrode, SHE) by correcting for the potential of the Ag/AgCl reference in 3.0 M KCl at T = 22°C, *i.e.* +207 mV. E_h values were converted to pe (with $pe = -\log a_{e-}$) as $E_h = -RT \ln(10) F^{-1} \log a_{e-}$, where R is the ideal gas constant ($8.3144\ J \cdot mol^{-1} \cdot K^{-1}$) and F is the Faraday constant (96,485.3 C mol^{-1}). Uncertainties of pH and E_h measurements (calculated as 2σ of averaged measurements) ranged between ±0.05/±0.10 and ±15/±40 mV, respectively.

2.4 Sorption experiments with ^{63}Ni, ^{152}Eu and ^{242}Pu in the absence and presence of proxy ligands

All batch sorption samples were prepared using the HCP and cement porewater described in Section 2.2. Stock solutions of the proxy ligands were titrated with 1.0 M NaOH to pH ≈ 12.5 in order to avoid any impact on the pH of the cement porewater.

Suspensions of HCP and cement porewater (10 mL) at the targeted S:L ratio were equilibrated for 2 days before the addition of the corresponding radionuclide. In the experiments with plutonium, the HCP was mixed with cement porewater containing 2 mM of either HQ or Sn(II), and the suspension was equilibrated for 2 days, after which pH and E_h were determined as described in Section 2.3. Small volumes (14–351 µL) of the diluted radionuclide stock solutions were pipetted into these systems, aiming at $\log[^{63}Ni(II)]_0 = -8/-9$, $\log[^{152}Eu(III)]_0 = -8/-8.67$ and $\log[^{242}Pu(IV)]_0 \approx -8$. After the addition of the corresponding radionuclides, the values of pH, E_h (only in the case of Pu) and total radionuclide concentration $[RN]_{aq}$, in the aqueous phase were monitored for ≤4 months $[RN]_{aq}$ was measured after phase separation, *i.e.,* ultrafiltration with 10 kD filters at 3,400–3,900 *g* (Nanosep®, Pall Life Sciences; pore size ≈ 2-3 nm) (Ni, Eu, Pu) or ultracentrifugation (694,000 g, 1 h; Beckman XL-90, rotor type 90Ti) (Eu). After each sampling, the volume of the original sample was restored with cement pore water. The aliquots obtained after phase separation were diluted with 2% HNO_3 (Suprapur). In the samples containing nickel, the acidified aliquot was mixed with 10 mL of liquid scintillation counting (LSC) cocktail (Ultima Gold XR, Perkin Elmer) and measured for 30 min in a LSC Tri-Carb 3110 TR (Perkin Elmer) equipment considering an energy window between 0 and 100 keV. Detection limits achieved with this counting time and sample characteristics were $\approx 6 \cdot 10^{-12}$ M, calculated as three times the standard deviation of blank solutions. The concentration of Eu was determined by gamma counting (Wizard2 10—Detector Gamma Counter, Perkin Elmer) for an energy window between 15 and 2000 keV and a counting time of 30 min. Detection limits calculated for these conditions were $\approx 10^{-13}$ M. Pu was quantified by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS; type Element XR, Thermo Fisher), with a detection limit of $\approx 10^{-13}$ M in the conditions of the present study. The solutions in the HCP-Ni system were additionally quantified for total nickel concentration by ICP-MS.

The same sequence was used in the preparation of the sorption samples in the ternary systems HCP-RN-proxy ligands. Two days after the addition of the corresponding radionuclide, the suspensions were spiked with appropriate volumes of GTA, HIBA and HBA stock solutions (0.2, $5 \cdot 10^{-2}$ and $5 \cdot 10^{-3}$ M) targeting the range of initial ligand concentrations $-4 \leq \log([L]_0/M) \leq -1$. Note that the sorption of the proxy ligands on HCP at the S:L ratio used in the ternary system HCP-RN-proxy ligands is very minor (Szabo et al., 2022a), and thus $[L]_0$ is considered equal to the concentration of the ligand in equilibrium conditions $[L]_{aq}$. After the addition of the proxy ligands, the values of pH, E_h (only in the case of Pu) and $[RN]_{aq}$ were monitored for ≤3 months. The sampling procedure was the same as described above for the binary system HCP-RN. After each sampling, the volume of the original sample was restored with cement pore water containing the corresponding proxy ligand and ligand concentration. The sorption of Ni(II) and Eu(III) on the walls of the vessels was evaluated after terminating the sorption experiments. Hence, the

TABLE 1 Summary of the experimental conditions considered for the sorption studies with the binary and ternary systems HCP-RN and HCP-RN-proxy ligands, with L = HIBA, HBA and GTA.

