Impact of Ca(II) on the aqueous speciation, redox behavior, and environmental mobility of Pu(IV) in the presence of EDTA

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HIGHLIGHTS
• Previous models overestimate Pu solubility with EDTA under alkaline conditions.
• Reevaluation of log β°(1,x,1) based on new experimental data and published results.
• Newly defined model accurately describes trends across a wide range of parameters.
• Evidence for the formation of a quaternary Ca Pu(IV) OH EDTA complex was found.
• Pu interactions with organic ligands and other di/trivalent cations can be relevant.

GRAPHICAL ABSTRACT

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ABSTRACT

The impact of calcium on the solubility and redox behavior of the Pu(IV) EDTA system was investigated using a combination of undersaturation solubility studies and advanced spectroscopic techniques. Batch solubility experiments were conducted in 0.1 M NaCl NaOH HCl EDTA CaCl₂ solutions at constant [EDTA] = 1 × 10⁻³ M, 1 ≤ pH ≤ 11, and 1 × 10⁻³ M ≤ [CaCl₂] ≤ 2 × 10⁻² M. Additional samples targeted brine systems represented by 3.5 M CaCl₂ and WIPP simulated brine. Redox conditions were buffered with hydroquinone (pe + pH ≈ 9.5) with selected samples prepared in the absence of any redox buffer. All experiments were performed at T = 22 °C under Ar atmosphere. In situ X ray absorption spectroscopy indicated that PuO₂(ncr,hyd) was the solubility controlling phase during the lifetime of all experiments and that aqueous plutonium was present in the +IV oxidation state across all experimental conditions except at pH ≈ 1, where a small fraction of Pu(III) was also identified. Current thermodynamic models overestimate Pu(IV) EDTA solubility in the absence of calcium by approximately 1 1.5 log₁₀ units and do not describe the nearly pH independent, increased solubility observed with increased calcium concentrations. The ternary Pu(IV) OH EDTA system without calcium was reevaluated using solubility data obtained in this work and reported in the literature. An updated thermodynamic model including the complexes Pu(OH)(EDTA)⁻, Pu(OH)₂(EDTA)²⁻, and Pu(OH)₃(EDTA)³⁻ was derived. Solubility data collected in the presence of calcium follows a pH independent trend (log m(Pu) vs. pH), which can only be explained by assuming the formation of a quaternary complex, tentatively defined as CaPu(OH)_4(EDTA)_2⁻, in solution. The significant enhancement of plutonium solubility observed in the investigated brine systems supports the formation of a quaternary complex that is not outcompeted by Ca(EDTA)²⁻, even in concentrated CaCl₂ solutions. Although the

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1. Introduction

The consensus among the international community is that the most favored means of disposal for high level and long lived radioactive wastes is in a deep geologic repository (Geckis et al., 2019; IAEA, 2003). To support international waste disposal efforts, interactions and processes that could potentially lead to the release of radionuclides into the geosphere in case of water intrusion or damage to the integrity of such a facility must be well understood. Of these radionuclides, plutonium is important due to its prevalence in both commercial waste and defense related transuranic waste, high alpha radiotoxicity, and long half life ($t_{1/2}^{239}Pu = 2.41 \times 10^4$ a), which allows it to persist and contribute to the overall activity of the waste for over one hundred thousand years.

The design of deep geologic repositories involves a combination of both natural and engineered barriers that define the geochemical boundary conditions within the repository. After repository closure, strongly reducing conditions are expected to develop due to the anoxic corrosion of iron and steel present in the repository. The use of cementitious materials is considered in repository concepts for the stabilization of the waste and for construction purposes. Upon interaction with groundwater, the progressive degradation of cement or the presence of other engineered barrier materials, such as MgO, will buffer the pH in the hyperalkaline range, respectively, strongly affecting the chemical behavior of the radionuclides.

Ethylenediaminetetraacetic acid (EDTA) has been used extensively in the nuclear industry through the processing of plutonium containing wastes, in the defense production of plutonium, and as a decontamination agent (Ayers, 1970; McFadden, 1980; Rai et al., 2008). It has been co-disposed with plutonium in many waste streams, some of which were inadvertently released into the environment (Freeman Pollard et al., 1994; Rai et al., 2008). EDTA is a strong chelating ligand that forms a wide range of stable aqueous complexes with plutonium in the +III, +IV, and +V oxidation states (AlMahamid et al., 1996; Boukhalfa et al., 2004; DiBlasi et al., 2021; Hummel et al., 2005; Reed et al., 1998) and several other metal cations. Depending upon the boundary conditions, plutonium EDTA complexation may enhance the solubility of plutonium and decrease its retention, thus having a notable impact on the environmental mobility of this radionuclide (Boukhalfa et al., 2004; Meyer et al., 2007; Rai et al., 2008).

Plutonium has four relevant oxidation states in aqueous systems: +III, +IV, +V, and +VI. Each oxidation state has its own characteristic environmental chemistry and mobility. Because the reduction potentials of plutonium are similar between vicinal states under pertinent boundary conditions, preferential complexation can have a significant influence on the final oxidation state distribution of plutonium in the presence of a ligand. Reed et al. (1998) observed the reduction of Pu(VI) to Pu(V) and Pu(IV) in the presence of three organic complexants that are expected to be present in geologic repositories: EDTA ($C_{10}H_{14}N_{2}O_{8}$), citrate ($C_{6}H_{5}O_{7}$), and oxalate ($C_{2}H_{2}O_{4}$). While the reduction kinetics vary for each organic molecule, the authors reported the stabilization of plutonium in its +IV oxidation state in the presence of each of the three ligands. Additionally, a recent paper by DiBlasi et al. (2021) presented evidence on increasing Pu(IV) fraction over time originating from both Pu(V/VI) or Pu(III) aqueous species under alkaline conditions in the presence of EDTA and absence of any redox buffer. Thus, organic complexation may contribute to plutonium oxidation state distribution, which is constantly evolving in complex matrices with other redox active elements, such as iron, present.
means of ion exchange, solvent extraction, solubility, spectrophotometry, electromigration, polarography, cyclic voltammetry, and potentiometric titration since the late 1950s (AlMahamid et al., 1996; Boukhalfa et al., 2004; Cauchetier and Guichard, 1975, 1973; Foreman and Smith, 1957a, 1957b; Gel’mann et al., 1959; Merciny et al., 1978; Meyer et al., 2007; Mikhailov, 1969; Moskvin and Art'yukhin, 1959; Poczynajko, 1989, 1991; Rai et al., 2001, 2008, 2010; Reed et al., 1998; Stepanov and Makarova, 1965; Thakur et al., 2009). The most comprehensive critical review of thermodynamic studies dedicated to the interaction of radionuclides with selected organic ligands of relevance for nuclear waste disposal (oxalate, citrate, EDTA, and isosaccharinic acid) was published in 2005 within the Thermochemical Database project of the Nuclear Energy Agency (NEA TDB) (Hummel et al., 2005). Thermodynamic data selected for the Pu EDTA system within the NEA TDB is the basis of the thermodynamic calculations performed in this work. Only Pu(III) EDTA complexes are currently selected in the NEA TDB, with log β’(Pu(EDTA)−) = (20.180 ± 0.370) and log β’(Pu(HEDTA)aq) = (22.020 ± 0.260). Thermodynamic studies available on the Pu(IV) EDTA system were not considered reliable by the NEA reviewers, who recommended the use of data selected for U(IV) and Np(IV) for scoping calculations with Pu(IV).

