The redox behaviour of uranium was investigated in 0.1 and 5.0 M NaCl solutions at 2 ≤ pHm ≤ 14.5 (pHm = –\log [H^+]) in the presence of different reducing chemical systems (Sn(II), Na2S2O4, Sn(II) + TiO2, Sn(II) + Fe(0), Sn(II) + Fe3O4). All experiments were performed under Ar atmosphere at T = (22 ± 2) °C. Uranium was added to independent batch samples as U(VI) (with [U]0 = 3.0 \times 10^{-5} or 4.2 \times 10^{-4} M), and the evolution of uranium concentration monitored for t ≤ 635 days. After attaining equilibrium conditions, [U] was found in all cases clearly below the solubility of U(VI) solid phases (UO3 \cdot 2H2O(cr) or Na2U2O7 \cdot H2O(cr)) and in good agreement with the solubility of tetravalent UO2(am, hyd) as calculated with available thermodynamic data. This observation is in line with (pe + pHm) measurements, which in all cases fell in the stability field of U(IV). Solvent extraction and XANES confirmed also that uranium is predominantly found as U(IV) in the aqueous and solid phases investigated. No evidence on the formation of anionic hydrolysis species of U(IV) was obtained up to pHm = 14.5. Based on our long-term redox study, we conclude that previous investigations reporting the formation of U(OH)5^– and U(OH)6^{2−} are possibly flawed by insufficient equilibration time, which prevented the complete reduction of U(VI) to U(IV). Our results further confirm that experimental pHm and Eh values measured in buffered systems can be considered as reliable parameters to predict the redox behaviour of U in dilute to concentrated NaCl systems.

1. Introduction

Uranium is a relevant actinide for the long-term safety assessment of underground repositories for the disposal of nuclear waste due to the large inventory in spent nuclear fuel, the long half-life of U isotopes in the waste (mostly 238U with t1/2 = 4.47\times10^{10} years, but also 235U with t1/2 = 7.04\times10^{8} years and 236U with t1/2 = 2.34\times10^{7} years) and the formation of stable redox states (+IV and +VI) with remarkably different chemical behaviour. After the closure of a deep geological repository, reducing conditions are expected to develop due to the anoxic corrosion of iron. Water intrusion into the repository may lead to the generation of aqueous systems, whose composition is defined by the groundwater of the host-rock, the technical barriers used in the repository (e.g. cement) and the waste itself. This imposes a variety of boundary conditions, which range from dilute systems (in granite and most repository concepts in clay) to concentrated brines as those expected in salt-rock-based repositories (Kim and Grambow, 1999; Metz et al., 2003, 2012; Bube et al., 2013). Cementitious environments as those used for the stabilization of the waste (especially for L/ILW) and for construction purposes will buffer the pH in the hyperalkaline range (10 ≤ pH ≤ 13.3) (Wieland and Van Loon, 2002).

The thermochemical database (TDB) project of the Nuclear Energy Agency (NEA) provides the most comprehensive and authoritative selection of thermodynamic data currently available for uranium (Grenthe et al., 1992; Guillaumont et al., 2003; Hummel et al., 2005). Data selection includes thermodynamic quantities of redox reactions, solubility phenomena, hydrolysis and complexation with inorganic and organic ligands.

U(VI) shows an amphoteric behaviour and precipitates as UO3 \cdot 2H2O(cr) and M–U(VI)–OH(s) with M = Na+, K+ or Ca2+ (among other cations) under acidic and alkaline conditions, respectively. It hydrolyses strongly forming polymeric hydrolysis species in acidic conditions where U(VI) shows higher solubility, whereas monomeric anionic hydrolysis species dominate in near-neutral to hyperalkaline pH conditions. Based upon
We use here a generic notation for solids, (s). This accounts for the different degrees of crystallinity of UO₂(s) (Spahiu et al., 2000, 2004). A decrease of the initial U(VI) from amorphous to crystalline and very likely including also colloidal phases.

Most of the publications available in the literature on the solubility chemistry of U(IV) at pH > 4 are solubility studies with UO₂(s) (Gayer and Leider, 1957; Galkin and Stepanov, 1960; Tremaine et al., 1981; Ryan and Rai, 1983; Bruno et al., 1986; Parks and Pohl, 1988; Rai et al., 1990; Casas et al., 1998; Neck and Kim, 2001; Fujiwara et al., 2003, 2005). Three relevant but controversial aspects arise from these studies:

- Solubility studies with U(IV) are challenged by difficulties in solid phase characterization. U(IV) (as well as other An(IV)) tends to form amorphous oxo-hydroxide phases, whose stability can be strongly impacted by effects such as particle size, aging, degree of hydration or surface alteration (including sorption). Several of these effects are easily missed with standard characterization approaches.

- The formation of anionic hydrolysis species of U(IV) (U(OH)₅⁻ and U(OH)₆³⁻) under alkaline conditions has been proposed in some studies (Gayer and Leider, 1957; Galkin and Stepanov, 1960; Tremaine et al., 1981; Fujiwara et al., 2005) and disregarded by others (Ryan and Rai, 1983; Parks and Pohl, 1988; Neck and Kim, 2001). We note that the first volume of the NEA–TDB series (Grenthe et al., 1992) included a limiting value for ΔG°ₘ(U(OH)₇⁻) in the selected data set, which was based on the assumption that a U(OH)₅⁻ > a(U(OH)₆³⁻) at pH > 12.

- Several reducing systems have been used to retain uranium in +IV redox state: H₂(g), Na₂S₂O₄, Zn, Fe(0), EuCl₂, hydrazine, among others (Ryan and Rai, 1983; Bruno et al., 1986; Parks and Pohl, 1988; Casas et al., 1998; Fujiwara et al., 2003, 2005; Zhao et al., 2014). In spite of this, oxidation of U(IV) to U(VI) (especially under hyperalkaline pH conditions) was reported in some studies and suspected in some others.

A large number of experimental studies have investigated the reduction of U(IV) in the presence of magnetite and other corrosion products of Fe (Cantrell et al., 1995; Grambow et al., 1996; Fiedor et al., 1998; El Aamrani et al., 1999; Farrell et al., 1999; Liger et al., 1999a; Cui and Spahiu, 2002b; Missana et al., 2003; O’Loughlin et al., 2003; Scott et al., 2005; Duro et al., 2008; Ilton et al., 2010; Huber et al., 2012; Latta et al., 2012; Bruno et al., 2018). These studies highlight the role of surfaces in the catalysis of the reduction process, and to point to a number of variables affecting the reduction kinetics such as pH, Eh, composition of the ionic media or Fe(II) content (in magnetite). We note that most of these studies target weakly acidic to weakly alkaline pH conditions, with the exception by Huber et al. (2012) and Bruno et al. (2018) covering up to pH = 11 and = 13, respectively.

Spahiu and co-workers investigated the redox behaviour of U(VI) in the presence of H₂(g) and carbonate, both in the absence and presence of UO₂(s) (Spahiu et al., 2000, 2004). A decrease of the initial U(VI) concentration (~8 × 10⁻⁶ M) was only observed after the addition of UO₂(s) to the system. The authors concluded that H₂(g) does not reduce U(VI) carbonate species in the absence of a catalyst, but that reduction takes place in the presence of UO₂(s) surfaces. Under similar experimental conditions but in the absence of H₂(g), Cui and Spahiu reported the reduction of U(VI) by UO₂(s) and proposed the formation of a layer of UO₂+x on fresh UO₂(s) surfaces (Cui and Spahiu, 2002a).

