PAPER

Impact of the degradation leachate of the polyacrylonitrile-based material UP2W on the retention of Ni(II), Eu(III) and Pu(IV) by cement†

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The uptake of [63]Ni(II), [152]Eu(III) and [242]Pu(IV) by hardened cement paste (HCP, CEM I) in the degradation stage II (pH $\approx$ 12.5, [Ca] $\approx$ 0.02 M) was investigated in the presence of a degradation leachate of UP2W, a polyacrylonitrile-based (PAN) material used as a filter aid in nuclear power plants. The degradation leachate with a concentration of dissolved organic carbon of $\sim$40 ppm was obtained from the degradation of UP2W in portlandite-buffered solutions for *ca.* 1100 days. Redox conditions in the Pu systems were buffered with hydroquinone, which defines mildly reducing conditions (pe + pH $\approx$ 10) where Pu(IV) is the predominant oxidation state. The degradation leachate investigated in this work is moderately sorbed by cement, with distribution ratios (R_d) of (0.35 $\pm$ 0.15) m³ kg⁻¹. These values are 30 to 100 times greater than distribution ratios previously reported for proxy ligands of PAN degradation products, *i.e.*, glutaric acid, α-hydroxyisobutyric acid and 3-hydroxybutyric acid. The presence of the degradation leachate induces a moderate decrease in the uptake of [63]Ni(II), [152]Eu(III) and [242]Pu(IV) by cement, as compared to the sorption in the presence of the proxy ligands. Nevertheless, retention in the presence of the degradation leachate remains high for all investigated radionuclides, with R_d([63]Ni(II)) $\approx$ 2 m³ kg⁻¹, R_d([152]Eu(III)) $\approx$ 100 m³ kg⁻¹ and R_d([242]Pu(IV)) $\approx$ 30 m³ kg⁻¹. These observations possibly reflect that the multiple functionalities (–COOH, –OH, amide groups) expected in the macromolecules (10–15 kDa) present in the degradation leachate, can offer further binding/chelating capabilities compared to the small organic proxy ligands with at most bidentate binding.

1. Introduction

UP2W is a polyacrylonitrile-based polymer (PAN) used as a filter aid in nuclear power plants.[1,2] Significant amounts of used UP2W are disposed of in SFR, the final repository for short-lived low and intermediate level wastes (L/ILW) in Sweden.[1–4] 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 $\leq$ pH $\leq$ 13.3) and Ca concentrations ranging from $\sim$10⁻⁴ M to $\sim$0.02 M.[5] Cementitious materials, in particular calcium silicate hydrate (C–S–H) phases, are known to sorb radionuclides strongly, primarily metal ions and other cationic species.[6,7]

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The degradation of UP2W under the hyperalkaline conditions defined by cementitious systems may result in the formation of organic ligands that can complex radionuclides and therefore decrease their retention by cement. Previous degradation studies with UP2W emphasize the complexity of the degradation products forming in cementitious environments.[2,3] The impact of the UP2W degradation leachates on the retention of radionuclides by cement systems has been investigated in a number of experimental studies. Holgersson and co-workers studied the uptake of [134]Cs(I), [60]Co(II) and [152]Eu(III) by cement in the presence of UP2W degradation leachates, which were generated at room temperature both with pH $\approx$ 12.5 and $\approx$13.3 solutions after a contact time of 300 days.[8] The porewater used in the degradation experiments was saturated with respect to portlandite. The dissolved organic carbon (DOC) quantified in the degradation leachates was $\approx$30 ppm. No effect of these degradation leachates was observed for [134]Cs(I) and [60]Co(II). The authors reported high detections limits for [152]Eu(III) (with log $R_{d,max}$ $\approx$ 0.4, with R_d in m³ kg⁻¹), which prevented conclusive observations on the impact of the degradation leachates on the uptake of this radionuclide by cement. Dario and co-workers investigated the uptake of [152]Eu(III) by cement

and TiO_2 in the presence of UP2W degradation leachates, as well as in the presence of other selected organic ligands.[2] The degradation leachates were generated at T = 60 °C in solutions with pH = 12.5 (adjusted with NaOH) in the absence and presence of 0.01 M Ca. This study was further extended by Duro *et al.* (in cooperation with Dario and co-workers), providing new experimental data and additional modelling insights.[3] Degradation leachates used in the sorption experiments by Duro *et al.* were generated in systems equilibrated at pH ≈ 12.5 and 13.4, with T = 25 and 60 °C, after a contact time of 276 days. Degradation experiments at T = 25 °C were conducted in the presence of 100 g dm^{-3} Ca(OH)$_2$, whereas in those at T = 60 °C Ca was either absent or with an initial concentration of 0.01 M (but absence of Ca(OH)$_2$). Leachates generated at elevated temperature and higher pH were characterized by significantly higher DOC concentrations (~1000 ppm), as compared to the degradation leachates obtained at T = 25 °C and pH ≈ 12.5 (~10 ppm). Distribution ratios for the uptake of Eu(III) by cement correlated well with the total DOC concentrations, with a significant decrease in the R_d values observed only for the systems with DOC ≈ 1000 ppm. Tasdigh studied the impact of UP2W degradation leachates on the retention of Ni(II) and Eu(III) by cement.[9] Degradation leachates were generated at T = 32 °C with pH ≈ 12.5 and 13.3 solutions for a contact time of 6 months. Significantly higher concentrations of total organic carbon (TOC) were quantified as compared to Holgersson *et al.* and Dario *et al.*, *i.e.*, 900 and 5100 ppm at pH ≈ 12.5 and 13.3, respectively. These high TOC values are possibly an artefact caused by the use of cellulose acetate filters for the filtration of the leachate solutions. In contrast to previous studies, Tasdigh used inactive Ni(II) and Eu(III). This resulted in higher detection limits for both metal ions, but also imposed some limitations for the interpretation of nickel data due to the large inventory of inactive Ni(II) in pristine cement and in cement porewater. The authors did not determine the R_d values of Eu(III) in the absence of degradation leachates, but reported significantly low distribution ratios in the presence of UP2W degradation leachates with TOC ≈ 900 ppm, *i.e.*, log R_d ≈ −1 to −0.5 (R_d in m^3 kg^{-1}).

