Impact of nitrate on the redox chemistry and solubility of Tc(IV) in alkaline, dilute to concentrated aqueous NaCl solutions

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A B S T R A C T

The impact of nitrate on the redox behaviour and solubility of ^{99}Tc(IV) was investigated in 0.1–5.0 M NaCl–NaNO$_3$–NaOH solutions with 0.1 M ≤ [NO$_3$$^-$] ≤ 1.0 M and 8.5 ≤ pH$_m$ ≤ 14.5 (with pH$_m$ = –log [H$^+$]) in the presence or absence of reducing agents (as Fe powder, Na$_2$S$_2$O$_4$, Sn(II)). The evolution of the redox conditions as a function of time (for t ≤ 450 days) was investigated: (i) in the absence of technetium (inactive samples), (ii) in the presence of ^{99}Tc(IV) (added as 1–2 mg of TcO$_2$·0.6H$_2$O(am)), and (iii) in the presence of ^{137}Cs(I) (and absence of ^{99}Tc). All experiments were conducted in an Ar-glovebox (O$_2$ < 1 ppm) at T = (22 ± 2) °C. An improved understanding of Tc redox processes in nitrate-rich alkaline solutions is relevant to predict Tc behaviour in specific nuclear waste disposal scenarios and a topic of fundamental scientific interest.

Nitrate induces a clear increase in E_h over time in the investigated aqueous solutions both in the presence and absence of reducing agents. In the case of Fe powder, this increase is observed almost immediately whereas in the presence of Na$_2$S$_2$O$_4$ or Sn(II) the oxidizing effect is only observed after several months in inactive systems (absence of Tc). In the presence of technetium, the increase in E_h occurs within a few days (5–50, depending upon reducing system, pH$_m$ and ionic strength). The evolution of E_h in the presence of ^{137}Cs (with similar β dose as in solubility experiments with ^{99}Tc) was analogous to that in the inactive systems. These observations indicate that the solid TcO$_2$·0.6H$_2$O(am) may play a role in catalysing nitrate reduction and radiation induced reactions have no significant impact in our experiments. Liquid-liquid extraction and XANES measurements confirm that technetium in the aqueous phase is mostly present as Tc(VII). Colorimetric nitrate/nitrite tests show the formation of nitrite, confirming that the oxidation of Tc(IV) to Tc(VII) is coupled to the reduction of nitrate. Our experimental observations support that, although kinetically hindered, nitrate can effectively oxidize Tc(IV).

1. Introduction

^{99}Tc is one of the main fission products of ^{235}U and ^{239}Pu in nuclear reactors. Due to its long half life (2.1 10^5 a) and redox sensitive che mical behaviour, ^{99}Tc is a very relevant radionuclide in the Safety Case of repositories for radioactive waste. Tc can be present in different oxidation states ranging from 0 to + VII (Rard et al., 1999; Guillaumont et al., 2003). Tc(VII) and Tc(IV) are predominant oxidation states in aqueous solutions in the absence of strong complexing ligands. Tc(VII) is known to be very soluble in aqueous media and forms the highly mobile TcO$_4$$^-$ aqueous species under weakly reducing to oxidizing conditions. In reducing alkaline systems as those expected in deep un derground repositories for the disposal of nuclear waste, Tc is found as

Tc(IV) which forms the sparingly soluble hydrous oxide TcO$_2$·xH$_2$O(am) (Duro et al., 2006; SKB, 2010; Giffaut et al., 2014).

Nitrate is a relevant component in certain waste forms expected in repositories for nuclear waste disposal. Nitrate containing radioactive waste mostly originates from reprocessing activities (e.g. PUREX pro cess) and is often conditioned as bituminized (ANDRA, 2005; International Atomic Energy Agency (IAEA), 1970; Irisawa et al., 2014; Kienzler, 2017; Weetjens et al., 2006) or cementitious (Atkins and Glasser, 1992; Bénard et al., 2008; Borkel et al., 2016; International Atomic Energy Agency (IAEA), 1993; Kienzler, 2017; Palmer and Fairhall, 1992) waste forms. The contact of water with this type of waste may lead to the formation of highly concentrated nitrate plumes (up to 10 M, especially in the case of bitumen) (André et al., 2007;

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Table 1
Chemical composition of the samples prepared for the redox experiments in 0.1 and 5.0 M NaCl–NaNO$_3$–NaOH systems.