The summary above highlights that relevant uncertainties still exist with regard to the solubility and hydrolysis of uranium. These uncertainties mostly affect U(IV), but translate also to ill-defined redox boundaries with U(VI), especially under alkaline conditions. In this context, our study aims at (i) investigating the reduction of U(VI) to U(IV) in a range of reducing systems covering 2 ≤ pHₘ ≤ 14.5, but with special focus to alkaline to hyperalkaline conditions; (ii) evaluating the impact of high salinity (as 5.0 M NaCl) on the redox chemistry of uranium; (iii) studying the reduction kinetics defined by different reducing systems; (iv) assessing the formation of anionic hydrolysis species of U(IV) under hyperalkaline pH conditions; and (v) contrasting newly generated experimental data with thermodynamics calculations, and contributing (whenever possible) to reducing existing uncertainties. The redox experiments designed for this purpose start from oversaturated U(VI) solutions, and consider differences in solubility between U(VI) and U(IV) solid phases as main criteria to probe the reduction to U(IV). Considering the relevance of kinetics described in previous investigations, very long equilibration times (t ≤ 635 days) have been allowed for these systems. Because of the known role of (given) surfaces in catalysing redox reactions, a series of experiments were performed in the presence of TiO₂, Fe(0) and Fe₂O₃(cr). Titanium dioxide is a well-known and widely used photocatalyst, whereas Fe(0) and Fe₂O₃(cr) are very relevant solid phases in the context of nuclear waste disposal, also with known reducing properties. For selected solid and aqueous samples, the redox state of uranium is determined using solvent extraction and XANES techniques. Further insights on the U(IV) / U(IV) redox boundaries are gained by comparing systematic pHₘ and Eh measurements with calculations performed using thermodynamic data available in the literature.

2. Thermodynamic background

Data selected in the update book of the NEA–TDB (Guillaumont et al., 2003) are taken as basis for the thermodynamic model considered in this study. Thermodynamic data selected in the NEA–TDB for U(IV) are updated with the recent study by Altmaier et al. (2017), where both solubility and hydrolysis were systematically investigated over a large range of ionic strength. NEA–TDB data selection for U(VI) is complemented with the comprehensive review work by Neck and Kim (2001) on An(IV) solubility and hydrolysis. Although most of the thermodynamic data reported by these authors are consistent with the NEA–TDB selection, Neck and Kim provide equilibrium constants for the second and third hydrolysis species of U(IV), currently not selected in the NEA–TDB. Equilibrium constants considered in the thermodynamic calculations in this study (Pourbaix diagrams and solubility curves) are summarized in Table 1. The combination of U(IV) and U(IV) solubility and hydrolysis constants summarized in the table provides a clear insight on the ill-defined redox borderline for the couple U(IV) / U(IV) in alkaline conditions. We note that uncertainties in the equilibrium constants of the key redox reactions (1)–(3) are very large and range from ± 1.0 to ± 1.5.

Main redox reactions in aqueous phase (pH > 8)

\[
\begin{align*}
\text{UO}_2\text{(OH)}_3^{2-} + 3 \text{H}^+ + 2 \text{e}^- &\leftrightarrow \text{U(OH)}_4^{aq} + \text{H}_2\text{O} \quad (1) \\
\log K &= (19.7 \pm 1.5) \\
\text{UO}_2\text{(OH)}_4^{3-} + 4 \text{H}^+ + 2 \text{e}^- &\leftrightarrow \text{U(OH)}_5^{aq} + 2 \text{H}_2\text{O} \quad (2) \\
\log K &= (30.9 \pm 1.4) \\
\end{align*}
\]

Main redox reaction in solid phase (pH > 8, [Na⁺] > 0.01 M)

\[
\begin{align*}
0.5 \text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O} &\leftrightarrow 2 \text{e}^- + 3 \text{H}^+ \leftrightarrow \text{UO}_2\text{(am, hyd)} + \text{Na}^+ + 2 \text{H}_2\text{O} \quad (3) 
\end{align*}
\]
log *K* = (19.7 ± 1.0)

The specific ion interaction theory (SIT) (Ciavatta, 1980) is the method adopted by the NEA–TDB (Grenthe et al., 1992; Guillaumont et al., 2003) for the correction of ion interaction processes. The basic formulism in SIT considers:

\[ \log \gamma_j = z_j^2 D + \Sigma c_j(k, I_m) m_k \]  

with

\[ D = \frac{A_m}{1 + B_m \sqrt{m}} \]

where \( z_j \) is the charge of the ion \( j \), \( D \) is the Debye–Hückel term, \( m_k \) is the mobility of the oppositely charged ion \( k \), and \( c_j(k, I_m) \) is the specific ion interaction parameter. \( A \) and \( B \) in the Debye–Hückel terms are constants which are temperature and pressure dependent, whereas \( a \) is an ion size parameter for the hydrated ion \( j \). At 25 °C and 1 bar, the terms \( A \) and \( B \) have a value of 0.509 kg mol^{-0.5} and 1.5 kg mol^{-0.5} and 1.5 kg mol^{-0.5}, respectively. SIT ion interaction coefficients used in the present work for activity corrections are summarized in Table 2.

### 3. Experimental

#### 3.1. Chemicals

Sodium chloride (NaCl, EMSURE®), sodium hydroxide (NaOH, Titrisol®), hydrochloric acid (HCl, Titrisol®), nitric acid (HNO₃, SUPRAPUR), sodium dithionite (Na₂S₂O₄, ≥87%), titanium dioxide (TiO₂, ≥ 99.5%), metallic iron powder (≥99.5%, grain size 10 μm) and xylene (97.5%) were obtained from Merck, SnCl₃ (98%), MES (2-(N-morpholino)ethanesulfonic acid, ≥ 99.5%; pKₐ = 6.15) and TRIS (2-Amino-2-(hydroxymethyl)propane-1,3-diol, ≥ 99.5%; pKₐ = 8.3) were purchased from Sigma Aldrich. PMBP (1-phenyl-3-methyl-4-benzoyl-2-pyrazolin-5-on, ≥ 99.0%) was provided by Fluka. Magnetite (α-Fe₃O₄(cr), 60–120 nm) was prepared hydrothermally at KIT–INE followed the protocol previously described in the literature (Schwertmann and Cornell, 2000).

All solutions were prepared with ultrapure water purified with a Milli-Q-academic (Millipore) apparatus and purged with Ar before use.

### 3.2. pHm and Eh measurements

The hydrogen ion concentration (pHm = −log [H⁺], in molal units) was measured using combination pH electrodes (ROSS, Orion) calibrated with standard pH buffers (pH 1–12, Merck). Experimentally measured pHm values were corrected with empirical “A” factors to obtain pHi(hm = pHm + A). Such corrections are required in solutions of ionic strength I ≥ 0.1 mol·kg⁻¹, where pHm is an operational value significantly deviating from pH. “A” factors entail both the liquid junction potential of the electrode and the activity coefficient of H⁺ at a given background electrolyte concentration. “A” factors reported in literature for NaCl systems were used for the determination of pHm (Almaier et al., 2003). In NaCl–NaOH solutions with [OH⁻] > 0.03 M, [H⁺] was calculated from the given [OH⁻] and the activity coefficient of H⁺ at a given background electrolyte concentration.
Sn(II) forms sparingly soluble oxo-hydroxides that show an amphoteric behavior with a conditional ion product of water.