In the context of an on-going collaboration between Karlsruhe Institute of 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,[10] the low molecular weight organic ligands glutaric acid (GTA), α-hydroxyisobutyric acid (HIBA) and 3-hydroxybutyric acid (HBA) were proposed as proxies for the degradation products of UP2W. The structure of these proxy ligands is consistent with ^{13}C-NMR data obtained for a degradation leachate of UP2W under hyperalkaline conditions.[11] The impact of these proxy ligands on the uptake of ^{63}Ni(II), ^{152}Eu(III) and ^{242}Pu(III/IV) by cement in the degradation stage II was recently investigated by us.[12] We reported a negligible effect of the proxy ligands on the uptake of ^{152}Eu(III) up to $[L]_{tot}$ = 0.1 M, whereas a slight decrease in the distribution ratios of ^{63}Ni(II) and ^{242}Pu(III/IV) was observed at $[L]_{tot}$ > 10^{-2} M (equivalent to 4000–7000 ppm C).

In this context, the present study aims at investigating the uptake of ^{63}Ni(II), ^{152}Eu(III) and ^{242}Pu(III/IV) by HCP in the presence of a UP2W degradation leachate generated in hyperalkaline systems representative of the cement degradation stage II, *i.e.*, pH ≈ 12.5 and [Ca] ≈ 20 mM. ^{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). The results obtained for the sorption of these radionuclides in the presence of UP2W degradation leachates are compared with previous analogous experiments performed with the proxy ligands HIBA, HBA and GTA.[12] The present work further complements experimental studies by Szabo *et al.* dedicated to the proxy ligands of UP2W, *i.e.*, evaluating their effect on the solubility of selected radionuclides and assessing their uptake by HCP.[13,14]

2. Experimental

2.1. Chemicals and radiotracers

All experiments were conducted at T = (22 ± 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 hour to remove traces of O$_2$ and CO$_2$.

^{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 ^{nat}Ni in the ^{63}Ni stock solution and ^{nat}Eu in the ^{152}Eu stock solutions were quantified as 3.0 × 10^{-5} M and 1.1 × 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 by α- and γ-spectrometry and by ICP-MS. The original Pu(VI) stock solution ($[Pu]_{tot}$ = 5.63 × 10^{-2} M) in 3 M HClO$_4$ was diluted to $[Pu]_{tot}$ = 2.64 × 10^{-6} M in 0.2 M HCl. The latter solution was used for the preparation of the sorption samples containing plutonium. Pu(IV) is expected to prevail in the mildly reducing conditions of the experiments,[15] 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.[16]

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,[16] 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 g^{-1} for the HCP powder material used in the present study.

A cement porewater representative of the degradation stage II was used in all sorption experiments. The cement porewater

was prepared using the protocol described by Tasi *et al.* and further used in the solubility and sorption studies with proxy ligands for UP2W degradation products.[12–14] 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 ($\leq 3 \times 10^{-4}$ 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 that binary system.[14]

2.3. Degradation leachate of UP2W

UP2W material provided by SKB was washed with Milli-Q water at $T = 65\ °C$, filtered and dried under ambient conditions. The degradation leachate was prepared in PTFE vessels containing 50 g L⁻¹ UP2W and 50 g L⁻¹ Ca(OH)₂, with a total volume of 1 L. The vessel was continuously stirred using a (PTFE-covered) magnetic stirrer. The supernatant solution was systematically monitored for pH, non-purgeable organic carbon-content (NPOC) and after dilution with 2% HNO₃ for total calcium concentration ([Ca]$_{tot}$) *via* inductively coupled plasma – optical emission spectroscopy (ICP-OES, Optima 8300 DV, PerkinElmer). NPOC content of the degradation leachate was determined before and after filtration with PTFE filters (pore diameter = 0.1 or 0.45 μm GE Healthcare, Lifesciences, Whatman™). Filters were washed three times with 1 mL of background solution equilibrated with Ca(OH)₂ to remove possible contributions of the filters to the overall NPOC values. All background solutions were likewise stored in PTFE flasks. Before filtration, 5–10 mL of supernatant solution was centrifuged at 4020*g* for 10 min to remove suspended particles. Background concentrations of NPOC in UP2W-free systems were quantified following the same protocol, and subtracted from the NPOC values measured for the degradation leachate. All solutions were acidified with ultrapure HCl before quantification of NPOC with a Multi N/C 2100 S instrument (Analytik Jena).

The degradation leachate used in the sorption experiments was taken from the mother suspension at $t \approx 1122$ days, with an NPOC concentration of ~40 ppm. Different dilutions of this leachate were contacted with cement in the absence (binary system) and presence (ternary system) of radionuclides (see Table 1 and Section 2.5).

2.4. pH and E_h measurements

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

Redox potentials of plutonium systems containing either hydroquinone (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.[17] 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 mol⁻¹ K⁻¹) and F is the Faraday constant (96 485.3 C mol⁻¹). Uncertainties of measured E_h values (calculated as 2σ of averaged measurements) ranged between ±15 and ±40 mV.