Radionuclide	Ionic strength I([NaCl] + [NaNO$_3$] + [NaOH]) in [mol·l^{-1}]	[NaNO$_3$] in [mol·l^{-1}]	Reducing agent	pH$_m$-range
no Tc, "inactive"	0.1	0.1, 0.09[a]	none	≈9, 11.8
	0.1	0.1	Fe powder	≈9
	0.1	0.09	Na$_2$S$_2$O$_4$	11.8
	0.1	0.1, 0.09[a]	Sn(II)	≈9, 11.8
	5.0	1.0	none	≈9, 11.8, 14.2
	5.0	1.0	Fe powder	≈9
	5.0	1.0	Na$_2$S$_2$O$_4$	11.8, 14.2
	5.0	1.0	Sn(II)	≈9, 11.8, 14.2
1–2 mg ^{99}TcO$_2$·0.6H$_2$O(am) "active"	0.1	0.1, 0.09[a]	none	≈9, 11.8
	0.1	0.1	Fe powder	≈9
	0.1	0.09	Na$_2$S$_2$O$_4$	11.8
	0.1	0.1, 0.09[a]	Sn(II)	≈9, 11.8
	5.0	1.0	none	≈9, 11.8, 14.2
	5.0	1.0	Fe powder	≈9
	5.0	1.0	Na$_2$S$_2$O$_4$	11.8, 14.2
	5.0	1.0	Sn(II)	≈9, 11.8, 14.2
5·10^5 Bq ^{137}Cs	0.1	0.09	none	11.8
	0.1	0.09	Na$_2$S$_2$O$_4$	11.8
	0.1	0.09	Sn(II)	11.8
	5.0	1.0	none	11.8
	5.0	1.0	Na$_2$S$_2$O$_4$	11.8
	5.0	1.0	Sn(II)	11.8

[a] Nitrate concentration was decreased to 0.09 M in those samples with [NaOH] = 0.01 M, in order to maintain constant ionic strength (I = 0.1 M).
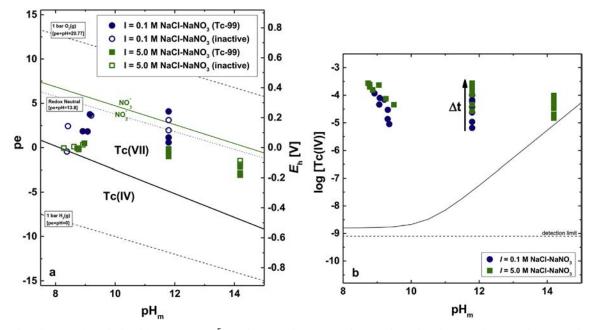

Fig. 1. (a) Pourbaix diagram of Tc calculated for [Tc]$_{tot}$ = 10^{-5} M and I = 0, and experimental pH$_m$ and pe values determined in 0.1 and 5.0 M NaCl–NaNO$_3$–NaOH systems with [NaNO$_3$] = 0.1 and 1.0 M. Samples marked as "inactive" do not contain Tc; (b) Experimental solubility data of Tc(IV) (added as 1–2 mg of TcO$_2$·0.6H$_2$O (am)) in NaCl–NaNO$_3$–NaOH systems at 8.5 ≤ pH$_m$ ≤ 14.5. Black solid line provides the reference Tc(IV) solubility at I = 0. All Tc calculations performed with thermodynamic data reported in (Yalçıntaş et al., 2016) and (Guillaumont et al., 2003). Redox borderline NO$_3^-$/NO$_2^-$ calculated at I = 0 using thermodynamic data reported in (Puigdomenech and Taxen, 2000).