Three major Pu(IV) EDTA thermodynamic studies were published after the most recent NEA TDB review, and thus were not included in the thermodynamic data selection process (Boukhalfa et al., 2004; Meyer et al., 2007; Rai et al., 2008). Boukhalfa et al. (2004) utilized a combination of techniques, including spectrophotometry under acidic conditions with l = 1.0 M, potentiometric titration from pH 0 to 10 with l = 0.1 M, and cyclic voltammetry at pH ≤ 8.2 with l = 0.1 M, to develop their speciation model. All experiments were performed using sodium salts as the ionic media (i.e., NaCl/HClO4, NaNO3, or NaCl). The model consists of six Pu(IV) EDTA species: Pu(EDTA)aq, Pu(OH)(EDTA)−, Pu(OH)2(EDTA)2−, Pu(EDTA)3−, Pu(EDTA)4−, and Pu(EDTA)5−. Plutonium (−93% 239Pu) concentrations ranged from 2.49·10−10 M for potentiometric titrations to 1.9·10−3 M for spectrophotometry, and as high as 5·10−3 M for cyclic voltammetry. Due to these relatively high concentrations, precipitation was observed for titrations above pH 7.5, limiting the data analysis to lower pH. Additionally, calculations by Boukhalfa et al. (2004) involved the use of formation constants at various ionic strengths without the implementation of ionic strength correction. This oversight was later corrected by Rai et al. (2008) in their detailed analysis of these data.

Meyer et al. (2007) also utilized potentiometric titrations from pH 1.6 to 10 at l = 1.0 M and spectrophotometric titrations at pH 1.6 with constant l = 1.0 M using KNO3 as the ionic medium to develop their Pu(IV) EDTA speciation model. This model consists of five Pu(IV) EDTA species: Pu(EDTA)aq, Pu(OH)(EDTA)−, Pu(EDTA)2−, Pu(EDTA)3−, and Pu(EDTA)4−. Unlike Boukhalfa et al. (2004), Meyer et al. (2007) implemented SIT ionic strength corrections to extrapolate equilibrium constants to zero ionic strength, and additional complexation interactions with ionic media were considered and corrected for during data analysis. Plutonium (−98% 239Pu) concentrations were kept sub millimolar with very low titration rates to minimize localized over saturations that would lead to colloid or solid formation. Even so, precipitates were observed at pH ≥ 7. Equilibrium constants were determined using only potentiometric titration data with one or two equivalents of EDTA. Similar to Boukhalfa et al. (2004), spectrophotometry was only performed under acidic conditions and thus provided very little supporting evidence regarding Pu(IV) EDTA speciation, particularly at higher pH where the solubility models differ and precipitation may have affected the potentiometric titration data. The authors address the precipitation within their work and limit their data to pH ≤ 6.5, but still extrapolate to produce a speciation model out to pH 10 that does not agree with either of the two other Pu(IV) EDTA speciation models discussed above.

The third and final study not included in the most recent NEA TDB review is Rai et al. (2008). This paper is based on the experimental results reported in a previous publication by the same authors, Rai et al. (2001), which was also not discussed within the NEA TDB review. Rai and co-workers conducted solubility experiments from undersaturation conditions using PuO2(am, hyd), which overcomes the problems under alkaline conditions reported by both Boukhalfa et al. (2004) and Meyer et al. (2007) that resulted in the formation of colloidal or nanocrystalline solid phases. Solubility data was collected from pH 2 to 11 and the aqueous plutonium oxidation state was verified using solvent extraction procedures. The authors used their solubility data points after 7 to 10 days of equilibration to derive thermodynamic and Pitzer activity models, which consist of three predominant Pu(IV) EDTA species: Pu(OH)(EDTA)−, Pu(OH)2(EDTA)2−, and Pu(OH)3(EDTA)3−. Rai et al. (2008) evaluated the possible formation of the unhydrolyzed Pu(EDTA)aq complex in their study but found that this species was not needed to effectively model their solubility data. The main differences between the 2001 and 2008 publications were the acidity constants of EDTA and the solubility product of PuO2(am, hyd) used; in the 2008 publication the selected values were consistent with the NEA TDB (Guillaumont et al., 2003; Hummel et al., 2005). It is of note, however, that the solid phase was not characterized in the original publication by Rai et al. (2001). In addition to evaluating their own data, Rai et al. (2008) also reevaluated the data of Boukhalfa et al. (2004) to determine the importance of 1:2 Pu(IV) EDTA complexes. Upon revisiting the data of Boukhalfa et al. (2004) with appropriate ionic strength corrections and consistent equilibrium constants, Rai et al. (2008) determined that the model proposed by Boukhalfa et al. (2004) no longer fit their data. More specifically, the 1:2 Pu(IV) EDTA complexes proposed by Boukhalfa et al. (2004) were not necessary to describe their data at pH ≤ 9.

All of the models include mixed Pu(IV) OH EDTA species and, hence, depict a pH dependent trend in the solubility curve where total plutonium concentrations are expected to smoothly decrease with increasing alkalinity of the system. Even with the short equilibrium times utilized in their study (7 to 10 days), Rai et al. (2008) is considered the most reliable study due to the extensive variation of the applied experimental parameters and the use of an experimental approach which overcomes artifacts in alkaline conditions. For these reasons, the work of Rai et al. (2008) is taken as the basis for the discussion of the Pu(IV) EDTA system.

The NEA TDB selects two Ca EDTA species Ca(EDTA)2− and Ca(HEDTA)− and both complexes have been considered in this work for the thermodynamic calculations in the presence of calcium (Hummel et al., 2005). The possible formation of the complex Ca2(EDTA)aq was reported in Schwarzenbach and Ackermann (1947), Anderegg et al. (1975), and Arena et al. (1983), but these references were not considered reliable by the NEA TDB. Due to the great stability of the Ca(EDTA)2− complex, the presence of calcium has been generally assumed to outcompete the complexation of EDTA with other metal ions present in significantly lower concentrations (see for instance the discussion in Rai et al. (2008)). Additionally, calcium has been shown to form ternary Ca Pu(IV) OH complexes, as reported by Almaier et al. (2008). The ternary complex Ca2[ Pu(OH)]4+ is expected form and impact plutonium solubility in concentrated calcium solutions ([Ca(II)] ≥ 2.0 M) at pH ≥ 11; to assess its role in the quaternary Ca Pu(IV) EDTA H2O system, we have included this complex in the calculations performed within this work.