2.5. Sorption experiments: binary and ternary systems

All batch sorption samples were prepared using the HCP, cement porewater and degradation leachate as described in Sections 2.2 and 2.3. The degradation leachate was added to the system after a centrifugation step at 2600*g* for 10 minutes.

Sorption samples for the binary system (cement + degradation leachate (DL)) were prepared by mixing HCP, cement porewater and degradation leachate (DL) at solid-to-liquid ratios (S : L) of 1 and 20 g L⁻¹ and [DL]$_0$ = 14.5, 26.0 and 28.9 ppm. NPOC values were regularly monitored up to $t \leq 64$ days following the protocol described in Section 2.3.

Sorption samples for the ternary systems (cement + radionuclide (RN) + degradation leachate (DL)) were prepared at S : L = 1 g L⁻¹ following two sequences for the addition of individual components: (i) "(cement + RN) + DL", and (ii) "(DL + RN) + cement". The addition of the third component (DL in (i) and cement in (ii)) was done after a pre-equilibration time of 2 days. Small tracer volumes (14–351 μL) were pipetted to each system, aiming at log[Ni(II)]$_0$ = −8, log[Eu(III)]$_0$ = −8.67 and log[Pu(IV)]$_0$ = −8 (with all concentrations in M). The degradation leachate was diluted with cement porewater to attain [DL]$_0$ = 20 and 36 ppm C in the sorption samples. Redox conditions in samples containing Pu were buffered with 2 mM HQ, which is known to set mildly reducing conditions in alkaline systems.[12,15,18]

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 up to $t \leq 225$ days. [RN]$_{aq}$ was measured after phase separation, involving a first centrifugation step at 3400–3900*g* (5 minutes) followed by ultrafiltration with 10 kDa filters (Nanosep®, Pall Life Sciences; pore size ≈ 2–3 nm) (10 minutes). The filtrate was diluted with 2% HNO₃, and radionuclide concentration quantified by means of liquid scintillation counting (LSC, ⁶³Ni), gamma counting (¹⁵²Eu) and sector field inductively coupled plasma mass spectrometry (SF-ICP-MS, ²⁴²Pu). Samples containing ⁶³Ni were mixed with LSC cocktail (Ultima Gold XL, PerkinElmer) and measured with a PerkinElmer Tri-Carb 3110TR equipment within the energy window 0–100 keV for 30 minutes. ¹⁵²Eu was quantified using a PerkinElmer Wizard2 10-2480 Detector Gamma Counter with a counting time of 30 minutes for the energy window 15–2000 keV. The concentration of ²⁴²Pu was determined using a Thermo Fisher Element XR equipment. Detection limits for these nuclides/techniques considering the corresponding dilution factors were ~10⁻¹³ M (⁶³Ni), ~10⁻¹² M (¹⁵²Eu) and ~3 × 10⁻¹² M (²⁴²Pu).

Volume of batch samples was systematically restored using cement porewater after each sampling. The main experimental conditions for the binary and ternary systems are summarized in Table 1.

Table 1 Summary of the experimental conditions considered for the sorption studies with the binary and ternary systems HCP−DL and HCP−RN−DL, with DL = degradation leachate of UP2W

RN	Order of addition	S : L [g dm^{-3}]	log([RN]$_0$/[M])	[DL]$_0$ [ppm C]	Redox buffer	Number of samples	Contact time [days]	Measurements
No RN		1	—	14.27, 25.6	—	2	64	NPOC
		20	—	28.54		1		
^{63}Ni	(HCP + Ni) + DL	1	-8^a	20, 36	—	2	≤20	pH, LSC
	(Ni + DL) + HCP	1	-8^a	36		1	≤140	
^{152}Eu	(HCP + Eu) + DL	1	-8.67^b	20, 36	—	2	≤62	pH, γ-counting
	(Eu + DL) + HCP	1	-8.67^b	36		1	≤225	
^{242}Pu	(HCP + Pu) + DL	1	-8.0	20, 36	2 mM HQ	2	≤76	pH, E_h, SF-ICP-MS
	(Pu + DL) + HCP	1	-8.0	36	2 mM HQ	1	≤225	

^{a} Containing also [^{nat}Ni] = $(1.6 \pm 0.8) \times 10^{-7}$ M in the cement porewater, as quantified in this work. ^{b} With [^{nat}Eu]$_0$ = 1.1×10^{-7} M, as added in this experimental series ([^{nat}Eu] = 1.0×10^{-7} M) and present in the ^{152}Eu commercial stock and considering the corresponding dilution factors ([^{nat}Eu] = 6.6×10^{-9} M).

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:

$$R_d = \frac{[M]_{solid}}{[M]_{aq}} \times \frac{1}{1000} = \frac{[M]_0 - [M]_{aq}}{[M]_{aq}} \times \frac{V}{m} \qquad (1)$$

where [M]$_0$ is the initial radionuclide concentration in the aqueous phase, V is the volume of sample (m^3) and m is the mass of HCP (kg). Distribution ratios were corrected for the radionuclide sorbed on the vessel's wall as described in our previous study.[12]

3.   Results and discussion

3.1.   Uptake of the UP2W degradation leachate by HCP

Fig. 1 shows the uptake of the UP2W degradation leachate by HCP at S : L = 1 g dm^{-3} and [DL]$_0 \approx$ 14 and 26 ppm. The figure shows also the results of the sorption experiments with glutaric acid (GTA) as previously reported by us,[14] where the reported concentrations in molar units (M) have been converted to ppm C for comparison purposes. Note that GTA was previously defined as a proxy ligand for the degradation products of polyacrylonitrile in hyperalkaline conditions.