Radionuclide	S:L [g·dm^{-3}]	log ($[RN]_0$/[M])	log ($[L]_0$/[M])	Redox buffer	Batch samples	Contact time (days)	Measurements
^{63}Ni(II)	1, 2, 4, 10, 20	−8[1], −9[1]	–	–	10	≤113	pH, LSC, ICP-MS (inactive Ni)
	1	−8[1]	−4, −1.5, −1		9	≤85	
^{152}Eu(III)	1, 2, 3, 4	−8[2]	–	–	5	≤125	pH, γ-counting
	1	−8.67[3]	−3, −2.5, −2, −1.5, −1		15	≤56	
^{242}Pu(III/IV)	0.5, 1	−8.2, −8.0, −7.8	–	2 mM HQ	5	≤80	pH, E_h, SF-ICP-MS
	1	−8.0	−4, −3, −2.5, −2, −1.5, −1	2 mM HQ/ Sn(II)	36	≤80	

[1] Containing also stable [Ni] = (1.6 ± 0.8)·10^{-7} M in the cement pore water, as quantified in this work.

[2] With stable $[Eu]_0$ = 3.1·10^{-8}. M, as present in the ^{152}Eu commercial stock and considering the corresponding dilution factors.

[3] With stable $[Eu]_0$ = 1.1·10^{-7} M, as added in this experimental series ([Eu] = 1.0·10^{-7} M) and present in the ^{152}Eu commercial stock and considering the corresponding dilution factors ([Eu] = 6.6·10^{-9} M).

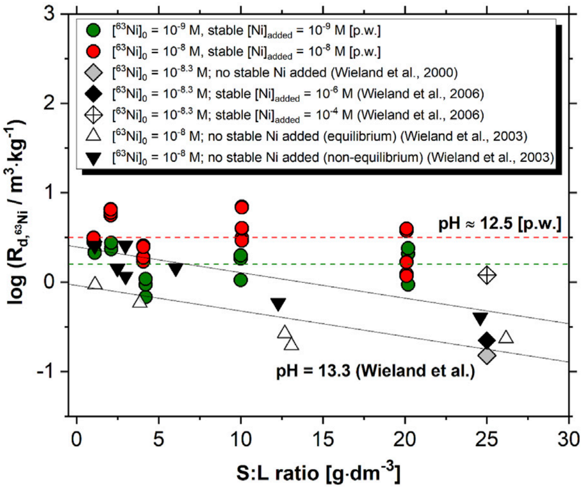

FIGURE 2
Uptake of ^{63}Ni(II) by HCP in the absence of proxy ligands as determined in this present work (p.w., red and green, pH ≈ 12.5) or reported by Wieland and co-workers (triangles and inverted triangles) (Wieland et al., 2000; Wieland and Van Loon, 2003; Wieland et al., 2006). Dashed and solid lines show the trend of R_d values with increasing S:L ratios as determined in this work and reported in Wieland and Van Loon, (2003), respectively.

suspension remaining in the vessel was discarded, the vessel was washed three times with MQ-water, filled in with 2% HNO_3 and left overnight. The concentration of Ni and Eu in the resulting solution was quantified by LSC and gamma counting, respectively. From these results, the fraction of ^{63}Ni and ^{152}Eu sorbed on the vessel's walls was determined as 30% and 4%, respectively. Distribution ratios determined in this work are corrected accordingly. A negligible sorption of Pu on the vessel's walls under analogous experimental conditions was previously reported by Tasi et al. (2021a). The main experimental conditions considered in this work for the binary HCP-RN and ternary HCP-RN-proxy ligands systems are summarized in Table 1.

Sorption was evaluated in terms of distribution ratios, R_d (in m^3·kg^{-1}), calculated as the ratio of radionuclide concentration in the solid ($[RN]_{solid}$, in mol·kg^{-1}) and aqueous ($[RN]_{aq}$, in M) phases:

$$R_d = \frac{[M]_{solid}}{[M]_{aq}} \cdot \frac{1}{1000} = \frac{[M]_0 - [M]_{aq}}{[M]_{aq}} \cdot \frac{V}{m} \tag{1}$$

where $[M]_0$ is the initial radionuclide concentration in the aqueous phase (M), V is the volume of sample (m^3) and m is the mass of HCP (kg).