Cannière et al., 2010; Hicks et al., 2017). Very high nitrate concentrations are also present in several waste tanks of the Hanford Site (Washington, USA) (Chaiko et al., 1995; Hill et al., 2011; Serne and Rapko, 2014).

The biotic and abiotic reduction of nitrate (mostly to N$_2$(g) and NH$_4^+$) under repository conditions has been described in a number of studies (Albrecht et al., 2012; André et al., 2007; Bertron et al., 2014; Libert, 2011; Truche et al., 2013). Such reduction processes are facilitated by high H$_2$ pressures, elevated temperatures, presence of Fe or bacterial activity, but the fate of this electron acceptor in the repository is yet largely unclear. Under environmental conditions, nitrate has been shown to oxidize different types of Fe phases (Fe(0), green rust, Fe(II)

silicates, pyrite, etc.) (Alowitz and Scherer, 2002; Hansen et al., 2001; Jørgensen et al., 2009; Postma, 1990), although kinetics of such redox processes are strongly affected by pH, surface area of the corresponding Fe phase or presence of certain reducing bacteria.

Previous studies have shown that in the absence of nitrate and in the presence of strongly reducing chemicals (such as Sn(II), Na$_2$S$_2$O$_4$, hydrazine, Eu(II) or Fe powder), Tc is characterized by a very low solubility (controlled by TcO$_2$·xH$_2$O(am)) and an amphoteric behaviour (predominance of cationic and anionic hydrolysis species in acidic and alkaline pH conditions, respectively) (Baumann et al., 2017; Eriksen et al., 1992; Guillaumont et al., 2003; Hess et al., 2004; Kobayashi et al., 2013b; Liu et al., 2007; Meyer et al., 1991; Warwick et al., 2007;
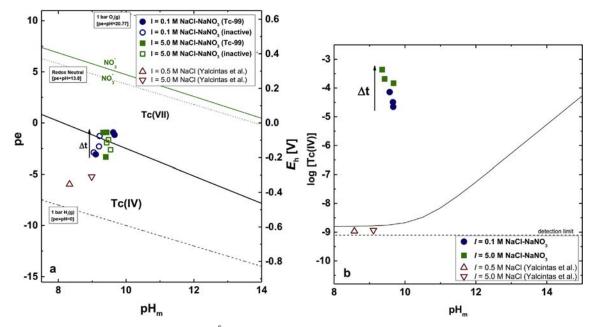
Fig. 2. (a) Pourbaix diagram of Tc calculated for $[Tc]_{tot} = 10^{-5}$ M and $I = 0$, and experimental pH_m and pe values determined in 0.1 and 5.0 M NaCl–NaNO$_3$–NaOH systems with [NaNO$_3$] = 0.1 and 1.0 M NaNO$_3$ in the presence of 10 mg Fe powder. Samples marked as "inactive" do not contain Tc. (b) Experimental solubility data of Tc(IV) (added as 1–2 mg of TcO$_2$·0.6H$_2$O(am)) in NaCl–NaNO$_3$–NaOH systems at $8.5 \leq pH_m \leq 14.5$ in the presence of Fe powder. Black solid line provides the reference Tc(IV) solubility at $I = 0$. All Tc calculations performed with thermodynamic data reported in (Yalçıntaş et al., 2016) and (Guillaumont et al., 2003). Redox borderline NO$_3^-$/NO$_2^-$ calculated at $I = 0$ using thermodynamic data reported in (Puigdomenech and Taxen, 2000). Triangles in figures a and b correspond to experimental data (pH_m, E_h and [Tc]) reported in (Yalçıntaş et al., 2015) under analogous conditions but absence of nitrate.
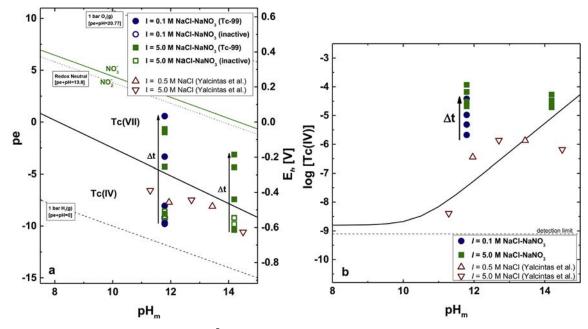