Redox potentials were measured with Pt combination electrodes with Ag/AgCl reference system (Metrohm). The measured potentials were converted to $E_0$ (versus standard hydrogen electrode, SHE) by correcting for the potential of the Ag/AgCl inner-reference electrode with 3 M KCl and $T = 22\, {^\circ}\text{C} \pm 207{^\circ}\text{mV}$. Stable $E_0$ readings were normally obtained within 10–30 min. The apparent electron activity ($pe = -\log a_e$) was calculated from $E_0 = -\left(\text{RT/F}\right)\ln a_e$, according to the relation $pe = 16.9\, E_0\, (V)$.

### 3.3. Preparation and characterization of redox samples

Oversaturation experiments with U(VI) were performed in 0.1 M and 5.0 M NaCl solutions with $2 \leq \, pH_{m} \leq 14.5$. Inactive solutions (without uranium) were pre-equilibrated in independent batch samples with the following reducing systems: Sn(II), Na2S2O4, Sn(II) + TiO2, Sn(II) + Fe(0) and Sn(II) + Fe3O4(cr). The $pH_m$ values were adjusted using HCl–NaCl and NaCl–NaOH solutions with $l = 0.1$ or 5.0 M. MES (5 mM) and TRIS buffers (1 mM) were used to fix the $pH_m$ at 6 and 8, respectively. Two different initial uranium concentrations were used in the experiments: $[U(VI)]_0 = 4.2 \times 10^{-4}$ and $3 \times 10^{-5}$ M. Table 3 provides a detailed summary of the experimental conditions used in this study.

The concentration of uranium was quantified at regular time intervals (up to 635 days) after phase separation by ultrafiltration (10 kD). Correcting for the potential of the Ag/AgCl inner-reference electrode was clearly below than the original $[Sn(II)]$, although $[Sn]$ was not quantified with the following reducing systems: Sn(II), Na2S2O4, Sn(II) + TiO2, Sn(II) + Fe(0) and Sn(II) + Fe3O4(cr). The $pH_m$ values were adjusted using HCl–NaCl and NaCl–NaOH solutions with $l = 0.1$ or 5.0 M. MES (5 mM) and TRIS buffers (1 mM) were used to fix the $pH_m$ at 6 and 8, respectively. Two different initial uranium concentrations were used in the experiments: $[U(VI)]_0 = 4.2 \times 10^{-4}$ and $3 \times 10^{-5}$ M. Table 3 provides a detailed summary of the experimental conditions used in this study.

The concentration of uranium was quantified at regular time intervals (up to 635 days) after phase separation by ultrafiltration (10 kD filters Nanosep and Mikrosep, Pall Life Sciences; 2–3 min cut-off). Aliquots of the original samples were diluted in 2% HNO3 in 5 ml screw-cap tubes (100–5000 dilution factor, depending upon NaCl and uranium concentration) and measured using ICP-MS (Perkin Elmer ELAN 6100). Measurement of blank samples normally resulted in 0.001–0.002 ppm U, leading to detection limits of $10^{-7}$ to $10^{-11}\, M$ (depending upon dilution factor), as calculated considering 3σ of the blank.

After attaining equilibrium conditions (constant $pH_m$, $E_h$ and [U] measurements), a solvent extraction approach was used to determine the oxidation state of U in the aqueous phase of samples containing [U] $\geq 10^{-5}$ M (Coronel et al., 1982; Fellhauer, 2013). 250 μL of the supernatant of the sample containing 20 mM Sn(II) in 0.1 M NaCl at $pH_m = 11.9$ was vigorously shaken for 3–5 min and centrifuged at 12000 g for 5 min to separate organic and aqueous phases. The concentration of uranium in the aqueous phase was quantified by ICP-MS and attributed to presence of U(VI).

### 3.4. XANES measurements

Uranium $L_{III}$-edge X-ray absorption near-edge structure (XANES) spectra were recorded at the INE-Beamline and ACT-Beamline at KIT Synchrotron (formerly ANKA), KIT Campus North, in Karlsruhe, Germany (Rothe et al., 2012; Zimina et al., 2017). Both solid (INE-beamline) and aqueous (ACT-Beamline) phases were characterized to determine the redox state of U. Three samples were investigated: (i) supernatant of the sample containing 20 mM Sn(II) in 0.1 M NaCl at $pH_m = 2.2$, (ii) solid phase of the sample equilibrated in 20 mM Sn(II) + 15 mg Fe(0) in 0.1 M NaCl at $pH_m = 10.9$ (iii) solid phase of the sample equilibrated in 20 mM Sn(II) in 5.0 M NaCl at $pH_m = 11.9$. U(IV) and U(VI) standards (both aqueous and solids) were prepared for the identification of the redox state of uranium in the unknown samples. A nitrate-free 0.01 M U(VI) stock solution was prepared in 1.0 M HCl after a series of dissolution / precipitation steps with UO2(NO3)2 in HCl / NaOH. A solid Na2UO2H2O4(cr) synthesized in our previous study (Altmair et al., 2017) was contacted with a $pH_m = 12$ solution and used as a reference for U(VI) solid phases. A 0.01 M U(IV) stock solution was prepared by electrolysis of the U(VI) stock in 1.0 M HCl. The redox purity of the resulting solution was confirmed by UV-vis (see Supporting Information). A fraction of the U(IV) stock solution was precipitated in a $pH_m = 12$ solution containing Na2S2O4 as holding reducing agent. The resulting UO2(am, hyd) solid was aged for 2 months and used as reference for U(IV) solid phases in the XANES measurements.

In all cases, approximately 300 μL of the suspension were transferred to a 400 μL polyethylene vial under an Ar atmosphere and centrifuged at 4020 g for 10 min to obtain a compacted solid phase at the bottom of the vial. The vials were mounted in a gas-tight cell with windows of Kapton® film (polymide) inside the Ar-glovebox and transported to ANKA. The measurements were conducted within a few hours after sample preparation.

Uranium $L_{III}$-edge (17166 eV) XANES spectra (7–9 replications per sample) were collected at room temperature under a continuous flow of Ar. The INE-Beamline is equipped with a Ge(422) double crystal monochromator (DCM) coupled with a collimating and a focusing Rh coated mirrors before and after the DCM, respectively. The DCM-crystals were detuned at 70%. The ACT-Beamline is equipped with these measurements with Si(111) double crystal monochromator (DCM) coupled with a collimating and a focusing Rh coated mirrors before and after the DCM, respectively. At both beamlines, the beam spotsize on the sample is below 1 mm diameter. The energy calibration was performed by assigning the energy of 17038 eV to the first inflection point of the K-edge absorption spectrum of the Y metal foil. The incident and transmitted beam intensities were measured by argon-filled ionization chambers. XANES data reduction and analysis were performed with the ATHENA software of the Demeter 0.9.26 package following standard procedures (Ravel and Newville, 2005).

### 4. Results and discussion

The redox behaviour and solubility of uranium are discussed in the following sections as classified by reducing system: Sn(II), Na2S2O4, Sn(II) + TiO2, Sn(II) + Fe(0) and Sn(II) + Fe3O4(cr). Experimentally measured $E_h$ and $pH_m$ values are plotted in Pourbaix diagrams calculated for 0.1 M or 5.0 M NaCl using the dynamic and activity models summarized in Section 2. Pourbaix diagrams are prepared with the code Medusa developed by Ignasi Puigdomènech (Puigdomènech, 1983) using the above data selection. For each reducing system, the concentration of U determined at
9 ≤ t [days] ≤ 635 is plotted as a function of pHm, and compared with the solubility calculated for the main U(VI) (UO₂\(2\)H₂O(orange) and Na₂U₂O₇-H₂O(orange)) and U(IV) (UO₂(am, hyd)) solid phases expected to form in the conditions of our study. The difference in solubility between U(VI) and U(IV) solid phases is used as main criterion to assess the reduction of U(VI) to U(IV) behaviour in neutral to alkaline pH region, and complemented in specific cases with solvent extraction and XANES techniques.