3 Results and discussion

3.1 Uptake of Ni(II) by HCP in the absence and presence of proxy ligands

Figure 2 shows the uptake of ^{63}Ni(II) by HCP in the absence of proxy ligands, as determined in this work for the degradation stage II of cement (pH ≈ 12.5). The figure shows also sorption data reported by Wieland and co-workers for the sorption of ^{63}Ni(II) by HCP in the degradation stage I (pH = 13.3), both in the absence and presence of added stable Ni(II) (Wieland et al., 2000; Wieland and Van Loon, 2003; Wieland et al., 2006).

R_d values determined in this work remain mostly constant within the investigated range of S:L ratios (1–20 g·dm^{-3}). Slight differences in the quantified R_d values are identified between sorption experiments with $[^{63}Ni]_0 = 10^{-8}$ and 10^{-9} M, *i.e.* (3.6 ± 1.8) m^3·kg^{-1} and (1.8 ± 0.7) m^3·kg^{-1}, although both values agree within the respective uncertainties. In contrast to this, Wieland and co-workers observed a systematic decrease of the measured R_d values with increasing S:L ratio (see Figure 2). The authors proposed isotopic exchange with stable nickel present in pristine HCP as main mechanism for the uptake of ^{63}Ni, and used the partition coefficient (α) to describe the isotopic distribution of ^{63}Ni between the HCP and the cement pore water:

$$\alpha = \frac{\left(n_{solid,^{63}Ni} / n_{solid,Ni}\right)}{\left(n_{aq,^{63}Ni} / n_{aq,Ni}\right)} = \frac{R_{d,^{63}Ni}}{R_{d,Ni}} \tag{1a}$$

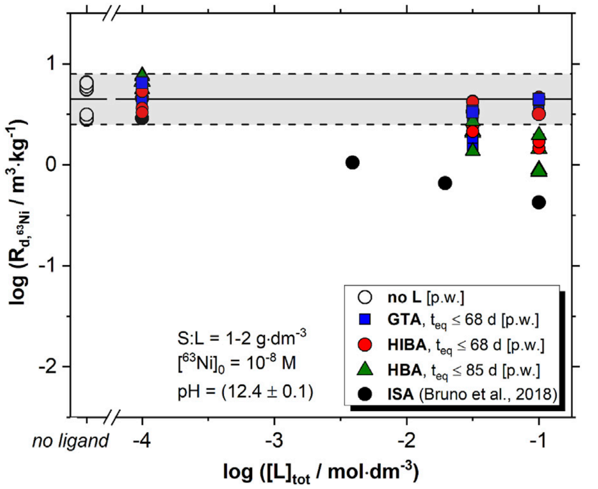

FIGURE 3
Uptake of ^{63}Ni(II) by HCP under increasing concentrations of proxy ligands, with 10^{-4} M ≤ $[L]_{tot}$ ≤ 0.1 M and S:L = 1 g·dm^{-3}. White circles and grey-shaded area correspond to the uptake of ^{63}Ni(II) by HCP in the absence of proxy ligands, as reported in Figure 2 for S:L = 1-2 g·dm^{-3}. Black symbols show the effect of ISA on the uptake of ^{63}Ni(II) by HCP, as reported by Bruno et al. (2018). All data correspond to degradation stage II of cement, with pH = (12.4 ± 0.1). [p.w.] stands for present work.