Fig. 3. (a) Pourbaix diagram of Tc calculated for $[Tc]_{tot} = 10^{-5}$ M and $I = 0$, and experimental pH_m and pe values determined in 0.1 and 5.0 M NaCl–NaNO$_3$–NaOH systems with [NaNO$_3$] = 0.1 and 1.0 M NaNO$_3$ in the presence of 2 mM Na$_2$S$_2$O$_4$. Samples marked as "inactive" do not contain Tc. (b) Experimental solubility data of Tc(IV) (added as 1–2 mg of TcO$_2$·0.6H$_2$O(am)) in NaCl–NaNO$_3$–NaOH systems at $11.5 \leq pH_m \leq 14.5$ in the presence of Na$_2$S$_2$O$_4$. Black solid line provides the reference Tc(IV) solubility at $I = 0$. All Tc calculations performed with thermodynamic data reported in Yalçıntaş et al. (2016) and (Guillaumont et al., 2003). Redox borderline NO$_3^-$/NO$_2^-$ calculated at $I = 0$ using thermodynamic data reported in (Puigdomenech and Taxen, 2000). Triangles in figures a and b correspond to experimental data (pH_m, E_h and [Tc]) reported in Yalçıntaş et al. (2015) under analogous conditions but absence of nitrate.

Yalçıntaş et al., 2015, 2016). As a rather hard Lewis acid, the solubility of Tc(IV) can be enhanced by the complexation with strong Lewis bases such as carbonate (Alliot et al., 2009; Baumann et al., 2018; Eriksen et al., 1992). Weaker ligands can hardly outcompete hydrolysis, and thus complexes of Tc(IV) with chloride are only described in extremely acidic conditions with very high chloride concentrations (Poineau et al.,

2006; Vichot et al., 2002, 2003) and hydroxide complexes prevail at higher pH conditions. No Tc(IV) nitrate complexes are described so far in the literature. Based on the similar strength reported for complexes of chloride and nitrate with hard Lewis cations (Brown et al., 2005; Gamsjäger et al., 2012; Guillaumont et al., 2003; Pearson, 1988; Wiberg and Hollemann, 2008), no Tc(IV) nitrate complexes are expected to
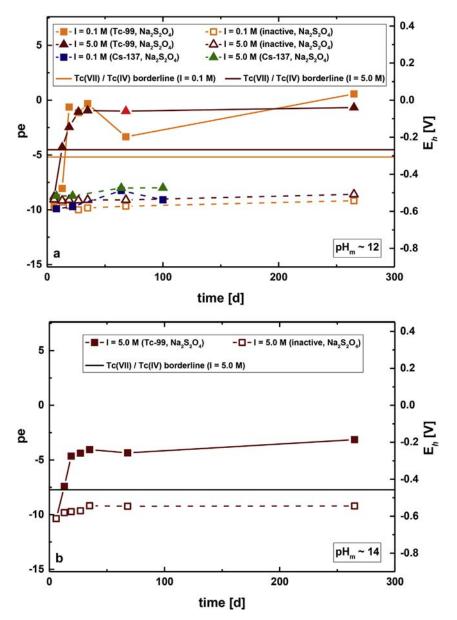
Fig. 4. Evolution of pe with time in NaCl–NaNO₃–NaOH systems in the presence of Na₂S₂O₄, both in the absence and presence of TcO₂·0.6H₂O(am) (denoted as "inactive" and "Tc-99", respectively). Selected systems investigated also in the presence of Cs-137 (and absence of Tc-99). Figure a: pH_m ~ 12; Figure b: pH_m ~ 14. Sample selected for XANES marked as red triangle. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

form in the weakly alkaline to hyperalkaline pH conditions of relevance in the context of repositories for nuclear waste disposal.