Fig. 1 shows a slight decrease of log[NPOC]$_{aq}$ relative to log[NPOC]$_0$ for the degradation leachate in contact with HCP at S : L = 1 g dm^{-3}. This observation suggests that the degradation leachate may experience a stronger uptake by HCP than GTA (empty symbols in Fig. 1). In order to validate this hypothesis, additional experiments were conducted at greater solid-to-liquid ratio (S : L = 20 g dm^{-3}). The results are plotted in Fig. 2, together with the sorption isotherms previously reported for GTA (S : L = 20 g dm^{-3}, pH = 12.5, Szabo et al.[14]) and iso-saccharinic acid (ISA, S : L = 25–500 g dm^{-3}, pH = 13.3, Van Loon et al.[19]) (in both cases, with reported ligand concentrations converted in this work to ppm C). Fig. 2 confirms the significantly stronger sorption of the UP2W degradation leachate compared to GTA, whereas the uptake is similar to the
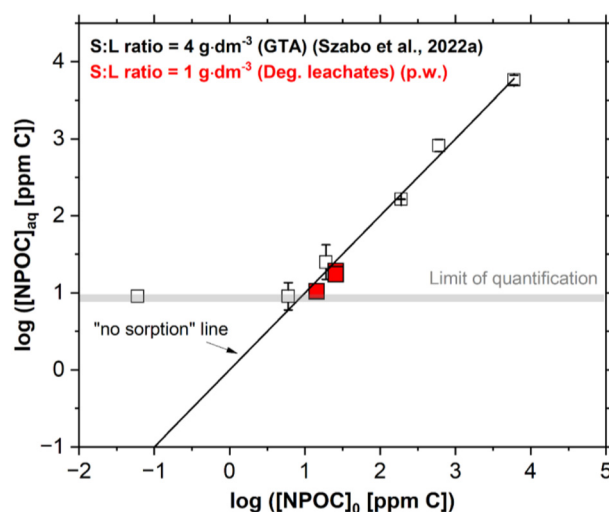

Fig. 1 Uptake of the UP2W degradation leachate by HCP in the degradation stage II. Data represented as log[DL]$_{aq}$ vs. log[DL]$_0$, with concentrations reported in ppm of C. Experiments performed at S : L = 1 g dm^{-3}. Shadowed grey areas correspond to the limit of quantification, which is imposed by the organic content leached from cement. Empty symbols show the sorption data reported by Szabo et al. for the uptake of glutaric acid (GTA) under analogous boundary conditions but at S : L = 4 g dm^{-3}.[14] (p.w.) stands for present work.

ISA-system in absolute terms. Distribution ratios determined in this work for the uptake of UP2W by HCP remain mostly constant within the investigated S : L ratios (1 and 20 g dm^{-3}), resulting in R_d = (0.35 ± 0.15) m^3 kg^{-1}. This value is *ca.* 30 times greater than the distribution ratio previously reported by us for glutaric acid, R_d = $(1.0 \pm 0.5) \times 10^{-2}$ m^3 kg^{-1},[14] and it is of the same order (though slightly higher) than the values reported for the uptake of ISA by HCP in the degradation stage II, *i.e.* $R_d \approx 0.1$ m^3 kg^{-1}.[16,20]

In our previous study, we discussed the impact of the number and type of functional groups (–COOH, –OH) present in low molecular weight organics on the sorption of these ligands onto cement.[14] The following classification was pro-
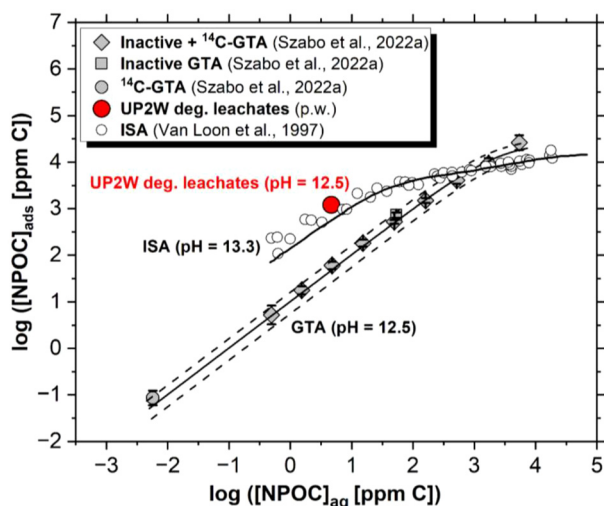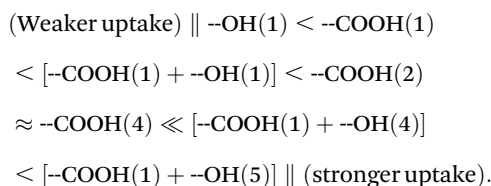
Fig. 2 Uptake of the UP2W degradation leachate by HCP in the degradation stage II. Data represented as log[DL]$_{solid}$ vs. log[DL]$_{aq}$, with concentrations reported in ppm of C. Experiments performed at S : L = 20 g dm^{-3}. Empty and grey symbols show the sorption data reported for GTA (Szabo et al.[14]) and ISA (Van Loon et al.[19]). See text for details.