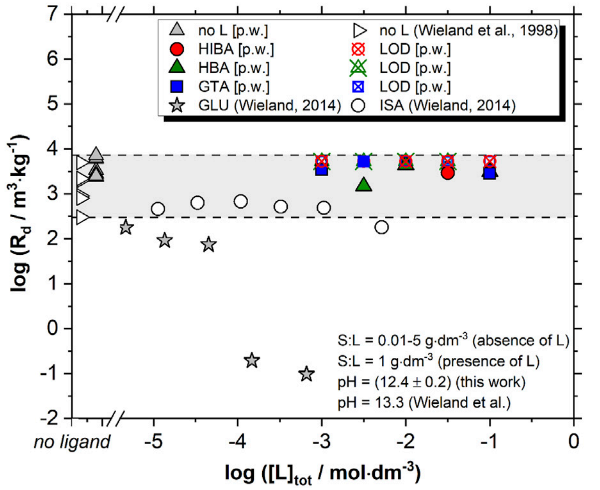

FIGURE 4
Uptake of ^{152}Eu(III) by HCP in the absence and presence of proxy ligands (with 10^{-3} M ≤ $[L]_{tot}$ ≤ 0.1 M) as determined in this work. Data reported by Wieland and co-workers for the uptake of ^{152}Eu(III) by HCP (degradation stage I) in the absence and presence of ISA and GLU provided for comparison (Wieland et al., 1998; Wieland, 2014). Grey-shaded area covers the range of R_d values determined in this work (S:L = 1–4 g·dm^{-3}) or reported by Wieland and co-workers (S:L = 0.01–0.1 g·dm^{-3}) in the absence of organic ligands. Experiments in the presence of organic ligands were conducted at S:L = 1 g·dm^{-3}. LOD and [p.w.] stand for limit of detection and present work, respectively.

where $n_{solid,^{63}Ni}$ and $n_{solid,Ni}$ are the number of moles of ^{63}Ni and stable Ni in HCP, $n_{aq,^{63}Ni}$ and $n_{aq,Ni}$ denote the number of moles of ^{63}Ni and stable Ni in the cement pore water, and $R_{d,^{63}Ni}$ and $R_{d,Ni}$ are the distribution coefficients of ^{63}Ni and stable Ni, respectively. The values of α approach 1 if the total inventory of ^{63}Ni in HCP is accessible to isotopic exchange.

Wieland *et al.* reported α = (3.3 ± 1.7)·10^{-2} (absence of added stable Ni), α = (2.9 ± 0.6)·10^{-2} (with stable $[Ni]_{added} = 10^{-6}$ M) and α = (4.5 ± 1.0)·10^{-2} (with stable $[Ni]_{added} = 10^{-4}$ M) for the uptake of ^{63}Ni by HCP (in the degradation stage I) (Wieland et al., 2006). On the basis of these results, Wieland and co-workers argued that only a small fraction of stable Ni present in pristine HCP is available for isotopic exchange with ^{63}Ni.

Measurements of stable Ni in the HCP and corresponding pore water used in this work resulted in (3.7 ± 1.0)·10^{-4} mol·kg^{-1} and (1.6 ± 0.8)·10^{-7} M,[1] respectively, which allow the calculation of $R_{d,Ni}$ = (2.3 ± 0.9) m^3·kg^{-1}. The combination of this value with $R_{d,^{63}Ni}$ determined in this work results in α = (1.0 ± 0.5) and (1.9 ± 1.0) for experiments conducted at $[^{63}Ni]_0 = 10^{-9}$ and 10^{-8} M, respectively. The partition coefficients (α) determined in this work are clearly higher than those reported in Wieland et al. (2006). Such discrepancies can be possibly explained by the different boundary conditions considered in both studies, *i.e.* cement degradation stage II (this work; pH ≈ 12.5) and I (Wieland et al., 2006; pH = 13.3). Hence, measured zeta potentials of the HCP surface sharply decrease from ≈20 mV at pH ≈ 12.5 to ≈ −20 mV at pH = 13.3 (Pointeau et al., 2006; Pointeau et al., 2008; Tasi et al., 2021a; Szabo et al., 2022a), whereas Ni(II) speciation is expected to change from $Ni(OH)_2(aq)$ to $Ni(OH)_3^-$ for the same variation of pH (González-Siso et al., 2018; Missana et al., 2022). In a recent study, Missana and co-workers reported $R_{d,^{63}Ni} \approx 1$ m^3·kg^{-1} (*i.e.* log $R_{d,^{63}Ni} \approx 0$) for the uptake of ^{63}Ni by C-S-H with Ca:Si = 1.4. Higher $R_{d,^{63}Ni}$ were obtained with decreasing pH and Ca:Si ratios, *i.e.* log $R_{d,^{63}Ni} \approx 1$ at Ca:Si = 0.8.

The concentration of stable Ni in the cement porewater is by a factor of 10 or 100, respectively, higher than the added ^{63}Ni. At the relatively high stable Ni concentration which is most likely determined by solubility of a Ni-bearing solid phase (LDH phases or $Ni(OH)_2$(am)) we can expect that Ni species are not only abundant in a solid phase and as dissolved $Ni(OH)_2(aq)$, but also as surface sorbed onto or incorporated into cement phases such as *e.g.*, C-S-H. Spiked ^{63}Ni will undergo the same reactions as stable Ni so that isotope exchange is assumed to be the dominant retention mechanism under our experimental conditions. Note further that the partition coefficients measured in this work are consistent (within the uncertainties) with α = 1, which suggests the full availability of stable Ni in pristine HCP (in the degradation stage II) for isotopic exchange with ^{63}Ni.