The thermodynamic calculations in this work are based on the reactions and associated constants reported in the literature (Table A1) or as updated within this work (Table 2). Literature complexation constants with EDTA were selected from Rai et al. (2008) and the NEA TDB (Hummel et al., 2005). The Specific Ion interaction Theory (SIT) was used for ionic strength corrections (Ciavatta, 1980; Pitzer, 1991), and the ion interaction parameters (Table A2) were either taken from the literature (Grenthe et al., 2020; Guillaumont et al., 2003; Hummel et al., 2003; Neck et al., 2009; Neck and Kim, 2001) or estimated based on the charge correlation approach described by Hummel (2002).
3. Experimental

3.1. Materials

Experiments with plutonium were performed in specialized labora-
tories in the controlled area of KIT INE. All experiments were conducted
in argon gloveboxes with \( O_2 < 2 \) ppm and under carbonate exclusion.
All experimental solutions were prepared with ultra pure water puri-
fi ed with a Milli Q apparatus (Millipore, 18.2 MΩ, 22 ± 2 °C). Before
use, Milli Q water was boiled for several hours while being purged
with argon gas. EDTA stock solutions were prepared from \( H_2EDTA \) (pu-
rified grade ≥ 99.5%) and corresponding sodium salts (Sigma Aldrich)
to target specific pH values: \( Na_2H_2EDTA \) (pH = 9.0, 101.0%), \( Na_2HEDTA:xH_2O \)
(≥95%), and \( Na_2EDTA·2H_2O \) (99.0 101.0%). Calcium containing solu-
tions were prepared with \( CaCl_2·2H_2O \) (Merck, p.a.). Redox buffers
were prepared using hydroquinone (Merck, p.a., hereafter denoted as
HQ) and \( Na_2S_2O_4 \) (Merck, ≥ 87%). TRIS buffer solutions were prepared with
pre determined ratios of Trizma® base and Trizma® hydrochloro
ride, as purchased (Sigma Aldrich, p.a.). Ionic strength in indicated sys-
tems was kept constant at \( I = 0.1 \) M using \( NaCl \) (Merck, p.a.). The 0.1 M
\( NaOH \) and \( HCl \) solutions used for \( \text{pH} \) adjustments were prepared from
standard solutions (Merck, Titrisol®). Plutonium solids were prepared
from a plutonium stock in 2.0 M \( HClO_4 \) with an isotopic composition
of 99.4%\(^{242}\)Pu, 0.58%\(^{239}\)Pu, 0.005%\(^{238}\)Pu, and 0.005%\(^{241}\)Pu.

3.2. Preparation of plutonium solid phases

Details on the synthesis procedure and the characterization results of
the nanocrystalline PuO\(_2\) (ncr, hyd) solid phase used in the current
study are published elsewhere (Tasi et al., 2018c). By the initialization
of the nanocrystalline PuO\(_2\) (ncr, hyd) solid phase used in the current
never exceeded 10 mA. The procedure was monitored by
three electrodes were connected to a potentiostat (Princeton Applied
Electrolyte, ionic strength, temperature, and pressure. Empirical \( A_m \) values for
NaCl and CaCl\(_2\) systems were adapted from elsewhere (Altmair et al.,
2003, 2008).

The redox potential in solution was determined with combined Pt or
Au and Ag/AgCl reference electrodes (Metrohm). The measured poten-
tials were converted to \( E_0 \) through a standard correction for the poten-
tial of the Ag/AgCl inner reference electrode at 3 M KCl and \( T = 22 ^\circ C \)
(+207 mV). \( E_0 \) values were further converted to \( \text{pe} \) (\( \text{pe} = -\log(a_e) \))
by Eq. (1):

\[
E_h = -RTln(10)\times F \times \log a_e
\]

where \( R \) is the ideal gas constant (8.31446 J mol\(^{-1}\) K\(^{-1}\)), \( F \) is the Faraday constant (96,485.33 C mol\(^{-1}\)) and \( a_e \) is the activity of the electron. Each
redox potential measurement was allowed a minimum of 15 min for equili-
 ration until the absolute drift of the value was observed to be
low 3.0 mV min\(^{-1}\). Additional, hour long measurements were taken pe-
riodically after cleaning the electrode with 1.0 M HCl to verify

To avoid overheating, the current never exceeded 10 mA. The procedure was monitored by
means of visible near infrared (Vis NIR) absorption spectroscopy on a
single beam diode array photometer (\( \lambda = 400 \) 1020 nm, Carl Zeiss
AG, MSC 501). The electrochemically prepared Pu(III) stock solution
was precipitated as Pu(OH)\(_3\) (am) by its slow addition to a TRIS
buffer solution (\( \text{pH}_a \approx 9.47 \)) with 5 mM \( Na_2S_2O_4 \) redox buffering agent pres-
ent. The resulting solid phase was used as the reference material in the
X ray absorption near edge structure (XANES) study.

3.3. Solubility experiments

Batch type undersaturation solubility experiments using PuO\(_2\) (ncr,
hyd) were carried out at a constant total EDTA concentration of 1 mM
with varying \( \text{pH}_a \) and total \( CaCl_2 \) concentrations. Table A3 details the experi-
mental conditions for each individual batch experiment. The
ionic strength in most systems was kept constant at 0.10 M accounting
for the contribution of all the components: \( Na_2EDTA \ Na_2HEDTA \ Na_2H_2EDTA \ NaCl \ HCl \ NaOH \ CaCl_2 \). Exceptions were the samples with
the highest calcium concentration ([\( CaCl_2 \] = 3.5 M, \( I = 10.5 M \) ) and
the samples prepared in the WIPP simulated brine (see Table A4 for
brine formulation). The \( \text{pH}_a \) of each sample was adjusted using appro-
priate concentration solutions of \( HCl \) and \( NaOH \) to maintain constant
ionic strength. After the specific amounts of suspended PuO\(_2\) (ncr, hyd)

solid phase (in aliquots of 0.1 M NaCl solutions) were added to the sam-
ple, values of \( \text{pH}_m \), \( E_0 \), and aqueous plutonium concentrations (after
10kD ultrafiltration) were monitored in all systems up to 73 days.

3.4. Solution characterization analytical methods

All \( \text{pH} \) measurements were performed using a combination \( \text{pH} \) elec-
trode (type Orion Ross, Thermo Scientific™) freshly calibrated against
standard \( \text{pH} \) buffers (\( \text{pH} = 3 13 \), Merck). To account for any ionic
strength effects, we report \( \text{pH} \) as \( \text{pH}_m \) (\( \text{pH}_m = -\log(F^+) = \text{pH}_exp + \text{A}_m \) ), or the total free concentration of protons in molal units. In aqueous
solutions of ionic strength \( I \geq 0.1 M \), the measured \( \text{pH} \) value (\( \text{pH}_\text{exp} \) ) is an
operational, apparent value related to (\( H^+ \)) by \( A_m \), an empirical param-
eter that includes the activity coefficient of the proton (\( \gamma H^+ \)) and the
liquid junction potential of the electrode for a given background electrolyte.

Solid phases were retrieved and characterized by XANES and EXAFS
studies. The conversion factors reported elsewhere (Grenthe et al.,
2020).

The redox potential of solution was determined with combined Pt or
Au and Ag/AgCl reference electrodes (Metrohm). The measured poten-
tials were converted to \( E_0 \) through a standard correction for the poten-
tial of the Ag/AgCl inner reference electrode at 3 M KCl and \( T = 22 ^\circ C \)
(+207 mV). \( E_0 \) values were further converted to \( \text{pe} \) (\( \text{pe} = -\log(a_e) \))
by Eq. (1):

\[
E_h = -RT\ln(10)\times F \times \log a_e
\]

where \( R \) is the ideal gas constant (8.31446 J mol\(^{-1}\) K\(^{-1}\)), \( F \) is the Faraday constant (96,485.33 C mol\(^{-1}\)) and \( a_e \) is the activity of the electron. Each
redox potential measurement was allowed a minimum of 15 min for equili-
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low 3.0 mV min\(^{-1}\). Additional, hour long measurements were taken pe-
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To avoid overheating, the current never exceeded 10 mA. The procedure was monitored by
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buffer solution (\( \text{pH}_a \approx 9.47 \)) with 5 mM \( Na_2S_2O_4 \) redox buffering agent pres-
ent. The resulting solid phase was used as the reference material in the
X ray absorption near edge structure (XANES) study.