vided, from weaker to stronger sorption (*i.e.*, from higher to lower R_d values):

$$(\text{Weaker uptake}) \parallel --\text{OH}(1) < --\text{COOH}(1)$$

$$< [--\text{COOH}(1) + --\text{OH}(1)] < --\text{COOH}(2)$$

$$\approx --\text{COOH}(4) \ll [--\text{COOH}(1) + --\text{OH}(4)]$$

$$< [--\text{COOH}(1) + --\text{OH}(5)] \parallel (\text{stronger uptake}).$$

Considering this sequence, R_d values determined in this work for UP2W degradation leachate strongly suggest that the number (and density) of functional groups per molecule in the main degradation products of UP2W is larger than in GTA (1 × (–COOH) + 1 × (–OH)). This hypothesis is in line with our recent results on the characterization of the UP2W degradation leachate after a degradation time of $t = 1122$ days.[21] Size fractionation data with LC–OCD–OND (size exclusion chromatography coupled to organic carbon detection and organic nitrogen detection)[22] indicates that the main degradation products of UP2W after this time have a size/molecular weight distribution with a maximum at 10–15 kDa, which represents fragments with approximately 200 equivalent monomer units (calculated as polyacrylic acid units). The presence of amide-groups in the degradation leachate is also reported by Tasi and co-workers,[21] and these groups may also contribute to the enhanced sorption onto cement. Note that on the basis of the structure of the initial PAN material, [CH$_2$CH(CN)]$_n$, a high density of functional groups (either as carboxylates or amides) can be potentially achieved through the hydrolysis of the nitrile groups.

3.2. Uptake of radionuclides by HCP in the presence of the UP2W degradation leachate

3.2.1. Uptake of ^{63}Ni(II). Fig. 3 shows the impact of the UP2W degradation leachate on the retention of ^{63}Ni(II) by HCP in the degradation stage II. For comparative purposes, the figure includes also sorption data determined in the presence of proxy ligands HIBA, HBA and GTA,[12] as well as data in the presence of ISA.[23]

The presence of the degradation leachate at $[DL]_0 = 20$–36 ppm C following the order of addition "(HCP + Ni) + DL" induces a slight but clear decrease of the R_d values with respect to DL-free systems, and also compared to the systems in the presence of the proxy ligands. Indeed, R_d values determined for systems containing UP2W DL are in line with those reported for analogous concentrations of ISA (expressed in ppm C).[23] Significantly lower R_d values are obtained in the presence of the degradation leachate following the order of addition "(Ni + DL) + HCP". However, R_d values determined for this system steadily increase with time, finally agreeing at $t = 21$ days with R_d values determined for the order "(HCP + Ni) + DL" (see Fig. SI-1 in the ESI†). This observation supports that equilibrium conditions have been attained in both systems. Similar observations were reported for the systems HCP–Pu(IV)–ISA[16] and HCP–Nb(V)–ISA,[24] although with a more remarkable kinetic hindrance for the order of addition "(Pu + ISA) + HCP".

Pronounced dissociation kinetics is well known for the metal ion interaction with macromolecular polyelectrolytes *e.g.* naturally occurring humic/fulvic acids.[25] Beside the
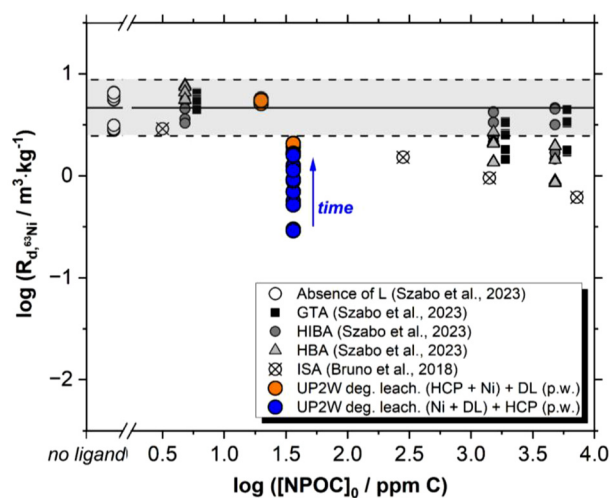

Fig. 3 Uptake of ^{63}Ni(II) by HCP in the presence of different concentrations of UP2W degradation leachate at S : L = 1 g dm^{-3}. Red and green symbols correspond to experiments conducted following the order of addition "(HCP + Ni) + DL" and "(Ni + DL) + HCP", respectively. Grey and black symbols correspond to the uptake of ^{63}Ni(II) by HCP in the presence of HIBA, HBA, GTA (Szabo et al.[12]) and ISA (Bruno et al.[23]). 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 Fig. 1 for S : L = 1–2 g dm^{-3}. All data correspond to degradation stage II of cement, with pH = (12.4 ± 0.1). Time evolution of samples containing the degradation leachate is shown in the ESI.†

coordination with multiple functional groups, macromolecules may in addition undergo intramolecular rearrangement or cation induced agglomeration leading to the kinetic stabilization of bound metal ions.[26]

Results obtained in this work under equilibrium conditions highlight that the uptake of ^{63}Ni(II) by HCP remains strong in the presence of the UP2W degradation leachate, with $\log R_d > 0$ (R_d in m^3 kg^{-1}). Note that, as discussed in previous publications, the uptake of radioactive nickel is primarily driven by isotopic exchange with natural nickel present in cement, either in the form of layered double hydroxide (LDH) phases or taken up by C–S–H.[7,12,27]

3.3. Uptake of ^{152}Eu(III)

Fig. 4a shows the uptake of ^{152}Eu(III) by HCP in the absence and presence of the UP2W degradation leachate, as determined in this work or reported in Duro et al.[3] For comparison purposes, Fig. 4b shows the impact of proxy ligands for the degradation products of UP2W as well as ISA and GLU on the uptake of ^{152}Eu(III) by HCP.[6,12,28]

The UP2W degradation leachate investigated in this work led to a slight decrease in the retention of Eu(III) by HCP in the degradation stage II when following the order of addition "(HCP + Eu) + DL", compared to DL-free systems, although distribution ratios remain high ($\log R_d \geq 2$, with R_d in m^3 kg^{-1}). As in the case of Ni(II), sorption is kinetically hindered when individual components are added following the order "(Eu + DL) + HCP". However, the significantly lower initial $\log R_d \approx 0.5$ increases to virtually the same values as for the sequence "(HCP + Eu) + DL" after ca. 100 days (see Fig. SI-2 in the ESI†). This observation supports that $\log R_d \approx 2$ represents equilibrium conditions for the investigated system.