Figure 3 shows the effect of proxy ligands (with 10^{-4} M ≤ $[L]_{tot}$ ≤ 0.1 M) on the uptake of ^{63}Ni by HCP in degradation stage II. The figure includes also data reported by Bruno and co-workers for the uptake of ^{63}Ni under the same conditions but in the presence of ISA (Bruno et al., 2018). HIBA, HBA and GTA have a minor impact on the retention of ^{63}Ni(II) by HCP, and a slight decrease in the $R_{d,^{63}Ni}$ is observed only at $[L]_{tot}$ = 0.1 M. These results are consistent with

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[1] This concentration is in line with previous data reported in the literature (Ochs et al., 2016) but higher than the solubility limit of β-$Ni(OH)_2$(cr) determined under analogous boundary conditions (González-Siso et al., 2018; Szabo et al., 2022b). This observation suggests that this solid phase is neither present in the cement not forming within the timeframe of our experiments. Solubility equilibrium involving other solid phases (*e.g.*, Ni-bearing LDH phases or $Ni(OH)_2$(am)) may instead be responsible of the measured concentrations of stable Ni in the cement pore water.

solubility data previously reported for β-Ni$(OH)_2$(cr) in the presence of the same proxy ligands (Szabo et al., 2022b), where an increase in the solubility was only observed at $[L]_{tot}$ = 0.1 M. In contrast to the proxy ligands investigated in this work, Figure 3 shows that ISA decreases the retention of ^{63}Ni by HCP in degradation stage II at $[ISA]_{tot} > 10^{-3}$ M (Bruno et al., 2018). This is again in line with solubility data reported for β-Ni$(OH)_2$(cr) in the presence of ISA, where the complexes Ni(OH)ISA(aq), $Ni(OH)_2(ISA)^-$ and $Ni(OH)_3(ISA)^{2-}$ were reported to control the aqueous speciation of Ni(II) in alkaline conditions (González-Siso et al., 2018). These observations support that the formation of stable complexes Ni(II)-OH-L is mostly responsible for the decrease in the retention of ^{63}Ni(II) by HCP. Differences observed between the proxy ligands and ISA are attributed to the presence of several alcohol groups in the latter ligand, which are known to form stable chelates with hard Lewis acids like Ni(II).

3.2 Uptake of Eu(III) by HCP in the absence and presence of proxy ligands

Figure 4 shows the uptake of ^{152}Eu(III) by HCP in degradation stage II, both in the absence and presence of increasing concentrations of proxy ligands. For comparative purposes, the figure shows also the sorption of Eu(III) by HCP in degradation stage I in the absence and presence of ISA and GLU, as reported by Wieland and co-workers (Wieland et al., 1998; Wieland and Van Loon, 2003; Wieland, 2014).

A very strong sorption is observed in the absence of proxy ligands, with R_d values ranging from ≈$3\cdot10^3$ $m^3\cdot kg^{-1}$ and ≈$1\cdot10^4$ $m^3\cdot kg^{-1}$ at S:L = 1–4 $g\cdot dm^{-3}$. These values are slightly higher but in line with sorption studies available in the literature. Wieland and co-workers reported R_d values ≥ 10^3 $m^3\cdot kg^{-1}$ at S:L = 0.01 $g\cdot dm^{-3}$ and > 10^2 $m^3\cdot kg^{-1}$ at S:L = 0.1 $g\cdot dm^{-3}$ (Wieland et al., 1998; Wieland and Van Loon, 2003). Our results are also consistent with the uptake observed for Eu(III) in the presence of C-S-H phases (Tits et al., 2000; Pointeau et al., 2001), thus strongly supporting that the latter phases are the main sink of Eu(III) (as well as An (III)) in cementitious systems. The uptake mechanism investigated by time-resolved laser fluorescence spectroscopy and X-ray absorption spectroscopy for Eu(III), Nd(III) and Cm(III) supports a fast adsorption with the formation of surface complexes, followed by the slower incorporation of the trivalent lanthanide or actinide in the C-S-H structure (Pointeau et al., 2001; Tits et al., 2003; Stumpf et al., 2004; Mandaliev et al., 2010a; Mandaliev et al., 2010b). Note that stable Eu(III) is also present in HCP (quantified as $2.7\cdot10^{-6}$ $mol\cdot kg^{-1}$ in the CEM I material used in this work), although the inventory is significantly lower than in the case of stable Ni(II) ($3.7\cdot10^{-4}$ $mol\cdot kg^{-1}$) and has a negligible effect in the retention of ^{152}Eu(III) in the current laboratory study.[2]