The oxidation of Tc(IV) to Tc(VII) is usually controlled by the heterogeneous reaction $TcO_2 \cdot 1.6H_2O(am) + 0.4H_2O(l) \rightleftharpoons TcO_4^- + 4H^+ + 3e^-$ with log K° = −37.8 (Guillaumont et al., 2003). The redox borderline Tc(VII)/Tc(IV) (1:1 distribution of both redox states) is calculated at pe ≈ 1 for pH = 7 and $[Tc]_{tot} = 10^{-5}$ M, thus indicating that the oxidation of Tc(IV) already takes place under mildly reducing conditions. The stepwise reduction of nitrate proceeds through the formation of nitrite according to $NO_3^- + 2H^+ + 2e \rightleftharpoons NO_2^- + H_2O(l)$, with log K° = 27.8 (Puigdomenech and Taxen, 2000). This chemical reaction and equilibrium constant define a N(V)/N(III) redox borderline at pe ≈ 7 as calculated for pH = 7. This implies that according to thermodynamic considerations and in the absence of other redox couples, nitrate should oxidize Tc(IV) to Tc(VII) with the consequent increase in Tc solubility. Existing literature on Tc redox in the presence of nitrate mostly focusses on sediment and aquifer systems

(Burke et al., 2005; Icenhower et al., 2010; Istok et al., 2004; Law et al., 2010; Li and Krumholz, 2008) or in Hanford wastetanks (Chaiko et al., 1995; Levitskaia et al., 2014; Qafoku et al., 2015; Schroeder et al., 2001), conditions which can hardly be extrapolated to deep underground repository conditions and nitrate containing wasteforms. Kobayashi, Sasaki, Kitamura and co workers performed the most comprehensive solubility study with Tc(IV) in the presence of nitrate available to date (Japan Atomic Energy Agency (JAEA), 2014; Kobayashi et al., 2013a). The authors observed a significant increase of the Tc(IV) solubility in some of the investigated systems, but did not provide conclusive evidence on the role of nitrate in the oxidative dissolution of TcO₂·xH₂O(am).

In this context, our work targets the investigation of Tc solubility and redox behaviour in nitrate containing solutions under repository relevant conditions, covering a broad range of nitrate and salt concentrations (0.1 1.0 M and 0.1 5.0 M, respectively), pH (8.5 ≤ pH_m ≤ 14.5) in presence of reductants (Sn(II), Fe(0), Na₂S₂O₄)
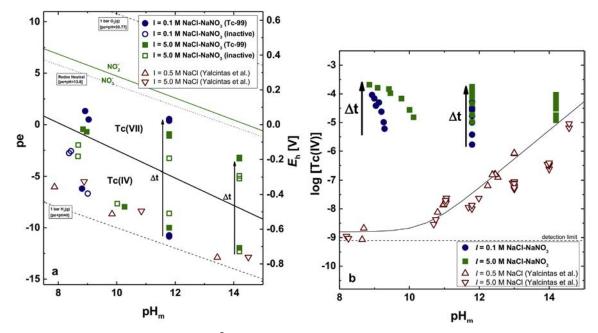
Fig. 5. (a) Pourbaix diagram of Tc calculated for $[Tc]_{tot} = 10^{-5}$ M and $I = 0$, and experimental pH_m and pe values determined in 0.1 and 5.0 M NaCl–NaNO$_3$–NaOH systems with $[NaNO_3]$ = 0.1 and 1.0 M NaNO$_3$ in the presence of 2 mM Sn(II). Samples marked as "inactive" do not contain Tc. (b) Experimental solubility data of Tc (IV) (added as 1–2 mg of TcO$_2$·0.6H$_2$O(am)) in NaNO$_3$–NaCl–NaOH systems at $8.5 \leq pH_m \leq 14.5$ in the presence of Sn(II). Solid line provides the reference Tc(IV) solubility at $I = 0$. All Tc calculations performed with thermodynamic data reported in (Yalçıntaş et al., 2016) and (Guillaumont et al., 2003). Redox borderline NO$_3^-$/NO$_2^-$ calculated at $I = 0$ using thermodynamic data reported in (Puigdomenech and Taxen, 2000). Triangles in figures a and b correspond to experimental data (pH_m, E_h and [Tc]) reported in (Yalçıntaş et al., 2015) under analogous conditions but absence of nitrate.

as well as in absence of reducing chemicals. For this purpose a combination of wet chemistry methods (solubility, pH and E_h measurements) and redox speciation approaches (solvent extraction and X ray Absorption Near Edge Structure, XANES) is used and compared with thermodynamic calculations (Pourbaix and solubility diagrams) using a consistent set of thermodynamic data (Baumann et al., 2017; Rard et al., 1999; Yalçıntaş et al., 2016).