3.5. X ray absorption spectroscopy

XANES and Extended X ray Absorption Fine Structure (EXAFS) of se-
lected aqueous and solid phases were recorded at the INE Beamline
for Actinide Research at the Karlsruhe Research Accelerator. (KARA), KIT
Campus North (Rothe et al., 2012, 2019). The storage ring operated at
2.5 GeV electron energy with a mean electron current of 120 mA. Solid phases were retrieved and characterized by XANES and EXAFS
analyses to gain insight on the plutonium solid phase controlling the
solubility in the undersaturation experiments. Aqueous phases were re-
trieved and characterized to experimentally determine the oxidation
state distribution of plutonium in solution.

For the purpose of these analyses, selected plutonium samples were
transferred into polyethylene vials under an argon atmosphere. A sus-
pension of approximately 1 mg of the solid material was pipetted into
the vial, tightly sealed with Parafilm® (Bemis Company, Inc.), and cen-
trifuged for a minimum of 10 min at 6000 rpm to compact the solid on
the bottom of the vial. Once the solid was sufficiently compacted, this
4.1. Impact of EDTA and calcium on the Pu(III)/Pu(IV) redox borderline measurements of (pe + pHm) and Pourbaix diagrams shows that the addition of EDTA shifts the aqueous Pu(III)/Pu(IV) boundary to more oxidizing conditions with a broad pH range (4–13), resulting in a larger aqueous Pu(III) predominance region in the presence of EDTA as opposed to in the absence of EDTA. The subsequent addition of calcium to the Pu EDTA system (Fig. A1c) shifts the aqueous Pu(III)/Pu(IV) boundary to more reducing conditions at pHm ≥ 7, slightly decreasing the aqueous Pu(III) predominance region as compared to the region in the absence of calcium. How ever, the aqueous Pu(III) predominance region in the presence of both EDTA and calcium is still larger than that in the absence of EDTA and calcium, indicating that even with calcium competition, EDTA changes the redox borderline between aqueous Pu(III) and Pu(IV) and increases the stability field of Pu(III) in solution.

Additional changes to Pu(III) and Pu(IV) predominance regions are observed for plutonium solid phases (Fig. 1). Upon the addition of calcium into the system, the Pu(III) solid phase predominance region in creases: the Pu(OH)3(am) predominance boundary shifts to significantly lower pH (pH ≥ 8) in the presence of both 1 mM EDTA and 20 mM CaCl2 as compared to the predominance region in the absence of calcium with 1 mM EDTA (pH ≥ 11). Similarly, the Pu(IV) solid phase predominance region also increases upon the inclusion of calcium in the calculations by shifting the lower boundary to more reducing conditions from pH ≈ 3.8. From these calculations, it is clear that both EDTA and calcium presence can significantly impact the redox boundary between both aqueous and solid Pu(III) and Pu(IV) phases.

Experimentally determined pHm and pe values are plotted on the Pourbaix diagrams of plutonium in Fig. 1 together with calculated predominance fields of plutonium solid compounds and aqueous species at different total calcium concentrations ([Ca]tot) and 1 mM total EDTA concentration ([EDTA]tot).

The comparison of experimental pHm and pe measurements with thermodynamic calculations in Pourbaix diagrams predicts different redox speciation for samples under alkaline (pHm > 8, absence and presence of calcium) and acidic (pHm < 6, only in the absence of calc ium) conditions (Fig. 1c). In alkaline systems, the predominance of aqueous Pu(IV) species is predicted, either as Pu(IV)/OH EDTA ternary complexes (samples in the absence of calcium) or as Pu(OH)4(aq) (samples in the presence of calcium). Solubility samples equilibrated under acidic conditions fall within the stability field of Pu(III) with the predominance of the complex Pu(III)(EDTA)−, indicating that more substantial dissolution of PuO2(nrc,hyd) is expected to take place under these conditions. Note, however, that the pe values in the absence of any redox buffer (red squares in Fig. 1) are considered less reliable and may not represent the real redox conditions of the system. Fig. 1 shows also that full dissolution of PuO2(nrc,hyd) should be expected for the solubility samples equilibrated in acidic conditions, at least those containing HQ for which reliable (pe + pHm) values are measured.

4.2. Solid and aqueous phase characterization by X-ray absorption spectroscopy

Fig. 2 shows the XANES Pu LIII edge absorption spectra for selected solid and aqueous phases, together with reference spectra of Pu(OH)3(am) and PuO2(nrc,hyd) solid phases (Tasi et al., 2018c) and Pu(III)aq and Pu(IV)aq aqueous phases (Brendebach et al., 2009). Table A5 summarizes the energies of the white line (WL) peaks and shifts in the XANES spectra of all samples and references. A comparison of the XANES spectra collected for the two solid phase samples with reference spectra shows that plutonium remained in the +IV oxidation state and may not represent the real redox conditions of the system. In both cases, white line and first feature positions are in excellent agreement with the data reported for Pu(IV)O2(nrc,hyd), considering the typical energy calibration error (±0.5 eV).
Pu LIII edge XANES spectra were collected for supernatant solutions of selected batch samples at pH<sub>m</sub> ≤ 6. Measurements at higher pH<sub>m</sub> values were not possible due to the low concentrations of plutonium in the aqueous phase of these experiments. As observed for the solid phases, the comparison of the XANES spectra collected for aqueous phases, white line locations and first feature positions (Table A5) to the reference spectra for Pu(III) and Pu(IV) from Brendebach et al. (2009) shows that the +IV oxidation state prevails at 4 ≤ pH<sub>m</sub> ≤ 6 for at least 41 days. Concurrent Vis NIR analyses (Fig. A2) displayed peaks at 504 nm and 495 nm that are consistent with Pu(IV) EDTA complex formation (AlMahamid et al., 1996; Cauchetier and Guichard, 1973; DiBlasi et al., 2021; Meyer et al., 2007). However, the XANES spectrum collected for the pH<sub>m</sub> = 1 sample exhibited shifts of ~1 eV towards lower energy for both the white line and first feature, indicating partial presence of the +III oxidation state of plutonium. While Pu(IV) still pre-dominates in this sample, it is clear that partial reduction has occurred in the aqueous phase. Vis NIR analyses provide supporting evidence for this result through the minor presence of a Pu(III) peak at 601 nm (Almaier et al., 2019; Clark et al., 2010; DiBlasi et al., 2021). Spectroscopic data collected for samples equilibrated under acidic conditions is not consistent with experimental pe and pH<sub>m</sub> measurements and thermodynamic calculations (see Fig. 1), which predict the predomiance of Pu(III) aqueous complexes at all pH<sub>m</sub> < 6, instead of Pu(IV) predominance in 4 ≤ pH<sub>m</sub> ≤ 6 samples and partial presence of Pu(III) observed for pH<sub>m</sub> = 1 samples. Further evidence on this discrepancy is discussed in the following sections.

Fig. A3 shows the Fourier transformed (FT) representation of k<sup>2</sup> weighted EXAFS data for solid phases recovered from a system at pH<sub>m</sub> = 4 in the absence of calcium and a system at pH<sub>m</sub> = 9 in the presence of hydroquinone and 20 mM CaCl<sub>2</sub>. Each dataset was fit with two coordination shells. The first shell at around 1.75 Å (R<sub>Δ</sub>) corresponds to plutonium bonding to bridging oxygen atoms and oxygen from terminal water and hydroxide units. The second shell at around 3.1 Å (R<sub>Δ</sub>) corresponds to single scattering from plutonium neighbors within the solid precipitate. All fitting ranges and generated parameters are listed in Table 1.