The uptake of Eu(III) by HCP is not affected by the presence of the proxy ligands up to ligand concentrations of $[L]_{tot}$ = 0.1 M, which is consistent with solubility data previously reported for $Nd(OH)_3$(s) in the presence of the same proxy ligands (Szabo et al., 2022b). Although these ligands are known to form stable complexes with Ln(III)/An(III) in acidic to near-neutral pH conditions (Deelstra and Verbeek, 1964;

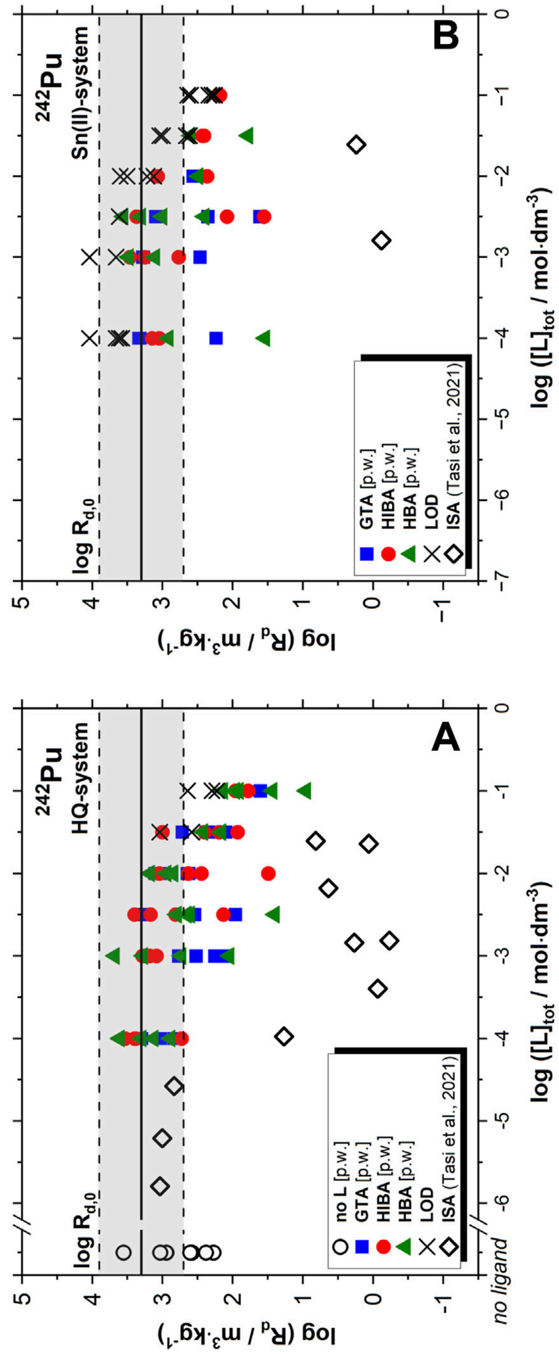

FIGURE 5
Uptake of ^{242}Pu(IV/III) by HCP (degradation stage II) in the absence and presence of proxy ligands (with 10^{-3} M ≤ $[L]_{tot}$ ≤ 0.1 M), with L = GTA, HIBA and HBA, in HQ **(A)** and Sn(II) **(B)** systems. Data reported by Tasi et al. for the uptake of ^{242}Pu(IV) by HCP (degradation stage II) in the presence of ISA provided for comparison (Tasi et al., 2021a). Experiments in the absence of organic ligands were conducted at S:L = 0.5–2 $g\cdot dm^{-3}$ (this work). The grey-shaded area indicates the range of log R_d values reported by Tasi and co-workers in the absence of organic ligands at S:L = 1 $g\cdot dm^{-3}$ (Tasi et al., 2021a). Experiments in the presence of organic ligands were conducted at S:L = 1 $g\cdot dm^{-3}$, both in this work and in (Tasi et al., 2021a). LOD and [p.w.] stand for limit of detection and present work, respectively.