2. Experimental

2.1. Chemicals

NaNO$_3$ (p.a.), NaCl (p.a.), Na$_2$S$_2$O$_4$ (p.a.), Fe powder, CHCl$_3$ (p.a.), NaOH (Titrisol®), HCl (Titrisol®) and colorimetric Nitrate Test (MQuant™) were purchased from Merck. Tetraphenylphosphonium chloride (TPPC, C$_{24}$H$_{20}$ClP, 98%) and SnCl$_2$ (98%) were purchased from Sigma Aldrich. The Fe powder was first washed with a HCl solution (pH ~ 3.5) and then with ultrapure water before adding the solid Fe to the NaCl NaNO$_3$ NaOH background solutions. A purified and radiochemically well characterized ^{99}Tc(VII) stock solution (1.3 M NaTcO$_4$) was used for the electrochemical preparation of an acidic Tc (IV) stock solution (see Section 2.4). A ^{137}Cs(I) stock solution (37 MBq Cs 137 in 0.1 M HCl) was purchased from Isotope Products Laboratories, Burbank, CA, USA and used in test redox systems in the absence of ^{99}Tc (see Section 2.4). Perkin Elmer Ultima Gold™ XR was used as liquid scintillation counting (LSC) cocktail.

All sample preparation and handling was performed in an Ar glovebox at T = (22 ± 2) °C. All solutions were prepared with ultrapure water purified with a Millipore Milli Q Advantage A10 (18.2 MΩ cm at 25 °C, 4 ppb TOC) with Millipore Millipak® 40 0.22 μm, purged with Ar for 1 h before use to remove traces of O$_2$(g) and CO$_2$(g).

2.2. pH_m measurements and E_h measurements

The determination of the proton concentration (pH_m = log [H$^+$], in molal units) was performed using combination pH electrodes (type

ROSS, Orion) calibrated against standard pH buffers (2 ≤ pH ≤ 12, Merck). In salt solutions of ionic strength $I_m \geq 0.1$ mol kg^{-1}, the measured pH value (pH_{exp}) is an operational apparent value related to [H$^+$] by $pH_m = pH_{exp} + A_m$. The empirical correction factor A_m entails both the liquid junction potential and the activity coefficient of H$^+$. The A_m values for the ternary system NaCl NaNO$_3$ were taken from (Herm et al., 2015). In NaCl NaOH solutions with [OH$^-$] ≥ 0.01 M, the proton concentration was calculated using γ_{H^+}, γ_{OH^-} (as calculated by SIT) and the activity of water (a_{H2O}), at each ionic strength, as reported in the NEA TDB (Rard et al., 1999).

Redox potential measurements were performed with Au and Pt combination electrodes with Ag/AgCl reference system (Metrohm) and converted to E_h versus the standard hydrogen electrode by correction for the potential of the Ag/AgCl reference electrode (+208 mV for 3 M KCl at 22 °C). All samples were measured for 15 30 min while agitating continuously. The apparent electron activity (pe = loga_e) was calculated from pe = 16.9 E_h [V], according to the equation $E_h = -\frac{RT\ln10}{F}\log a_{e^-}$. The performance of the redox electrode was tested with a standard redox buffer solution (Schott, +220 mV vs. Ag/AgCl) and provided readings within ± 10 mV of the certified value.