4.1. Redox behaviour and solubility of uranium in reducing systems

4.1.1. Sn(II) systems in 0.1 and 5.0 M NaCl

In Fig. 1a., the \(E_{\text{H}}\) and \(pHm\) values measured in 0.1 M NaCl systems containing 2, 10 and 20 mM Sn(II) are shown. Experimental \(E_{\text{H}}\) and \(pHm\) values are plotted in a Pourbaix diagram of uranium calculated for the same boundary conditions and \([U] = 3.0 \times 10^{-5}\) M. The figure shows that Sn(II) sets very strongly reducing conditions, in all cases well below the calculated U(VI/IV) borderline. This suggests that U(VI) should reduce to U(IV) in the course of the experiment. Fig. 1a also shows that \(E_{\text{H}}\) values remain stable within the timeframe considered for this system (\(t = 238\) days).

Fig. 1b shows the concentrations of uranium measured in this system after 10 kDa ultrafiltration. Different shapes and colours of symbols correspond to the different concentrations of Sn(II) (2, 10 and 20 mM) and (initial) U(VI) (4.2 \times 10^{-4} and 3.0 \times 10^{-5} M). The figure also shows the solubility of U(VI) and U(IV) solid phases calculated for 0.1 M NaCl systems and according to thermodynamic data summarized in Section 2. A very significant decrease of uranium concentration (down to \(10^{-8} - 10^{-9}\) M) is observed in all investigated Sn(II) systems, which suggests the complete reduction of U(VI) to U(IV) and a solubility-control by UO₂(am, hyd). However, reduction kinetics are strongly affected by the initial [U(VI)]₀, [Sn(II)] and pHm:

- The fastest reduction (= 59 days) is observed for those samples with highest Sn(II) concentration (20 mM) and lowest [U(VI)]₀ (3.0 \times 10^{-3} M).
- Those samples with [U(VI)]₀ = 4.2 \times 10^{-4} M and [Sn(II)] = 10 mM show pHm-dependent reduction kinetics. Hence, fast reduction (=99 days) is observed within 10 ≤ pHm ≤ 12, whereas significantly longer contact time (= 238 days) is required to reduce U(VI) to U(IV) at pHm = 12.8. Such behaviour can be rationalized by the decreased driving force for the reduction of U(VI) to U(IV): \(A\Delta p_{\text{e}}\) (as \(|p_{\text{exp}} - p_{\text{borderline}}|\) becomes smaller with increasing pHm (Fellhauer, 2013; Kobayashi et al., 2013) (see Fig. 1a.).
- The sample with [U(VI)]₀ = 4.2 \times 10^{-4} M, [Sn(II)] = 2 mM and pHm = 12.8 shows the slowest reduction kinetics. A first, fast drop in uranium concentration is produced within 19 days leading to \([U] = 10^{-8}\) M, in excellent agreement with a solubility control by Na₂U₂O₇-H₂O(orange). This concentration of uranium is retained in solution up to \(t = 238\) days. A much longer contact time (635 days, black circle in Fig. 1b.) is required to decrease uranium concentration down to \(10^{-8} - 10^{-9}\) M, which corresponds to the complete reduction of U(VI) to U(IV). Very likely both Na₂U₂O₇-H₂O(orange) and UO₂(am, hyd) solid phases co-exist for a long time until the solid phase transformation is completed, but in such cases the solubility is controlled by the more soluble phase.

An additional series of samples in the presence of Sn(II) was prepared in 0.1 M NaCl covering a broader pHm-range, 2 ≤ pHm ≤ 12.8. Independent batch experiments were prepared with 20 mM Sn(II) and [U(VI)]₀ = 3 \times 10^{-3} M, conditions in which (based upon our previous experiments in alkaline pHm conditions) a faster reduction of U(VI) to U(IV) is expected. Fig. 2a shows that Sn(II) provides very reducing conditions (\(p_{\text{e}} + pHm = 2 ± 1\)) over the complete pHm-range investigated, in excellent agreement with previous redox investigations using Sn(II) as reducing chemical (Kobayashi et al., 2013; Yalcintas et al., 2015). Under these boundary conditions, the reduction of U(VI) to U(IV) is completed within \(t ≤ 177\) days for all investigated samples except the one at pHm = 5.9 for which significantly longer contact time (\(t = 574\) days) is required (see Fig. 2b.). The reason for the longer equilibration time required for this specific case remains unexplained, but might be related with the greater stability field of U(V) at this pHm. The shape of the solubility curve of U obtained within 2 ≤ pHm ≤ 12.8 is in excellent agreement with thermodynamic calculations performed for U(IV) according to thermodynamic and activity models summarized in Section 2. This observation strongly suggests that equilibrium conditions have been attained in the system, as well as hinting towards the expected predominance of UO₂(am, hyd) as solubility controlling solid...
phase in equilibrium with U(OH)$_2^{2-}$, U(OH)$_3^{+}$ and U(OH)$_4^{4-}$ hydration species.

The impact of high salinity on the redox behaviour of uranium was investigated in 5.0 M NaCl systems with $4 \leq \text{pH}_m \leq 14.5$. Independent batch samples were prepared with 20 mM Sn(II) and $[\text{U(VI)}]_0 = 3 \cdot 10^{-5}$ M.

Fig. 3a shows the Pourbaix diagram of uranium calculated for these boundary conditions, including experimental $E_h$ and $\text{pH}_m$ values measured in 5.0 M NaCl systems containing 20 mM Sn(II); b. concentrations of uranium measured after 10 kD ultrafiltration for 5.0 M NaCl systems with $[\text{Sn(II)}] = 20$ mM and $[\text{U(VI)}]_0 = 3 \cdot 10^{-5}$ M. Solid lines correspond to solubility curves of $\text{UO}_2\cdot2\text{H}_2\text{O}^{(cr)}$, $\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}^{(cr)}$ and $\text{UO}_2^{(am, hyd)}$ calculated using thermodynamic data in Section 2. Dashed horizontal line indicates the initial U(VI) concentration in the experiments. The different filling of the data points refers to the different equilibration times.