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[2] The ratio ^{152}Eu (total inventory): Stable Eu (inventory in HCP) ranges from 4:1 (at S:L = 1 $g\cdot L^{-1}$) to 1:1 (at S:L = 4 $g\cdot L^{-1}$). A much larger inventory of stable Eu in HCP would be required in order to make isotopic exchange a relevant retention mechanism in our experimental study, especially considering the very high log R_d values determined for this system (log R_d = 3-4, with R_d in $m^3\cdot kg^{-1}$).

Wang et al., 2000; Giroux et al., 2002), they cannot compete against hydrolysis in hyperalkaline systems or against the strong sorption occurring in HCP systems. This observation is further supported by thermodynamic calculations conducted by Keith-Roach and Shahkarami (Keith-Roach and Shahkarami, 2021). In contrast to the proxy ligands investigated in this work, the uptake of Eu(III) is strongly decreased in the presence of GLU and, to a lesser extent, ISA (Wieland, 2014) (see Figure 4). Even though HIBA and HBA contain a carboxylic group with an alcohol group in α- or β-position, this configuration is insufficient to form stable complexes with Eu(III) in hyperalkaline systems. As discussed in Szabo et al. (2022a), a greater number of alcohol groups (as occurs in ISA or GLU) is required to form stable chelates in hyperalkaline conditions and thus affect aqueous complexation and sorption phenomena.

3.3 Uptake of Pu(III/IV) by HCP in the absence and presence of proxy ligands

The measurements of pH and E_h in the Pu systems containing HQ and Sn(II) resulted in (pe + pH) = (10.0 ± 0.5) and (2 ± 1), respectively. These values are consistent with previous studies available in the literature using the same reducing chemicals (Tasi et al., 2018a; Tasi et al., 2018c). Considering the redox distribution of plutonium in alkaline reducing conditions, Pu(IV) is expected to prevail in the aqueous phase of HQ-buffered systems, whereas both Pu(III) and Pu(IV) may coexist in the strongly reducing conditions imposed by Sn(II) (Fellhauer, 2013; Tasi et al., 2018c; Grenthe et al., 2020). Figures 5A, B (HQ-system) and (Sn(II)-system) show the uptake of Pu (in terms of log R_d values) by HCP in the degradation stage II, both in the absence and presence of increasing concentrations of proxy ligands. The figure includes also sorption data reported for Pu in the presence of ISA under analogous experimental conditions (Tasi et al., 2021a).

Sorption data in the investigated Pu samples are characterized by a large dispersion. This is a common feature of An(IV) systems in pH-conditions where the neutral species $An(OH)_4(aq)$ prevails, and it is caused by difficulties in the phase separation and the possible presence of intrinsic colloids. A very strong sorption of Pu is observed in HQ-systems and absence of proxy ligands, with log R_d values ranging from 2.2 to 3.5 (with R_d in $m^3 \cdot kg^{-1}$). These results are consistent with sorption data reported by Tasi and co-workers under analogous experimental conditions (Tasi et al., 2021a). The reference book by Ochs et al. recommends a log R_d of 1.5 for the uptake of Pu(IV) by HCP in the degradation stage II, with log R_d = 3 defined as upper limit (Ochs et al., 2016), also in line with our experimental observations.

Strong sorption is observed also in the presence of proxy ligands, with analogous log R_d values determined in HQ- and Sn(II)-systems. Considering the strong sorption described also in Section 3.2 for Eu(III), the experimental observations for Pu in Sn(II)-systems do not allow the unequivocal assignment of the oxidation state prevailing under these very reducing conditions. A slight decrease in the log R_d values can be speculated at $[L]_{tot} > 10^{-2}$ M, especially in the case of HQ-systems. However, this observation is uncertain due to the large dispersion of the data, and by the increase of the detection limit with increasing ligand concentration caused by the steady increase of the dilution factors required for ICP-MS. In spite of this, R_d values remain high in all the investigated systems containing proxy ligands, *i.e.* log $R_d > 1$. The weak impact of the proxy ligands on the retention of Pu by HCP in degradation stage II is in line with the results of solubility experiments in the presence of analogous concentrations of proxy ligands, in which the solubility of PuO_2(ncr, hyd) remains unaffected up to $[L]_{tot}$ = 0.1 M, both in HQ- and Sn(II)-buffered systems (Szabo et al., 2022b). Although HIBA, HBA and GTA are known to form stable binary complexes with An (III/IV) under acidic conditions, these complexes can neither outcompete hydrolysis nor the strong sorption on HCP under the hyperalkaline pH conditions characteristic of the degradation stage II of cement.