Comparison with data reported by Duro and co-workers is not straightforward. Experiments conducted by the latter

authors at room temperature resulted in significantly lower NPOC values ($[DL]_0$ = 2–5 ppm C) than those considered in the present work ($[DL]_0$ = 20–36 ppm C), which had no evident impact on the retention of Eu(III) by HCP (black triangles in Fig. 4a). The degradation leachates in Duro et al. (2012) with NPOC values similar to those investigated in the present work were obtained at elevated temperature (empty triangles and grey pentagons in Fig. 4a), and thus may not be comparable to the degradation products generated in this study at room temperature. Moreover, note that sorption experiments in Duro et al. were conducted for a contact time of 1 day following the order of addition "(HCP + DL) + Eu". As per observations in this work, significantly larger contact times might be required to reach equilibrium conditions for this order of addition as well.

3.4. Uptake of ^{242}Pu(IV)

The measurements of pH and E_h in the Pu systems containing HQ resulted in (pe + pH) = (10.0 ± 0.5). These values are consistent with previous studies available in the literature using the same reducing chemicals.[15,29] Considering the redox distribution of plutonium in alkaline reducing conditions, Pu(IV) is expected to prevail in the aqueous phase of HQ-buffered systems.[15,18,30]

Fig. 5 shows that the UP2W degradation leachate induce a clear decrease in the distribution ratios of Pu(IV), compared to the DL-free systems. For the order of addition "(HCP + Pu) + DL", equilibrium conditions are attained after ~76 days, with $\log R_d \approx 1.5$. Clearly lower R_d values are determined at short equilibration times for the order of addition "(Pu + DL) + HCP", which however increase with time to finally match the values $\log R_d$ values determined following the order of addition "(HCP + Pu) + DL" after a contact time of ~225 days (see Fig. SI-3 in the ESI†). As for Ni(II) and Eu(III), the degra-
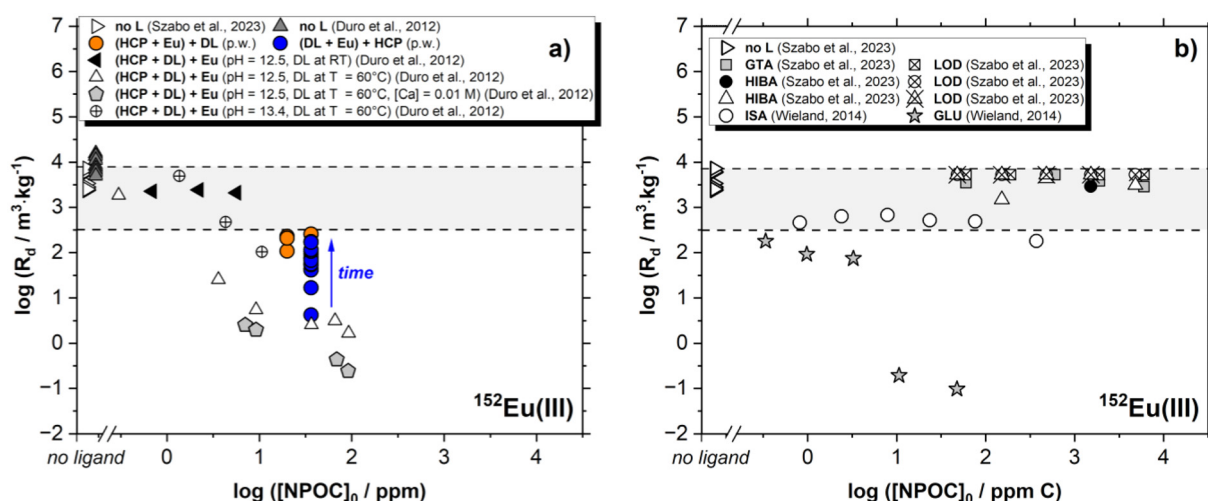

Fig. 4 (a) Uptake of ^{152}Eu(III) by HCP in the absence and presence of different concentrations of UP2W degradation leachate as determined in this work or reported in Duro et al.[3] (b) Uptake of ^{152}Eu(III) by HCP in the absence and presence of UP2W proxy ligands (pH = 12.5, Szabo et al.[12]), ISA and GLU (pH = 13.3).[6,28] 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.[6] Experiments in the presence of organic ligands were conducted at S : L = 1 g dm^{-3}. LOD stands for limit of detection. Time evolution of samples containing the degradation leachate is shown in the ESI.†
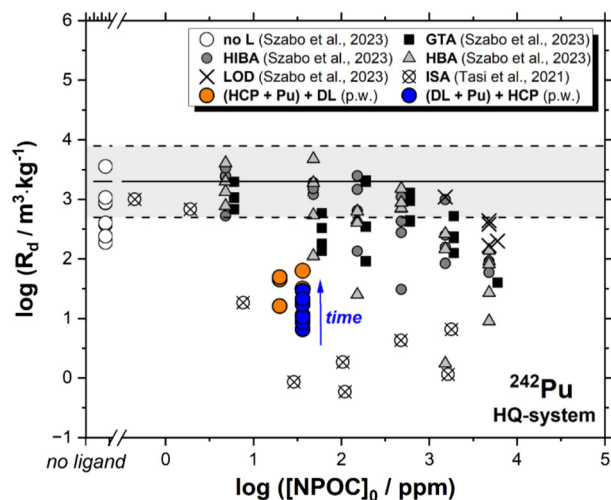
Fig. 5 Uptake of ^{242}Pu(IV) by HCP in the presence of the UP2W degradation leachate at S : L = 1 g dm^{-3}. Red and green symbols correspond to experiments conducted following the order of addition "(HCP + Pu) + DL" and "(Pu + DL) + HCP", respectively. Grey and black symbols correspond to the uptake of ^{242}Pu(IV) by HCP in the presence of HIBA, HBA, GTA (Szabo *et al.*[12]). All data correspond to degradation stage II of cement, with pH = (12.4 ± 0.1). Time evolution of samples containing the degradation leachate is shown in the ESI.† Solid line and grey-shaded area indicate the average R_d values and corresponding uncertainty reported in Tasi *et al.*[16] for the uptake of Pu(IV) by HCP under analogous experimental conditions in the absence of organic ligands. Crossed circles shown sorption data from the same experimental study but in the presence of ISA.