Fig. 2. a. Pourbaix diagram of uranium calculated for $[\text{U}] = 3 \cdot 10^{-5}$ M and 0.1 M NaCl. Calculations performed allowing the precipitation of $\text{UO}_2\cdot2\text{H}_2\text{O}^{(cr)}$, $\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}^{(cr)}$ and $\text{UO}_2^{(am, hyd)}$. Symbols represent experimentally measured $E_h$ and $\text{pH}_m$ values in 0.1 M NaCl systems containing 20 mM Sn(II); b. concentrations of uranium measured after 10 kD ultrafiltration for 0.1 M NaCl systems with $[\text{Sn(II)}] = 20$ mM and $[\text{U(VI)}]_0 = 3 \cdot 10^{-5}$ M. Solid lines correspond to solubility curves of $\text{UO}_2\cdot2\text{H}_2\text{O}^{(cr)}$, $\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}^{(cr)}$ and $\text{UO}_2^{(am, hyd)}$ calculated using thermodynamic data in Section 2. Dashed horizontal line indicates the initial U(VI) concentration in the experiments. The different filling of the data points refers to the different equilibration times.
Na2S2O4 systems in 0.1 M NaCl

4.1.2. Na2S2O4 systems in 0.1 M NaCl

The redox behaviour of uranium in the presence of 20 mM Na2S2O4 in 0.1 M NaCl solutions with \( \text{pH}_{\text{in}} = 11 \) is shown in Fig. 4. Na2S2O4 is a strong reducing agent that sets \( \text{pE_H} \) values at the border of water reduction (pe + \( \text{pH}_{\text{in}} \) = 0) (Fig. 4a). A fast decrease in uranium concentration to \([U] = 10^{-5} \) M was observed within 9 days for all investigated experiments (Fig. 4b). This observation indicates the reduction of U(VI) to U(IV) and a solubility-control by UO2(am, hyd). We note that very different \([U(VI)]_0\) were used in Fujiwara et al. (2005) (1-10^{-3} M) and in the present work (3.0·10^{-5} M). As discussed in Section 4.1.2, reduction kinetics are strongly affected by \([U(VI)]_0\) and this can expectedly be the reason for the different behaviour observed among the available studies. Such disagreement is discussed in detail in Section 4.3. Ryan and Rai (1983) performed solubility experiments with UO2(am, hyd) precipitated in alkaline conditions from an acidic U(IV) stock solution. The authors used Na2S2O4 as holding reducing agent in their experiments. Most of the solubility data reported by Ryan and co-workers in hyperalkaline conditions scatter around \(10^{-8} \) M (see Fig. 4b.), clearly below the solubility data reported in Fujiwara et al. (2005) and in good agreement with our final U concentrations. The increase in solubility observed by Ryan and co-workers at \( \text{pH}_{\text{in}} = 14 \) was explained by the authors with the oxidation to U(VI).

4.1.3. Sn(II) + TiO2 systems in 0.1 M NaCl

Fig. 5 shows the redox behaviour of uranium in the presence of 20 mM Sn(II) + 10 mg TiO2 in 0.1 M NaCl solutions with \( 2 \leq \text{pH}_{\text{in}} \leq 12.8 \). Experimental \( \text{pE_H} \) values summarized in Fig. 5a are in line with \( \text{pE_H} \) values measured in pure Sn(II) systems, and are in all cases situated within the stability field of U(IV). Fig. 5b shows that the initial concentration of uranium decreases rapidly (≈ 37 days) to values consistent with a complete reduction to U(IV) and a solubility control by UO2(am, hyd). As in pure Sn(II) systems, however, a significantly slower reduction takes place at \( \text{pH}_{\text{in}} = 6 \).

The comparison of Fig. 5b with Figs. 1b and 2b shows that under analogous (pe + \( \text{pH}_{\text{in}} \)) conditions, the presence of TiO2 accelerates the reduction of U(VI) to U(IV). This is consistent with the known role of TiO2 in catalysing redox processes (Wehrli et al., 1989; Amadelli et al., 1991; Tan et al., 2003). Enhanced kinetics are promoted by the strong sorption of U(VI) (and An(VI) in general) to TiO2 over a broad range of detection limit of ICP–MS (≈ 10^{-7} M for this NaCl concentration). Due to the high detection limit and the low solubility of Na2U2O7·H2O(cr) in 5.0 M NaCl solutions with \( \text{pH}_{\text{in}} = 7.6 \) and 11.9, these results do not provide conclusive insight on the redox behaviour of uranium within this \( \text{pH}_{\text{in}} \)-range. However, based upon measured (pe + \( \text{pH}_{\text{in}} \)) values and the solubility behaviour of uranium in acidic and hyperalkaline conditions, the reduction of U(VI) to U(IV) is to be expected also in these conditions. The decrease of uranium concentration observed at \( \text{pH}_{\text{in}} = 13.2 \) and 14.5 is consistent with the reduction of U(VI) to U(IV) and a solubility-control by UO2(am, hyd). The solubility of U(VI) calculated for the reaction \( 0.5\text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(cr) + 2\text{H}_2\text{O}(l) = \text{UO}_2(\text{OH})_4^{2-} + \text{Na}^+ + \text{H}^+ \) is 1–3 orders of magnitude greater than the experimentally measured \([U]\) (see Fig. 3b.), thus providing conclusive evidence that U(VI) does not control the solubility of uranium under these boundary conditions.

The observation of anionic hydrolysis species of U(IV) \( [\text{U(OH)}_5^{2-}]^- \) and \( [\text{U(OH)}_6^{2-}]^- \) was prompted in a previous study based upon solubility experiments with the in-situ reduction of U(VI) by Na2S2O4 (Fujiwara et al., 2005) (see discussion in Introduction and in Section 4.1.2). We note that our solubility data up to \( \text{pH}_{\text{in}} = 14.5 \) does not support the formation of such anionic hydrolysis species of U(IV) in significant proportions.

Fig. 4. a. Pourbaix diagram of uranium calculated for \([U] = 3.0\cdot10^{-5} \) M and 0.1 M NaCl. Calculations performed allowing the precipitation of UO2(am, hyd), Na2U2O7·H2O(cr) and UO2(am, hyd) and UO2(am, hyd) calculated using thermodynamic data in Section 2. Dashed blue solubility line corresponds to the solubility of \( \text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(cr) \) at \( I = 0.5 \) M calculated including the formation of \( [\text{U(OH)}_5^{2-}]^- \) and \( [\text{U(OH)}_6^{2-}]^- \) as reported by Fujiwara et al. (2005). Dashed horizontal line indicates the initial U(VI) concentration in the experiments. The different filling of the data points refers to the different equilibration times. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
4.1.4. Sn(II) + Fe(0) and Sn(II) + Fe3O4(cr) systems in 0.1 M NaCl

Fig. 6a and 7a show the experimental $E_{\text{h}}$ and $pH_m$ values measured in systems containing 20 mM Sn(II) + 15 mg Fe(0) and 20 mM Sn(II) + 10 mg Fe3O4(cr), respectively. Both datasets are plotted in Pourbaix diagrams of uranium calculated for 0.1 M NaCl solutions with [U] = 3.0·10$^{-5}$ M using thermodynamic data summarized in Section 2. Very similar and low $E_{\text{h}}$ values ($pH_m \approx 2 \pm 1$) are measured in both systems. These values are in excellent agreement with $E_{\text{h}}$ values measured in Sn(II) systems but in absence of Fe phases (see Section 4.1.1), thus indicating that redox potential is governed by Sn(II) rather than by Fe.