In contrast to the proxy ligands, Figure 5 shows the remarkable impact that ISA on the uptake of Pu, which results in a decrease of up to 3 orders of magnitude in the R_d values (Tasi et al., 2021a). This is attributed to the strong ternary and quaternary complexes (Ca-)Pu-OH-ISA forming in hyperalkaline conditions (Tasi et al., 2018a; Tasi et al., 2018b). Moreover, distinct trends are observed at high ISA concentrations, involving the formation of stable surface complexes than increase sorption. Tasi and co-workers explained this observation with the strong uptake of ISA by cement, which modifies the surface properties at $[ISA]_{tot} \geq 10^{-3}$ M. This again highlights the significantly different behaviour of proxy ligands and ISA, not only with respect to the interaction with radionuclides but also concerning the interaction with cement surfaces. Similar observations have been reported for the uptake of Pu(IV) and Th(IV) by HCP and C-S-H phases in the presence gluconate, a polyhydroxocarboxylic acid analogous to ISA (Moreton, 1993; Moreton et al., 2000; Wieland, 2014; Guidone et al., 2022).

4 Summary and conclusion

A comprehensive sorption study was conducted with the aim of quantitatively assessing the impact of α-hydroxyisobutyric acid, 3-hydroxybutyric acid and glutaric acid on the retention of Ni(II), Eu(III) and Pu(III/IV) by HCP in degradation stage II of cement. These low molecular weight organic ligands were identified within Work Package 3 CORI of the EURAD EU project as possible degradation products of UP2W, a polyacrylonitrile-based filter aid used in nuclear power plants.

Sorption experiments conducted in the absence of proxy ligands are consistent with literature data, with log $R_{d,^{63}Ni} \approx$ 0-1, log $R_{d,^{152}Eu} \geq$ 3.4–4 and log $R_{d,^{242}Pu} \approx$ 2.2–3.5 (all R_d in $m^3 \cdot kg^{-1}$). Considering the presence of nickel in the pristine cement and based on the quantification of $R_{d,^{63}Ni}$; $R_{d,^{nat}Ni}$ in the current study, we conclude that isotopic exchange with the complete species inventory of stable Ni present in pristine HCP (including Ni in solid phases and associated with surfaces, *e.g.*, of C-S-H phases) is the main retention mechanism of ^{63}Ni(II) in cement systems in degradation stage II. Differences compared to the retention mechanism proposed for cement in degradation stage I might be explained by differences in the surface properties of cement and the aqueous speciation of Ni(II) under these conditions.

The retention of ^{63}Ni(II) and ^{242}Pu(III/IV) is slightly decreased in the presence of proxy ligands at $[L]_{tot} > 10^{-2}$ M. The effect is less evident for Pu due to the dispersion of the data and to the increased detection limits with increasing ligand concentration. On the contrary, the uptake of ^{152}Eu(III) is not affected by the presence of proxy ligands up to concentrations of $[L]_{tot}$ = 0.1 M. These results are consistent with solubility studies conducted with β-$Ni(OH)_2$(cr), $Nd(OH)_3$(s) and PuO_2(hyd, ncr) under analogous conditions and in the presence of proxy ligands. Although HIBA and HBA share some functional groups with ISA and GLU, the investigated proxy ligands show a minor capacity for the mobilization of radionuclides in cementitious systems. These observations support that mono- and dicarboxylic acids can hardly outcompete the hydrolysis and sorption of Ni(II), Eu(III) and Pu(III/IV) in cement systems in the degradation stage II, except if several alcohol groups are also present in the organic ligand. With the aim to approaching systems of even higher complexity, the last step of this project will target the impact of the complex degradation leachates of UP2W on the retention of ^{63}Ni(II), ^{152}Eu(III) and ^{242}Pu(III/IV) by hardened cement paste in the degradation stage II.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

Author contributions

SH, AM, XG, MA, and HG defined the initial concept of the project. AT and XG contributed to conception and design of the experimental study. PS and AT performed the experiments. AT and PS conducted data evaluation. XG wrote the first draft of the manuscript. PS and AT wrote sections of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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Conflict of interest

AM and SH were employed by Svensk Kärnbränslehantering AB.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fnuen.2023.1117413/full#supplementary-material

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