dation leachate induces a greater decrease in $\log R_d$ for the uptake of Pu(IV) than the corresponding proxy ligands counterparts. These results confirm again the kinetic hindrance on sorption induced by the degradation leachate when introduced following the sequence "(Pu + DL) + HCP". Although the impact of the degradation leachate on the retention of Pu by cement is evident, distribution ratios remain high. These results emphasize also the need of performing sorption experiments with real degradation leachates, beyond the use of proxy ligands. Experimental observations in this work possibly reflect that the multiple functionalities expected in the macromolecules (10–15 kDa) present in the degradation leachate, can offer additional binding capabilities compared to the small molecular weight organic ligands considered as proxy ligands in Szabo *et al.*[12] with at most bidentate chelation. The comparison with sorption data for Pu(IV) reported in Tasi *et al.*[16] under analogous experimental conditions but in the presence of ISA (crossed circles in Fig. 5) supports that the UP2W degradation leachate investigated in this work has a weaker impact on the retention of plutonium than ISA.

4. Summary and conclusions

UP2W is a PAN-based material used as filter-aid in nuclear power plants and is disposed of in repositories for L/ILW. A comprehensive sorption study was conducted with the aim of quanti-

tatively assessing the impact of the degradation leachate of UP2W on the uptake of ^{63}Ni(II), ^{152}Eu(III) and ^{242}Pu(IV) by hardened cement paste (HCP, CEM I) in the degradation stage II (pH ≈ 12.5, [Ca] ≈ 0.02 M). The degradation leachate was generated under hyperalkaline conditions with 50 g L^{-1} UP2W and 50 g L^{-1} Ca(OH)$_2$. The leachate used in the sorption experiments was taken from the mother suspension at $t \approx 1122$ days, with a NPOC concentration of ~40 ppm. Results are compared with previous sorption studies conducted under analogous conditions with α-hydroxyisobutyric acid, 3-hydroxybutyric acid and glutaric acid. These low molecular weight organic ligands were identified within Work Package 3 CORI of the EURAD EU project as plausible proxies for the degradation products of UP2W.

Sorption experiments conducted for the binary system cement-degradation leachate with S : L = 1 and 20 g L^{-1} showed a moderate uptake, with R_d = (0.35 ± 0.15) m^3 kg^{-1}. These values are significantly higher than distribution ratios previously reported for UP2W proxy ligands. On the contrary, R_d values obtained for the degradation leachate are in line with those previously reported for cement-ISA systems. A moderate decrease in the uptake of ^{63}Ni(II), ^{152}Eu(III) and ^{242}Pu(IV) by cement is observed in the presence of the degradation leachate, as compared to DL-free systems or to sorption experiments in the presence of proxy ligands. In spite of this, significant retention in the presence of the degradation leachate remains for all investigated radionuclides, with $\log R_d(^{63}$Ni(II)$) \approx 0.3$, $\log R_d(^{152}$Eu(III)$) \approx 2$ and $\log R_d(^{242}$Pu(IV)$) \approx 1.5$ (all R_d in m^3 kg^{-1}). These observations possibly reflect that the multiple functionalities (–COOH, –OH, amide groups) expected in the macromolecules (10–15 kDa) present in the degradation leachate, can offer additional binding/chelating capabilities compared to the small molecular weight organic ligands considered as proxy ligands with at most bidentate bonding. Two different sequences were attempted for the addition of individual components, *i.e.*, HCP, radionuclide and degradation leachate. A relatively fast equilibrium is attained when following the order of addition "(HCP + RN) + DL". Clearly lower R_d values are determined at short equilibration times for the order of addition "(RN + DL) + HCP", which however increase with time to finally match the $\log R_d$ values determined following the order of addition "(HCP + RN) + DL" after contact times of ~100–200 days. This suggests the transient stabilization of RN–DL moieties, which are outcompeted by sorption in the long-term.

These results emphasize the importance of performing sorption experiments with degradation leachates, rather than using only proxy ligands of complex systems such as UP2W or other organic materials disposed in repositories for nuclear waste. This study provides key inputs for quantitatively assessing the impact of UP2W degradation products on the uptake of radionuclides by cement under conditions relevant for the disposal of L/ILW.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 M. Keith-Roach, M. Lindgren and K. Källström, Assessment of complexing agent concentrations for the post-closure safety assessment in PSAR SFR, SKB, R-20-04, 2021.

2 M. Dario, M. Molera and B. Allard, Effect of organic ligands on the sorption of europium on TiO_2 and cement at high pH, SKB, TR-04-04, 2004.

3 L. Duro, M. Grive, X. Gaona, J. Bruno, T. Andersson, H. Boren, M. Dario, B. Allard, J. Hagberg and K. Källström, Study of the effect of the fibre mass UP2 degradation products on radionuclide mobilisation, SKB, R-12-15, 2012.