Fig. 6b and 7b show the concentrations of U measured in Sn(II) + Fe(0) and Sn(II) + Fe3O4(cr) systems. For both systems and in samples at $pH_m \leq 10$, the initial concentration of U decreases very rapidly ($t \approx 37$ days) to very low values (< 10$^{-8}$ M), consistently with the reduction of U(VI) to U(IV) and a solubility-control by UO$_2$(am, hyd). Slower reduction kinetics are observed at $pH_m \geq 11$ in both Fe systems (up to 574 days are required at $pH_m \approx 11$). Similar observations were recently reported by Bruno et al. (2018), who investigated the redox behaviour of uranium under
alkaline reducing conditions. For a system at $pH_m = 12.8$ in the presence of Sn(II) + Fe$_3$O$_4$(cr), the authors reported the slow decrease of the original uranium concentration, and confirmed by XPS analysis that U(IV) was predominant in the solid phase. Rai et al. (1990) studied the solubility of U(IV) with UO$_2$(am, hyd) precipitated in alkaline conditions from an acidic U(IV) stock solution. The authors used Fe(0) as holding reducing agent to retain uranium in the +IV redox state. We note that very short equilibration times ($t \leq 6$ days) were considered in this solubility study. The solubility data reported by Rai et al. at $pH \leq 11$ is in good agreement with our long-term redox experiments in the presence of Sn(II) + Fe(0) (see Fig. 6b). The authors attributed the increased uranium concentration at $pH \approx 12$ to the likely oxidation of U(IV) to U(VI). We agree with this hypothesis, and provide a further insight on this discussion: although Fe(0) sets very reducing conditions (close to the border of water reduction) within a broad range of alkaline conditions ($pH_m < 11$), it has been shown that the passivation / corrosion of the surface of Fe(0) occurring in hyperalkaline $pH_m$ conditions results in a significant increase of the redox potential (Kobayashi et al., 2013; Bruno et al., 2018; Yalcintas et al., 2015). Bruno and co-workers showed that the (pe + pH$_m$) conditions set by Fe(0) at $pH_m = 12.8$ were above the redox borderline of U(VI) / U(IV), and confirmed that no reduction of U(VI) to U(IV) was observed in this system. Unfortunately, Rai et al. did not report $E_h$ values in their paper and our hypothesis (though plausible) cannot be confirmed. The discussion above highlights that in our redox experiments with Sn(II) + Fe(0) and Sn(II) + Fe$_3$O$_4$(cr), Sn(II) is indeed the system controlling the redox behaviour of uranium.

4.2. Redox speciation of uranium in the aqueous and solid phases

4.2.1. Solvent extraction

The solvent extraction method described in Section 3.3. was used to assess the redox state of uranium in samples with $[U] \gtrsim 10^{-5} \text{M}$. Because of the low solubility of U(IV) at $pH_m > 4$, the extraction method was restricted to samples with $2 \leq pH_m \leq 3.1$. The results obtained for selected acidic samples are summarized in Table 4. In all cases, solvent extraction confirms the predominance of U(IV) in solution ($\geq 97\%$) after attaining equilibrium conditions. This observation is in agreement with thermodynamic calculations provided in Figs. 2a – 5a.

4.2.2. XANES analysis

Fig. 8 shows the U L$_{III}$-edge XANES spectra of selected aqueous (Fig. a., ACT-Beamline) and solid (Fig. b., INE-Beamline) samples, including reference spectra of aqueous species / solid compounds of U(VI) and U(IV) collected at the same beamlines. The experimental conditions and edge positions (white line, WL) are summarized in Table 5. We note that significant differences arise in the WL of U(VI) and U(IV) for aqueous and solid samples. The use of different beamlines can be partly responsible for such differences. However, intrinsic differences between aqueous and solid moieties are known to impact edge positions for a given actinide and redox state (see for instance discussion on XAFS of Np(V) and Np(VI) aqueous species and solid compounds in alkaline systems Gaona et al., 2012). For these reasons, the use of similar reference systems measured at the same beamline is mandatory for the correct assessment of the redox state of a given (actinide) system.

The edge position of the aqueous sample containing 20 mM Sn(II) in 0.1 M NaCl at $pH_m \approx 2$ is in excellent agreement with the position of the U(IV) reference (see Fig. 8a and Table 5), thus confirming that uranium is found in the +IV redox state. This is in line with thermodynamic calculations and with results obtained for the same sample by solvent extraction.

Fig. 8b shows the XANES spectra of solid uranium samples collected

![Fig. 7. a. Pourbaix diagram of uranium calculated for $[U] = 3.0 \times 10^{-5} \text{M}$ and 0.1 M NaCl. Calculations performed allowing the precipitation of UO$_2$·2H$_2$O(cr), Na$_2$U$_2$O$_7$·H$_2$O(cr) and UO$_2$(am, hyd). Symbols represent experimentally measured $E_h$ and $pH_m$ values in 0.1 M NaCl systems containing 20 mM Sn(II) + 10 mg Fe$_3$O$_4$(cr); b. concentrations of uranium measured after 10 kD ultrafiltration for 0.1 M NaCl systems with $[\text{Sn(II)}] = 20 \text{mM} + 10 \text{mg Fe}_3\text{O}_4$(cr) and $[\text{U(VI)}]_0 = 3.0 \times 10^{-5} \text{M}$. Solid lines correspond to solubility curves of UO$_2$·2H$_2$O(cr), Na$_2$U$_2$O$_7$·H$_2$O(cr) and UO$_2$(am, hyd), calculated using thermodynamic data in Section 2. Dashed horizontal line indicates the initial U(VI) concentration in the experiments. The different filling of the data points refers to the different equilibration times.

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>$pH_m\pm$</th>
<th>$E_h$ [mV]$^b$</th>
<th>U(IV) [%]$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M NaCl, 20 mM Sn(II)</td>
<td>2.2</td>
<td>−284</td>
<td>98%</td>
</tr>
<tr>
<td>0.1 M NaCl, 20 mM Sn(II) + 10 mg TiO$_2$</td>
<td>2.1</td>
<td>−357</td>
<td>97%</td>
</tr>
<tr>
<td>5.0 M NaCl, 20 mM Sn(II)</td>
<td>3.1</td>
<td>−288</td>
<td>99%</td>
</tr>
</tbody>
</table>

$^a$: ± 0.05; $^b$: ± 20 mV; $^c$: ± 10%.
from solubility experiments in (i) 0.1 M NaCl at pHm = 10.9, with 20 mM Sn(II) + 15 mg Fe(0), and (ii) 5.0 M NaCl at pHm = 11.9, with 20 mM Sn(II). The edge position of the solid sample in 0.1 M NaCl is in excellent agreement with the edge position of UO2(am, hyd) reference. A significant shift to higher energies (≈+1.5 eV, compared to the edge position of UO2(am, hyd)) is observed for the uranium solid equilibrated in 5.0 M NaCl. The XANES spectra of this sample does not show, however, the typical shoulder of the uranyl or uranate (in Na2U2O7·H2O(cr)) moieties. These observations suggest the predominance of U(IV) in the solid phase, albeit with a significant contribution of U(VI).

The process of reduction of the initial aqueous U(VI) in alkaline NaCl solutions goes through a first, fast precipitation of Na2U2O7·H2O(cr) followed by a slow transformation of this solid phase into UO2(am, hyd). As discussed in Section 4.1, the kinetics of this transformation are affected by [U(VI)]0, [Sn(II)] and pHm. Beyond these parameters, the concentration of sodium in solution participates in the equilibrium reaction driving the transformation of Na2U2O7·H2O(cr) into UO2(am, hyd):

$$0.5 \text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O} (\text{cr}) + 2 e^- + 3 \text{H}^+ \leftrightarrow \text{UO}_2 (\text{am, hyd}) + \text{Na}^+ + 2 \text{H}_2\text{O} (\text{l})$$  \hspace{1cm} (6)

with

$$\log K^0\text{eq}(0.5 \text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O} (\text{cr})) = \log K^0\text{eq}((\text{UO}_2 (\text{am, hyd})) + \log [\text{Na}^+] + \log \gamma_{\text{Na}^+} + 3 \text{pH}_{\text{m}} - 3 \log \gamma_{\text{H}^+} + 2 \text{p}e + 2 \log a_w$$ \hspace{1cm} (7)

The combination of solubility data and XANES indicates that a contact time of 330 days was sufficient to transform completely Na2U2O7·H2O(cr) into UO2(am, hyd) in a 0.1 M NaCl solution with pHm = 11, but insufficient to complete such transformation in a 5.0 M NaCl solution.
NaCl solution with pH\textsubscript{m} = 12. This is in line with reaction (6) and corresponding equation (7), which indicate that such transformation is favoured at low pH\textsubscript{m}, pe and [Na\textsuperscript{+}].