Evaluation of the EXAFS spectra collected for the solids investigated in this work resulted in coordination numbers of N<sub>0</sub> = 5 and N<sub>Pu</sub> = 10 and distances R<sub>0</sub> ≈ 2.31 Å and R<sub>Pu-Pu</sub> ≈ 3.82 Å. Distances R<sub>0</sub> and R<sub>Pu-Pu</sub> determined in this study are in line with data reported for ideal fluorite type PuO<sub>2</sub> (R<sub>0</sub> = 2.32 Å, R<sub>Pu-Pu</sub> = 3.81 Å), whereas coordination numbers are smaller than those reported for the ideal crystalline material (N<sub>0</sub> = 8; N<sub>Pu</sub> = 12) (Conradson et al., 2003; Tasi et al., 2018a). An in-depth study of this solid phase in the Pu ISAX system by Tasi et al. (2018a) resulted in similar structural parameters (i.e., R<sub>0</sub> = 2.30 Å, N<sub>0</sub> = 6; R<sub>Pu-Pu</sub> = 3.80 Å, N<sub>Pu-Pu</sub> ≈ 4). The latter study argued that the nanocrystalline nature of the PuO<sub>2</sub> (ncr,hydr) solid phase resulted in distorted local order around plutonium centers, which can reduce the coordination number reported for ideal fluorite type PuO<sub>2</sub> due to the destructive interference of the backscattered photoelectron waves. Additionally, fixing S<sub>0</sub> = 1.0 can lead to slight underestimation of coordination numbers during fitting. These results provide evidence that the initial PuO<sub>2</sub> (ncr,hydr) solid phase remains stable throughout the lifetime of the batch experiments and thus controls the solubility of plutonium in the presence of EDTA and calcium.

4.3. Undersaturation solubility experiments in the presence of EDTA and calcium

Fig. 3 shows experimental concentrations of plutonium ([Pu]<sub>aq</sub>) in equilibrium with PuO<sub>2</sub> (ncr,hydr) in solutions containing 1 mM EDTA and 0 ≤ [CaCl<sub>2</sub>] ≤ 3.5 M or the WIPP simulated brine. The calculated solubility of Pu(IV) species from a PuO<sub>2</sub> (am,hydr) solid phase in the absence and in the presence of 1 mM EDTA is provided for comparison as a function of calcium concentration. Steady state was achieved after 6–27 days for experiments in the absence of calcium, 27–53 days for 1 mM 3.5 M CaCl<sub>2</sub> experiments, and after 25 days for WIPP simulated brine experiments. Experimental solubility data in all investigated systems are clearly above the calculated solubility of PuO<sub>2</sub> (am,hydr) in the absence...
S0

with 1 mM EDTA and this (blue lines) are shown for comparison. (For interpretation of the references to colour in Data range and parameters generated by least-squares Table 1 the calculated solubility of Pu(IV) species as a function of pH under

ence of EDTA and absence of calcium qualitatively follow the trend of Pu(IV) EDTA complexes in the aqueous phase. Solubility data in the presence of EDTA (black line in Fig. 3), thus supporting the predominance of Pu(IV) EDTA aqueous complexes in all acidic samples. For this reason, solubility calculations assuming the reductive dissolution of PuO2(am, hyd) at (pe + pHm) = 9, including all Pu(IV) OH EDTA and Pu(III) EDTA complexes listed in Table A1, were also conducted and are plotted as a gray line in Fig. 3a. The redox condition (pe + pHm) = 9 for these calculations was selected based off of the experimentally measured pH and pe values. These calculations largely overestimate the experimental solubility in the presence of EDTA and absence of calcium and are not able to explain the trends in the solubility observed with in ceasing pHm. In agreement with the spectroscopic observations summarized in Section 4.4, solubility data underpin the predominance of Pu(IV) EDTA aqueous complexes within the investigated systems.

In the presence of EDTA and calcium, thermodynamic calculations predict a clear decrease of the solubility of plutonium with increasing calcium concentrations (green and red lines in Fig. 3b). These predictions are not reproduced by our experimental data, which show consistent and systematically higher plutonium concentrations at both pHm ≈ 9 and 11 (red and green symbols in Fig. 3b). These observations provide indirect evidence on the possible formation of quaternary Ca Pu(IV) OH EDTA complexes. We note that the predominance of the anionic complexes Pu(OH)2(EDTA)2− and Pu(OH)3(EDTA)3− under alkaline conditions represents an appropriate ground for strong ionic interactions with Ca2+ present in solution. Solubility data in the presence of 1 mM and 20 mM CaCl2 follow a close to pHm independent trend, thus pointing to a solubility equilibrium that involves no exchange of protons.

Rai and co workers also observed higher plutonium concentrations than those predicted by thermodynamic calculations in systems containing both EDTA and calcium (Fig. 9 in Rai et al. (2008)). Although the authors did not propose any hypothesis to explain such disagreement, these results provide independent support for the formation of quaternary Ca Pu(IV) OH EDTA complexes.

Experiments conducted at high ionic strength (3.5 M CaCl2 and WIPP brine) exhibit systematically higher plutonium concentrations than those predicted by thermodynamic calculations conducted for EDTA free systems (Fig. 3b). Considering the large excess of calcium in the 3.5 M CaCl2 system and the high stability of the Ca EDTA complex (log β1,1 = (12.69 ± 0.06)), these observations can be only explained by the formation of quaternary Ca Pu(IV) OH EDTA complexes. Similar to dilute systems, solubility data of plutonium in 3.5 M CaCl2 solutions with pHm ≈ 9 and 11 follow pHm independent behavior. This observation points again to a solubility equilibrium involving no exchange of protons.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>k-range (Å⁻¹)</th>
<th>r-range (Å)</th>
<th>Shell</th>
<th>N</th>
<th>R (Å)</th>
<th>ΔE (eV)</th>
<th>σ² (Å²)</th>
<th>r-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pHm = 4</td>
<td>2.7–7.0</td>
<td>O</td>
<td>5.2</td>
<td>2.30</td>
<td>4.37</td>
<td>0.0082</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>[EDTA] = 1 mM</td>
<td>1–4</td>
<td>Pu</td>
<td>10.0</td>
<td>3.82</td>
<td></td>
<td></td>
<td></td>
<td>0.0220</td>
</tr>
<tr>
<td>pHm = 9, HQ</td>
<td>2.7–8.2</td>
<td>O</td>
<td>5.4</td>
<td>2.31</td>
<td>3.94</td>
<td>0.0077</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>[EDTA] = 1 mM</td>
<td>1.1–3.9</td>
<td>Pu</td>
<td>9.4</td>
<td>3.82</td>
<td></td>
<td></td>
<td></td>
<td>0.0220</td>
</tr>
<tr>
<td>[CaCl₂] = 20 mM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sf = 1.0 fixed (slightly underestimating N in all fits); Errors: Rrup, 0.02 Å, Rrup, 0.02 Å.