4 M. J. Keith-Roach, M. Lindgren and K. Källström, Assessment of complexing agent concentrations in SFR, SKB, R-14-03, 2014.

5 H. F. W. Taylor, Cement chemistry, T. Telford, London, 2nd edn, 1997.

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

7 M. Ochs, D. Mallants and L. Wang, Radionuclide and Metal Sorption on Cement and Concrete, in Topics in Safety, Risk, Reliability and Quality, Springer International Publishing: Imprint: Springer, Cham, 1st edn, 2016, p. 1 online resource (XXX, 301 pages).

8 S. Holgersson, I. Dubois and L. Börstell, Batch experiments of Cs, Co and Eu sorption onto cement with dissolved fibre mass UP2 in the liquid phase, SKB, P-11-24, 2011.

9 H. Tasdigh, Assessment of the impact of fiber mass UP2 degradation products on nickel(II) and europium(III) sorption onto cement, KTH, Master Thesis, 2015.

10 CORI-SOTA State of the art report on cement-organic-radionuclide interactions, Final version as of 19.05.2021 of deliverable D3.1 of the HORIZON 2020 project EURAD, EC grant agreement no.: 847593, 2021.

11 A. Tasi, P. Szabo, X. Gaona, M. Altmaier and H. Geckeis, Contribution by KIT-INE to CORI Task 2 (pers. co.), in Eurad European Joint Programme on Radioactive waste management, Milestone DMS97 – CORI Technical Report – Task 2 Hydrolytic/radiolytic degradation of organics: description of first results on hydrolytic and radiolytic organic degradation and identification of released species, ed. D. Ricard and J. Vandenborre, 2021.

12 P. Szabo, A. G. Tasi, X. Gaona, A. C. Maier, S. Hedström, M. Altmaier and H. Geckeis, Front. Nucl. Eng., 2023, 2, 1117413.

13 P. Szabo, A. Tasi, A. Gaona, R. Polly, A. Maier, S. Hedström, M. Altmaier and H. Geckeis, Dalton Trans., 2022, 51, 9432–9444.

14 P. Szabo, A. Tasi, A. Gaona, A. Maier, S. Hedström, M. Altmaier and H. Geckeis, Front. Nucl. Eng., 2022, 1, DOI: 10.3389/fnuen.2022.997398.

15 A. Tasi, X. Gaona, D. Fellhauer, M. Bottle, J. Rothe, K. Dardenne, D. Schild, M. Grive, E. Colas, J. Bruno, K. Kallstrom, M. Altmaier and H. Geckeis, Radiochim. Acta, 2018, 106, 259–279.

16 A. Tasi, X. Gaona, T. Rabung, D. Fellhauer, J. Rothe, K. Dardenne, J. Lutzenkirchen, M. Grive, E. Colas, J. Bruno, K. Kallstrom, M. Altmaier and H. Geckeis, Appl. Geochem., 2021, 126, 104862.

17 M. Altmaier, X. Gaona, D. Fellhauer and G. Buckau, Intercomparison of redox determination methods on designed and near-neutral aqueous systems, KIT-SR 7572, Karlsruhe Institute of Technology, Karlsruhe, 2010, p. 34.

18 D. Fellhauer, Untersuchungen zur Löslichkeit und Redoxchemie von Plutonium und Neptunium, Universität Heidelberg, 2013.

19 L. R. Van Loon, M. A. Glaus, S. Stallone and A. Laube, Environ. Sci. Technol., 1997, 31, 1243–1245.

20 I. Pointeau, N. Coreau and P. Reiller, Radiochim. Acta, 2008, 96, 367–374.

21 A. Tasi, P. Szabo, X. Gaona, M. Bouby, Y. Kouhail, A. Maier, S. Hedström, M. Altmaier and H. Geckeis, in Processes Influencing Radionuclide Transport and Retention – Investigations Across Scales, 2022, DOI: 10.5445/IR/1000142975.

22 S. A. Huber, A. Balz, M. Abert and W. Pronk, Water Res., 2011, 45, 879–885.

23 J. Bruno, M. R. González-Siso, L. Duro, X. Gaona and M. Altmaier, Key master variables affecting the mobility of Ni, Pu, Tc and U in the near field of the SFR repository. Main experimental findings and PA implications of the PhD thesis, SKB, TR-18-01, 2018.

24 N. Cevirim-Papaioannou, Y. Jo, K. Franke, M. Fuss, B. de Blochouse, M. Altmaier and X. Gaona, Cem. Concr. Res., 2022, 153, 106690.

25 W. Schussler, R. Artinger, J. I. Kim, N. D. Bryan and D. Griffin, J. Contam. Hydrol., 2001, 47, 311–322.

26 H. Geckeis, T. Rabung, T. N. Manh, J. I. Kim and H. P. Beck, Environ. Sci. Technol., 2002, 36, 2946–2952.

27 E. Wieland, J. Tits, A. Ulrich and M. H. Bradbury, Radiochim. Acta, 2006, 94, 29–36.

28 E. Wieland, J. Tits, P. Spieler and J. P. Dobler, Mater. Res. Soc. Symp. Proc., 1998, 506, 573–578.

29 A. Tasi, X. Gaona, D. Fellhauer, M. Bottle, J. Rothe, K. Dardenne, R. Polly, M. Grive, E. Colas, J. Bruno, K. Kallstrom, M. Altmaier and H. Geckeis, Appl. Geochem., 2018, 98, 247–264.

30 I. Grenthe, X. Gaona, A. V. Plyasunov, L. Rao, W. H. Runde, B. Grambow, R. J. M. Konings, A. L. Smith and E. E. Moore, Second Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium, Volume 14, Nuclear Energy Agency of the OECD (NEA), 2020, vol. 14.