4.3. Kinetic aspects of U(VI) reduction to U(IV): main results in the present study and comparison with literature data

Multielectron transfer processes involving changes in the structure of the redox counterparts are known to be kinetically hindered (Morel and Hering, 1996; Stumm and Morgan, 1996; Altmaier et al., 2011). Such impact on kinetics is also known in the case of light actinides U, Np, Pu and Am, which form two structurally different moieties (An\textsuperscript{(+3)} and AnO\textsubscript{2}\textsuperscript{(-2)}) for the lower (+3 and + 4, x = 3–4) and higher (+5 and + 6, y = 1–2) oxidation states (Sullivan et al., 1957; Lemire et al., 2001; Hennig et al., 2009, 2010). The kinetics of U(VI) reduction have been largely investigated in the literature, with special focus on systems containing Fe and often looking at the impact of surfaces on the reduction process (Liger et al., 1999b; Rovira et al., 2007; Duro et al., 2008; Yan et al., 2014). However, most of these efforts have been dedicated to the study of the near-neutral pH-range, leaving aside alkaline to hyperalkaline pH conditions as those defined by cementitious systems. This is possibly due to the experimental challenges related to these boundary conditions which require a strict exclusion of O\textsubscript{2} and CO\textsubscript{2}. Such experimental challenges are likely the reason for the discrepancies in the literature on the solution chemistry of U(IV) and the corresponding implications in the U(VI) / U(IV) redox boundaries.

Experimental results presented in Sections 4.1.1 to 4.1.4 demonstrate our success in retaining very reducing conditions for equilibration times up to 635 days. In these conditions, thermodynamic data summarized in Section 2 predict the predominance of U(IV) aqueous species and solid compounds within the complete pH\textsubscript{m}-range investigated in the present study (2 ≤ pH\textsubscript{m} ≤ 14.5, see Figs. 1 to 7). The discussion in Sections 4.1.1 to 4.1.4 already hint to a remarkable impact of kinetics on the reduction process, with [U(VI)]\textsubscript{0}, [Sn(II)]\textsuperscript{2+}, pe and [Na\textsuperscript{+}] identified as main parameters affecting kinetics of U(VI) reduction in the conditions of our study. This section provides an accurate rapport of the time-dependency observed for the systems investigated in the present work. Focus is given to hyperalkaline pH\textsubscript{m} conditions (10 ≤ pH\textsubscript{m} ≤ 13.5), and comparison with literature data is provided whenever available.

Fig. 9 evaluates the impact of [U(VI)]\textsubscript{0} and concentration of the reducing chemical on the reduction kinetics of U(VI) at pH\textsubscript{m} = 13. The figure includes also thermodynamic calculations for the solubility of U(VI) (as Na\textsubscript{2}U\textsubscript{2}O\textsubscript{7}·H\textsubscript{2}O(cr)) and U(IV) (as UO\textsubscript{2}(am, hyd)) using thermodynamic data summarized in Section 2. A third calculated solubility is appended to the figure using thermodynamic data reported in Fujiwara et al. (2005) for the anionic hydrolysis species of U(IV), U(OH)\textsubscript{5}\textsuperscript{2−} and U(OH)\textsubscript{6}\textsuperscript{3−}.

Fig. 9a shows that for the system at pH\textsubscript{m} = 13 with lowest [U(VI)]\textsubscript{0} (3·10\textsuperscript{-5} M) and highest [Sn(II)] (20 mM), U(VI) is completely reduced to U(IV) after ≈ 50 days. A much longer contact time (≈ 600 days) is required to reach a complete reduction for the system with highest [U(VI)]\textsubscript{0} (4·10\textsuperscript{-4} M) and lowest [Sn(II)] (2 mM). In the latter case and up to t = 250 days, the concentration of uranium in solution is consistent with the solubility of UO\textsubscript{2}(am, hyd) calculated including the formation of U(OH)\textsubscript{5}\textsuperscript{2−} and U(OH)\textsubscript{6}\textsuperscript{3−} as reported in Fujiwara et al. (2005). However, we note that this uranium concentration is also consistent with a solubility-control by the reaction 0.5 Na\textsubscript{2}U\textsubscript{2}O\textsubscript{7}·H\textsubscript{2}O(cr) + 2 H\textsubscript{2}O(l) ↔ UO\textsubscript{2}(am, hyd) + Na\textsuperscript{+} + H\textsuperscript{+} with log \( K_{\text{a}(\text{U})} = -(19.05 \pm 0.1) \) (calculated from Altmaier et al., 2017). As discussed in the previous section, the concentration of uranium in the reduction of U(VI) from oversaturation conditions is governed by two processes: a first, fast decrease in concentration controlled by the precipitation of U(VI) solid phases, followed by a slow transformation of this solid phase into UO\textsubscript{2}(am, hyd). In the system under discussion ([U(VI)]\textsubscript{0} = 4·10\textsuperscript{-4} M and [Sn(II)] = 2 mM), UO\textsubscript{2}(am, hyd) certainly forms from the beginning of the experiment, but the most soluble solid phase present in the system (Na\textsubscript{2}U\textsubscript{2}O\textsubscript{7}·H\textsubscript{2}O(cr)) controls [U\textsubscript{aq}] for contact times up to t = 250 days. Only after this very long contact time, [U\textsubscript{aq}] decreases further until reaching the level corresponding to a solubility-control by UO\textsubscript{2}(am, hyd) at t = 600 days.

Fig. 9b shows the reduction kinetics of U(VI) as determined at pH\textsubscript{m} = 13 for systems containing Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} as reducing chemical...
These concentrations correspond to the examples shown in Fig. 9b. Fujiwara et al. (2005) compared to the present work (1·10^{-3} M vs. 3·10^{-5} M). As discussed in section 4.1.1 and also shown in Fig. 9a, [U(VI)]_{i0} has a relevant impact on the reduction kinetics, and up to 600 days were required to completely reduce to U(IV) an initial U(VI) concentration of 4·10^{-4} M. Both experimental studies also differ in the concentration of Na used as background electrolyte (0.5 M NaClO4 in Fujiwara et al. vs. 0.1 M NaCl in the present work). As discussed in Section 4.2.2, the driving force for the transformation of Na2U2O7-H2O(Ocr) into UO2(am, hyd) decreases with increasing concentration of Na (see equilibrium reaction (6)). Based on these observations, we firmly believe that the interpretation in Fujiwara et al. (2005) is flawed by insufficient equilibration time. Solubility data reported after t = 50 days is likely controlled by the equilibrium

\[ \text{Na}_2\text{U}_2\text{O}_7\cdot\text{H}_2\text{O}(\text{cr}) + (x-2)\text{H}_2\text{O}(\text{l}) = \text{UO}_2(\text{OH})_{2-x}^x + \text{Na}^+ + (x-3)\text{H}^+ \]  

with x = 3–4.6. We hypothesize that the authors would have observed a second step in the overall decrease of [U]_{aq} at longer equilibration times corresponding to a solubility control by UO2(am, hyd). Similar conclusions can be drawn when comparing their and our observations at pH_{m} = 12 (data not shown).