Global parameter for both shells.
data at t = 7 days. The authors did not characterize the solubility product of this solid phase, and instead used thermodynamic data reported in the literature. In their first publication, Rai and co workers used log $K^*_{s,0} = -56.85$ for the interpretation of their solubility data (Rai et al., 2001). This value is in line with a solubility constant often assigned in the literature to the amorphous phase Pu(OH)$_4$(am) (i.e., log $K^*_{s,0} = -56.8 \pm 1.3$); see ThermoChimie TDB, Giffaut et al. (2014); originally reported in Lemire and Garisto (1989). However, in 2008, Rai and co workers reinterpreted their solubility using the thermodynamic product associated with the PuO$_2$(am,hyd) solid phase selected in the NEA TDB, and accordingly obtained complexation constants for the ternary system Pu(IV) OH EDTA that are ~1.5 log$_{10}$ units higher than those reported by the same authors in 2001. Considering the identical relative stability of the forming species (i.e., the trend of m[Pu] and $K^*_{s,0}$ of phPu is the same in both solubility studies (this work; Rai et al., 2001)) and ac counting for the well characterized log $K^*_{s,0}$ of the solid phase in our solubility study, it follows that the solubility constant used in Rai et al. (2008) is not representative of a freshly precipitated solid phase. Hence, the reason for the offset observed between our experimental data and thermodynamic calculations using the model reported in Rai et al. (2008) is the solubility product used in the latter publication, which underestimates the solubility of plutonium in the absence of EDTA and consequently leads to the overestimation of the equilibrium constants for the Pu(IV) OH EDTA complexes. To address these discrepancies, the following modeling strategy was considered:

(i) all solubility datasets obtained in this work and reported in Rai et al. (2001) were combined for the evaluation performed in the present work;
(ii) conditional solubility constants related to the formation of the ternary hydroxo species determined in Rai et al. (2008) were kept constant (e.g., PuO$_2$(am,hyd,fresh) + EDTA$^{4-} + (4 + x)H^+$ ⇔ Pu(OH)$_x$(EDTA)$^{x-} + (2 + x)H_2O(l)$, with log $K^*_{s,(1,x)}$ (see Table 2); and
(iii) the solubility constant of the freshly precipitated solid phase applied in the experiments of Rai et al. (2001) was readjusted by recalculating the overall stability constants of the given ternary species (log $\beta$ values, corresponding to the general equation $Pu^{n+} + EDTA^{4-} + (x+2)H_2O(l)$ + $Pu(OH)_x$(EDTA)$^{x-} + xH^+$, with $x = 1, 2$ and 3 to gain the best fit on all data sets.

Solubility calculations using this new thermodynamic model are shown in Fig. 4, confirming that the updated model is able to satisfactorily explain the two independent datasets, and a direct comparison of the model description of our experimental data before and after reevaluation can be found in Fig. A5. The resulting thermodynamic constants are summarized in Table 2, which also includes the solubility constant derived in this work for the freshly precipitated solid phase used by Rai et al. (2001). Solubility constants log $K^*_{s,(1,x)}$ derived in this work for the Pu(IV) OH EDTA system are approximately 1.2 log$_{10}$ units lower than those reported in Rai et al. (2008).

Experimental solubility data in the presence of EDTA and calcium cannot be explained without claiming the formation of a quaternary Ca Pu(OH)$_x$(EDTA)$^{(1–2)x}$ complex (see discussion in Section 4.3) with the general formula Ca$_x$PuOH$_y$(EDTA)$^{(56–2)x–y–6}$. Although the experimental dataset for this quaternary system is limited (only two pH$_m$ values and two calcium concentrations), we attempted to derive a preliminary thermodynamic model for this system. Taking the solubility and complexation model discussed above as the basis for the ternary Pu(IV) OH EDTA system, solubility data collected in the presence of EDTA and calcium were fitted to include quaternary CaPu(OH)$_x$(EDTA)$^{(1–2)x}$ complexes with Pu:OH ratios of 1:1, 1:2, 1:3, and 1:4 (i.e., $y = 1, 2$ and 3), although different stoichiometries of EDTA and calcium within the complex may also apply, the number of EDTA (z) and calcium (x) molecules/atoms in the complex was set to 1. This choice was made for the sake of simplicity, but also considering that Coulomb

4.4. Thermodynamic modeling

Datasets of Pu(IV) solubility in the presence of EDTA and absence of calcium determined in this work and reported by Rai et al. (2008) show consistent trends across the entire pH range, but hold a systematic offset in the concentration of plutonium of about 1.5 log$_{10}$ units (Fig. 3). These observations give support to a consistent aqueous speciation in both studies, while likely reflecting differences in the PuO$_2$(s) solid phase controlling the solubility. The solid phase used in the present work (PuO$_2$(ncr,hyd) aged for ca. 11 years) was extensively characterized in a previous study (Tasi et al., 2018c), and the solubility product was determined to be log $K^*_{s,0} = -(58.1 \pm 0.3)$. This value is in excellent agreement with the NEA TDB selection for an aged amorphous phase PuO$_2$(am,hyd) (i.e., log $K^*_{s,0} = -(56.8 \pm 1.3)$). In summary, the thermodynamic model reported by Rai and co workers (both in the 2001 and 2008 papers) was based on the validity of the solubility

Fig. 3. Experimentally measured m[Pu]$_{tot}$ in equilibrium with PuO$_2$(nCr,hyd) at [EDTA]$_{tot} = 1$ mM and $I = 0.1$ M NaCl (except 3.5 M CaCl$_2$ and WIPP brine) with (a) 0 M CaCl$_2$ (blue diamonds) and (b) 1 mM CaCl$_2$ (green triangles), 20 mM CaCl$_2$ (red squares), 3.5 M CaCl$_2$ (orange triangles), or WIPP simulated brine (gray circles). Solid and dotted lines correspond to the thermodynamically calculated solubility of PuO$_2$(am,hyd) under different solution conditions based on the values in Table A1. Gray dashed lines represent the ICP-MS detection limits for the experimental analyses and all error bars are contained within data symbols. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
repulsion is likely to prevent the coordination of a second EDTA$^{4-}$ ion to a highly hydrolyzed Pu(VI) central atom. Results of the different model attempts are summarized in Table A6, where the quality parameter represents the averaged square root of the sum of differences between the experimental and calculated plutonium concentrations, calculated as: $\sqrt{\sum \left[ \log \left( \frac{[Pu_{calc}]}{[Pu_{exp}]} \right) \right]^2}$. (n-1)^{-1}$ (where n is the number of data points). The best fit was obtained assuming the formation of the CaPu(OH)$(EDTA)^{2-}$ complex, with log $K^{°}(1,1,4,1) = (6.6 \pm 0.5)$ and log $K^{°}(1,1,4,1) = (8.9 \pm 0.1)$ for the solubility/complexation reactions PuO$_2$(n,cry,hyd) + $Ca^{2+} + Pu^{4+} + EDTA^{4-} + 2H_2O(l)$ = CaPu(OH)$(EDTA)^{2-}$ and Ca$^{2+} + Pu^{4+} + EDTA^{4-} + 4H_2O(l) = CaPu(OH)$(EDTA)^{3-} + 4H^+$. Apart from the numerical proof, it also appears to be evident from the nearly constant total plutonium concentrations in solutions with 1 mM and 20 mM CaCl$_2$, that this seemingly pH independent trend in the data (see Fig. 5) can only be represented by assuming the formation of a species with a Pu:OH ratio of 1:4. A direct comparison of the model with and without plutonium complexation in cluson can be found in Fig. A6. The lack of SIT or Pitzer ion interaction coefficients of the anionic species with $Ca^{2+}$, Mg$^{2+}$, or Na$^+$ hinders the proper assessment of plutonium solubility for this system in concen trated brines, but again, the formation of a quaternary complex with a Pu:OH ratio of 1:4 is consistent with the given trend in the data ob served in 3.5 M CaCl$_2$ solutions. This fitting exercise resulted in a tenta tive formula of CaPu(OH)$_4$(EDTA)$^{2-}$ for the quaternary complex, which is implemented throughout the rest of this discussion. However, further experimentai is required to define the precise stoichiometry of the quaternary CaPu(OH)$(EDTA)^{2-}$ complex (es).