Fig. 10 shows the reduction kinetics of U(VI) at pH_{m} = 8–13 in the presence of different reducing systems (Sn(II), Sn(II) + Fe(0), Sn(II) + Fe3O4(cr) and Sn(II) + TiO2). We note that concentration of Sn(II) was the same in all these systems (20 mM), and thus this exercise aimed at evaluating the impact of different surfaces on the overall reduction kinetics. Fig. 10 includes also thermodynamic calculations for the solubility of U(VI) (as Na2U2O7·H2O(Ocr) and U(IV) (as UO2(am, hyd)) solid phases using thermodynamic data summarized in Section 2.

Fig. 10 shows a relatively fast reduction in all systems investigated in the presence of 20 mM Sn(II). The interpretation of such diagrams requires a clear understanding of some key parameters:

- TiO2, Fe2O3(cr) and Fe(0) provide surfaces that can expectedly catalyse the reduction of U(VI) to U(IV). However, Sn(II) precipitates also as sparingly soluble SnO(s) (or analogous oxo-hydroxides). Sn(II) surfaces can possibly participate in the catalysis of U(VI) reduction.

- Sn(II) shows an amphoteric behaviour, forming cationic and anionic hydroxyl species in acidic and alkaline pH conditions, respectively. Consequently, all Sn(II) systems except those at pH_{m} = 13 include solid SnO(s) (approximately 50 mg). At this pH_{m}, the enhancement in the solubility due to the formation of Sn(OH)_{2-x}^x leads to the complete dissolution of SnO(s) (see Fig. S1 in Supporting Information).

- The solubility of Na2U2O7·H2O(Ocr) is about 2 orders of magnitude lower at pH_{m} = 8–11 than at pH_{m} = 13, whereas the solubility of UO2(am, hyd) remains the same within 8 ≤ pH_{m} ≤ 13. This leads to a greater difference in the solubility of U(VI) and U(IV) under hyperalkaline conditions, compared to weakly alkaline pH_{m}.

No significant differences can be identified in the reduction kinetics of U(VI) at pH_{m} = 8–11 for the systems Sn(II), Sn(II) + TiO2, Sn(II) + Fe(0) and Sn(II) + Fe3O4(Ocr). As discussed in Section 4.1.3 slightly faster reduction kinetics can be claimed in the presence of TiO2 at pH_{m} ≥ 12.

Most of the systems described in Fig. 10a–c show a first step in the decrease of [U(VI)]_{i0} where uranium concentration stabilizes at 10^{-7} – 10^{-6} M, followed by a final step where uranium concentration decreases clearly below 10^{-8} – 10^{-9.5} M. Although less evident than the process described above for samples at pH_{m} = 13, this observation might be attributed again to a first, fast decrease in concentration controlled by the precipitation of Na2U2O7·H2O(Ocr), followed by a slow transformation of this U(VI) solid phase into UO2(am, hyd).

5 The authors claim the identification of UO2(am, hyd) by XRD, but do not show the corresponding diffraction patterns in the publication. As reported in Altmair et al. (2017), Na2U2O7·H2O(Ocr) shows rather broad and less intense XRD reflections, which could have been easily missed by Fujiwara and co-workers in the evaluation of their XRD data.

6 These concentrations correspond to the examples shown in Fig. 9b. Fujiwara et al. performed also experiments in 1.0 and 2.0 M NaClO4-NaOH with similar results. Experiments performed in the present work in 5.0 M NaCl-NaOH solutions (in 20 mM Sn(II) and with [U(VI)]_{i0} = 3·10^{-3} M) showed: (i) a good agreement with the solubility of Na2U2O7·H2O(Ocr) at pH_{m} = 13 after an equilibration of 65 days (thus incomplete reduction to U(IV), see solubility data in Fig. 3b), and (ii) an incomplete transformation of Na2U2O7·H2O(Ocr) into UO2(am, hyd) at pH_{m} = 12 after 330 days (see XANES results in Section 4.2.2).

7 The redox behaviour of uranium was investigated in reducing, di- lute to concentrated NaCl solutions covering a broad pH_{m}-range (2–14.5). Special focus was put on alkaline to hyperalkaline systems due to the ill-defined U(VI)/U(IV) redox borderline under these conditions and the controversy on the existence of anionic species of U(IV). Uranium was added to independent batch samples as U(VI), and the evolution of uranium concentration in five different reducing systems (Sn(II), Na2S2O4, Sn(II) + Fe(0), Sn(II) + TiO2 and Sn(II) + Fe3O4) is followed by a slow transformation of this U(VI) solid phase into UO2 (am, hyd).

5. Conclusions

The redox behaviour of uranium was investigated in reducing, dilute to concentrated NaCl solutions covering a broad pH_{m}-range (2–14.5). Special focus was put on alkaline to hyperalkaline systems due to the ill-defined U(VI)/U(IV) redox borderline under these conditions and the controversy on the existence of anionic species of U(IV). Uranium was added to independent batch samples as U(VI), and the evolution of uranium concentration in five different reducing systems (Sn(II), Na2S2O4, Sn(II) + Fe(0), Sn(II) + TiO2 and Sn(II) + Fe3O4) was followed by a slow transformation of this U(VI) solid phase into UO2(am, hyd).

After attaining equilibrium conditions, the measured low uranium concentrations in solution was in most cases in good agreement with the solubility of UO2(am, hyd), strongly supporting the reduction of U(VI) to U(IV). This observation is in line with results obtained by solvent extraction and XANES, which confirm that uranion is predominantly found as U(VI) in the aqueous and solid phases investigated. Kinetics play a very important role in the reduction process, and are importantly affected by [U(VI)]_{i0}, pH_{m}, E_{0}. Concentration of the reducing chemical and presence of redox-active surfaces. Our results provide also insight in the mechanism driving the reduction of U(VI) to U(IV) in alkaline NaCl systems: a first, fast precipitation of Na2U2O7·H2O(Ocr) is followed by the slow transformation of this U(VI) solid phase into UO2(am, hyd). Such transformation is favoured at low pH_{m}, pe and Na concentrations. Our results strongly support the predominance of the species U(OH)_{2-x}aq (or analogous, neutral polyatomic species) up to pH_{m} values of 14.5, thus disregarding the formation of U(VI) anionic hydrolysis species (U(OH)_{2-x}^{2-x} and U(OH)_{3-x}^{3-x}) as proposed in previous studies. As discussed by Ryan and Rai (1983), oxidation of U(IV) is suspected to have occurred in Gayer and Leider (1957) and Tremaine et al. (1981). We suggest that also the study by Fujiwara et al. (2005) is possibly flawed by insufficient equilibration time, which prevented the complete reduction of the initial U(VI) to U(IV).

Experimental observations in the present work (pH_{m}, E_{0}, solubility) are in excellent agreement with thermodynamic calculations (Pourbaix diagrams, solubility curves) using the NEA-TDB thermodynamic selection, complemented with data reported in Neck and Kim (2001) and Altmair et al. (2017) for U(VI) and U(VII) species, respectively. This suggests that experimental pH_{m} and E_{0} values measured in buffers...
systems in combination with available thermodynamic data can be reliably used for the prediction of the redox state distribution of uranium in dilute to concentrated NaCl systems under boundary conditions relevant for nuclear waste disposal.

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