There is increasing evidence in the literature on the formation of ter nary and quaternary complexes of actinides with organic/inorganic li gands involving the interaction of $Ca^{2+}$ with a negatively charged central moiety (Bernhard et al., 1996; Endrizzi and Rao, 2014; Fellhauer et al., 2010, 2016; Kalmykov and Choppin, 2000; Lee and Yun, 2013; Neck et al., 2009; Rojo et al., 2021; Tasi et al., 2018b; Tits et al., 2005; Vercammen et al., 2001; among others). The best approach to assess the stability of these complexes requires the definition of a chemical reaction involving the aqueous species prevailing in solution. For the systems Ca U(VI) CO$_3$ (Endrizzi and Rao, 2014), Ca Pu(VI) ISA (Tasi et al., 2018b), and Ca Np(V) OH (Fellhauer et al., 2016), the fol lowing equilvrium reactions can be accordingly defined:

$$Ca^{2+} + UO_2^{2+} (aq)^{4} \Leftrightarrow CaUO_2(CO_3)_{2}^{2-} \log K°CaPu(OH)(EDTA)^{2-} = (5.15 \pm 0.06)$$ (1)

$$Ca^{2+} + UO_2^{2+} (aq)^{3} \Leftrightarrow CaUO_2(CO_3)_{3}^{2-}(aq) \log K°CaPu(OH)(EDTA)^{3-} = (3.85 \pm 0.06)$$ (2)

$^{a}$ As selected by the NEA-TEB, Guillaumot et al. (2003).

$^{b}$ The notation PuO$_2$(am,hyd,fresh) is assigned in this work to the freshly precipitated solid phase used in the solubility study by Rai et al. (2001). A similar nomenclature is used in the NEA-TEB books referring to freshly precipitated solid phases of tetravalent elements, e.g. ThO$_2$(am,hyd,fresh) or ThCaO$_2$(am,hyd,fresh) (Grentiehe et al., 2020; Rand et al., 2008).

$^{c}$ Derived in this work from solubility data in Rai et al. (2001).

$^{d}$ As detailed in Rai et al. (2008), the primary difference between Rai et al. (2008) and Rai et al. (2001) values was the implementation of acidity constants for EDTA sourced from the NEA-TEB values in Rai et al. (2008) calculations. For this reason, Rai et al. (2008) values were implemented within this work.

$^{e}$ Values corrected to l = 0 with the SIT model by Rai et al. (2008).

### Table 2

Comparison of solubility constants for Pu(IV) hydrous oxides and equilibrium constants for the formation of ternary Pu(IV)-OH-EDTA complexes as reported in Rai et al. (2008), Boukhalfa et al. (2004), or Rai et al. (2001) to solubility and formation constants derived in this work.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\log K°$ or $\log C°$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuO$_2$(am,hyd) + 2H$_2$O(l) = Pu$^{4+}$ + 4OH$^-$</td>
<td>$-(58.33 \pm 0.52)^a$</td>
</tr>
<tr>
<td>PuO$_2$(am,hyd,fresh)$^b$ + 2H$_2$O(l) = Pu$^{4+}$ + 4OH$^-$</td>
<td>$-(57.15 \pm 0.50)^b$</td>
</tr>
<tr>
<td>PuO$_2$(am,hyd,fresh)$^c$ + EDTA$^{4-}$ + 3H$^+$ = Pu(OH)(EDTA) + H$_2$O(l)</td>
<td>$(21.855 \pm 0.292)^d$</td>
</tr>
<tr>
<td>PuO$_2$(am,hyd,fresh)$^c$ + EDTA$^{4-}$ + 2H$^+$ = Pu(OH$_2$(EDTA)$^{2-}$</td>
<td>$(16.871 \pm 0.292)^d$</td>
</tr>
<tr>
<td>PuO$_2$(am,hyd,fresh)$^c$ + EDTA$^{4-}$ + H$^+$ + 2H$_2$O(l) = Pu(OH$_2$(EDTA)$^{3-}$</td>
<td>$(7.354 \pm 0.292)^d$</td>
</tr>
<tr>
<td>Pu$^{4+}$ + EDTA$^{4-}$ + 4OH$^-$ = Pu(OH)(EDTA) + H$_2$O(l)</td>
<td>$(23.00 \pm 0.30)^i$</td>
</tr>
<tr>
<td>Pu$^{4+}$ + EDTA$^{4-}$ + 2OH$^-$ = Pu(OH$_2$(EDTA)$^{2-}$ + 2H$^+$</td>
<td>$(18.02 \pm 0.30)^i$</td>
</tr>
<tr>
<td>Pu$^{4+}$ + EDTA$^{4-}$ + 3OH$^-$ = Pu(OH$_3$(EDTA)$^{3-}$ + 3H$^+$</td>
<td>$(8.50 \pm 0.30)^i$</td>
</tr>
</tbody>
</table>

$^a$ As selected by the NEA-TEB, Guillaumot et al. (2003).

$^b$ The notation PuO$_2$(am,hyd,fresh) is assigned in this work to the freshly precipitated solid phase used in the solubility study by Rai et al. (2001). A similar nomenclature is used in the NEA-TEB books referring to freshly precipitated solid phases of tetravalent elements, e.g. ThO$_2$(am,hyd,fresh) or ThCaO$_2$(am,hyd,fresh) (Grentiehe et al., 2020; Rand et al., 2008).

$^c$ Derived in this work from solubility data in Rai et al. (2001).

$^d$ As detailed in Rai et al. (2008), the primary difference between Rai et al. (2008) and Rai et al. (2001) values was the implementation of acidity constants for EDTA sourced from the NEA-TEB values in Rai et al. (2008) calculations. For this reason, Rai et al. (2008) values were implemented within this work.

$^e$ Derived from experimental data obtained in this work and reported in Rai et al. (2001) as described in the text.

$^f$ Values corrected to l = 0 with the SIT model by Rai et al. (2008).
The estimated amount of EDTA disposed in the Swedish LILW repository is 8.3 × 10^8 kg EDTA, which consists of used nuclear fuel or highly radioactive waste materials (i.e., fission products) that remain after fuel reprocessing, is not expected to contain EDTA (Clark and Ewing, 2006; US NRC, 2020). Processes for creation of specific waste forms for HLW, such as vitrification, will destroy any organic components of the waste prior to disposal. Low and intermediate level radioactive waste (LILW), or waste which contains radioactive and nonradioactive components that may adversely affect humans and the environment, can contain EDTA originating from either the waste itself or the waste packaging. The estimated amount of EDTA disposed in the Swedish LILW repository SFR 1 is 10 kg, which equates to a maximum of 3.9 × 10^{-4} M total ligand concentrations in different vaults of the repository (Bradbury and Van Loon, 1997; Chapman et al., 2002; Fanger et al., 2001). However, further disposal of EDTA into the facility is prohibited according to new regulations. Compared to current regulations for LILW, the Waste Isolation Pilot Plant (WIPP) in the United States, which is responsible for the deep geologic disposal of defense transuranic waste (TRU), contains large quantities of EDTA: an estimated 4.03 × 10^6 kg of EDTA has been deposited in the WIPP, which translates to 8 × 10^{-3} M EDTA accounting for the entire volume of the repository (Appendix SOTERM 2019, 2019). Finally, legacy waste, such as that disposed of at the Hanford Site and Maxey Flats, can also contain EDTA (Cleveland and Rees, 1981; Hakem et al., 2001; McFadden, 1980). The waste tanks at the H-35 (Yakima, USA) contain ~5 × 10^5 kg mixed radionuclides generated from more than 40 years of plutonium processing, and this waste is estimated to include ~8.3 × 10^8 kg EDTA (Campbell et al., 2000; Colburn and Peterson, 2021; Freeman Polland et al., 1994; Hakem et al., 2001; Rai et al., 2008; Samuels et al., 1994). An analysis of waste from Hanford Tank 241 SY 101 by Campbell et al. (2000) exhibited total organic carbon concentrations of ~2000 ppm, 70 90% of which could be attributed to organic chelators (i.e., primarily EDTA or oxalate); this equates to a maximum total ligand concentration of ~6 × 10^{-4} M within Tank 241 SY 101 at the Hanford Site. Ultimately, it is both appropriate and necessary to consider EDTA in the context of nuclear waste disposal for TRU, LILW, and legacy waste, although the concentrations are expected to vary for each specific disposal situation; herein, we use 0.1 mM EDTA to approximate both environmentally and repository relevant boundary conditions.

Thermodynamic data derived for the ternary Pu(IV) OH-EDTA system (Table 2) in combination with the tentative equilibrium constant proposed for the quaternary CaPu(OH)4(EDTA)2^- complex were considered to prepare updated Pourbaix diagrams of plutonium in the presence of EDTA (Fig. 6a) and plutonium in the presence of both EDTA and calcium (Fig. 6b). The updated diagram in Fig. 6a (0 M CaCl2) shows a smaller aqueous Pu(IV) predominance field than previously calculated using the thermodynamic model reported in Rai et al. (2008), which results in an increase of the stability field of aqueous Pu(III) species. This indicates that the dominant valence of plutonium for the acidic experiments reported within this work is still predicted to be Pu(III), even with the inclusion of revised thermodynamic constants within the calculations and suggests that the thermodynamic constants for Pu(III) EDTA species may not be reliable. To address this discrepancy, future experimentation and modeling will focus on reassessing the thermodynamics of the Pu(III) EDTA system. The Pourbaix diagram in Fig. 6b (20 mM CaCl2), while preliminary in nature, displays the overwhelming predominance of the quaternary CaPu(OH)4(EDTA)2^{-} complex in the presence of both EDTA and calcium under alkaline conditions. The formation of this quaternary complex increases the stability field of Pu(IV) to the detriment of the Pu(III) EDTA region at pH ≥ 6, thus highlighting the specific impact of calcium in the redox distribution of plutonium for systems containing EDTA. Colored regions in Fig. 6 correspond to the (pH + pE) conditions found in natural waters (groundwater, seawater, rain/streams) and expected in underground repositories for nuclear waste (Duro et al., 2012; Runde, 2000). Fig. 6a and Fig. 6b show that both Pu(IV) EDTA and Pu(III) EDTA complexes have large stability fields within the (pH + pE) conditions prevailing in natural waters (gray shaded area). In contrast to previous assumptions, the ubiquitous presence of calcium in environmental systems does not inhibit the complexity of plutonium with EDTA but rather promotes the stabilization of Pu(IV) in solution through the formation of quaternary complexes. Under the reducing conditions expected in underground repositories (orange colored region), our updated thermodynamic model predicts the coexistence of Pu(IV) EDTA or Pu(III) EDTA complexes over the range of 2–3 pH units. However, the large inventory of calcium in specific repository concepts/conditions (e.g., cementitious systems) is expected to enhance the stability field of Pu(IV), thus shifting the Pu(IV)/Pu(III) redox border towards more reducing conditions. The discussion above highlights the complexity of quaternary M Pu OH EDTA systems. In our view, the generally accepted outcompetition of Pu EDTA complexation by some environmentally relevant major cations such as calcium may need to be revisited. Experimental evidence collected in this work suggests the possible formation of quaternary complexes of plutonium in these systems. The formation of such complexes may significantly affect the chemical behavior of plutonium in the presence of EDTA under a wide range of geochemical conditions of
environmental relevance as well as in underground repositories for nuclear waste disposal.

5. Conclusions

Undersaturation solubility experiments using a well characterized PuO₂(ncr,hyd) solid phase and chemically controlled, well defined redox conditions in solution, in combination with advanced spectroscopic techniques, are considered to attain a thermodynamic description of the Ca Pu(IV) EDTA H₂O system, which includes previously unreported quaternary Ca Pu(IV) OH EDTA complex(es).

Although the current NEA TDB selection does not consider the formation of hydroxo species for any of the An(IV) EDTA systems, more recent literature provide evidence that these complexes dominate An(IV) aqueous speciation in the presence of EDTA under weakly acidic to hyperalkaline pH conditions. The use of thermodynamic models available in the literature for the Pu(IV) OH EDTA ternary system results in a systematic overestimation of the plutonium solubility data determined in the present study in the absence of calcium. By using the well defined solubility constant available for the solid phase used in this work and by adjusting the solubility product of the solid phase in the work of Rai et al. (2001), solubility data in both studies gave a proper basis for the reevaluation of the overall formation constants (log β₁,₁,₁) for the ternary complexes Pu(OH)₁(EDTA)⁰, Pu(OH)₂(EDTA)⁻, and Pu(OH)₃(EDTA)²⁻. This exercise resulted in a consistent thermodynamic model that is able to successfully explain both solubility data sets. The comparison of both solubility studies also provides a sound basis for the differentiation between the solubility products of an amorphous, freshly precipitated PuO₂ solid phase and an aged PuO₂ solid phase with higher crystallinity. Following the nomenclature considered in the NEA TDB for the case of Th(IV) (Rand et al., 2008), we propose the definition of the solid phase PuO₂(am,hydr,fresh) with a solubility product of log Kₛₚ₁₀ = (−57.15 ± 0.50).

The formation of quaternary Ca Pu(IV) OH EDTA complex(es) is strongly supported by solubility experiments conducted over a wide range of total calcium concentrations (1 mM < [Ca(II)]ₜ₀ < 3.5 M). The pH independent trend (i.e., nearly constant total plutonium concentrations quantified in the alkaline range) hinted towards a Pu:OH stoichiometric ratio of 1:4 in the quaternary complex, which is tentatively defined as CaPu(OH)₄(EDTA)²⁻. As a consequence of the stabilization effect of Ca(II) on the Pu(IV) OH EDTA system, the previously defined redox boundary for Pu(III)/Pu(IV) aqueous species suffers a significant shift towards lower (pe + pH) values, increasing the stability field of Pu(IV)ₚₐₜ species under conditions relevant in the context of nuclear waste disposal. However, additional experimental efforts are required to conclusively determine the stoichiometry of the quaternary complex and its impact on the Pu(III)/Pu(IV) aqueous redox boundary. In order to properly assess this effect, similar work will also be conducted with Pu(III) to evaluate the possible formation of stable Ca Pu(III) OH EDTA quaternary complexes.

Beyond the effect of calcium on the Pu(IV) OH EDTA system and in analogy to observations reported for other chelating ligands (e.g., citrate), such stabilization effects may be anticipated for other di and trivalent metal ions. The possible formation of quaternary M(II)/M(III) Pu(IV) OH EDTA complex(es) emphasizes the importance of reinterpreting the role of major cations of environmental relevance (e.g., calcium, iron, magnesium, lead) for defining the speciation and mobility of plutonium under repository and environmentally relevant conditions.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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