2.3. Determination of Tc total concentration and redox speciation in solution

The total concentration of Tc in the aqueous phase was quantified by LSC. For each sample, 500 μl of supernatant were removed from the sample and centrifuged in 10 kD filters (2 3 nm cut off, Nanosep® and Mikrosep® centrifuge tubes Pall Life Sciences) at 4020 g for 5 min to separate colloids or suspended solid phase particles. 400 μl of the filtrate were then pipetted into 600 μl of 1.0 M HCl. Under standard ambient temperature and pressure, 600 μl of this solution were added to 10 ml of LSC cocktail (Perkin Elmer Ultima Gold™ XR) in a screw cap (PP, 20 ml, Zinsser Analytic) and measured with a LKB Wallac 1220 Quantulus Liquid Scintillation Counter for 30 min each. The background count rate in LSC was determined by repeated measurements of inactive blanks, and the resulting detection limit (3 times the standard
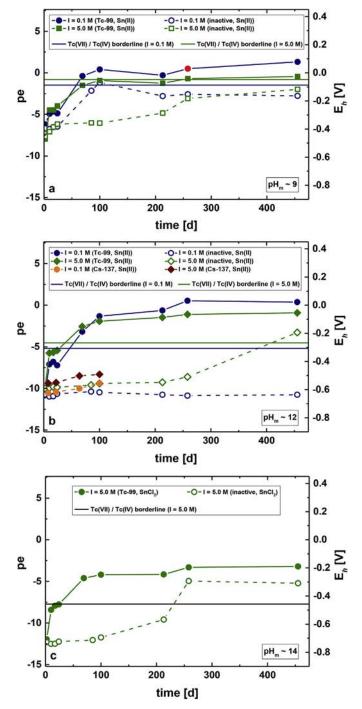
Fig. 6. Evolution of pe with time in for NaCl–NaNO₃–NaOH systems in the presence of Sn(II), both in the absence and presence of TcO₂·0.6H₂O(am) (denoted as "inactive" and "Tc-99", respectively). Selected systems investigated also in the presence of Cs-137 (and absence of Tc-99). Figure a: pH$_m$ ∼9; Figure b: pH$_m$ ∼12; Figure c: pH$_m$ ∼14. Sample selected for XANES marked as red circle. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

deviations of the blank) was calculated as $8 \cdot 10^{-10}$ M.

Liquid liquid extraction was used for the quantification of the redox speciation of Tc in the aqueous phase. 500 µl of the supernatant of each of the technetium containing samples were centrifuged in 10 kD ul trafiltration vials at 4020 g for 5 min 400 µl were then acidified with 1.0 M HCl and pipetted into 400 µl of a solution of 50 mM TPPC in chloroform and shaken for 60 s (Kopunec et al., 1998). After subsequent separation of the aqueous and organic phases by centrifugation, the

Table 2
Fraction of Tc(VII) in the supernatant solution of selected solubility samples as quantified by liquid-liquid extraction with TPPC. Uncertainties: pH$_m$ ± 0.1, liquid-liquid extraction ± 10%.

Reducing agent	Equilibration time	[NaNO₃] [M]	I [M]	pH$_m$	Tc(VII) [%]
none	245 d	0.1	0.1	9.0	99
none	245 d	0.1	0.1	11.8	85
none	245 d	1.0	5.0	8.8	96
none	245 d	1.0	5.0	11.8	92
none	245 d	1.0	5.0	14.2	67
Fe(0)	54 d	0.1	0.1	9.6	99
Fe(0)	54 d	1.0	5.0	9.4	97
Na₂S₂O₄	62 d	0.1	0.1	11.8	48
Na₂S₂O₄	62 d	1.0	5.0	11.8	82
Na₂S₂O₄	62 d	1.0	5.0	14.2	27
Sn(II)	245 d	0.1	0.1	9.0	99
Sn(II)	245 d	0.1	0.1	11.8	72
Sn(II)	245 d	1.0	5.0	9.0	95
Sn(II)	245 d	1.0	5.0	11.8	88
Sn(II)	245 d	1.0	5.0	14.2	67

technetium concentration in the aqueous phase was determined by LSC as described above and attributed to the presence of Tc(IV).

2.4. Redox behaviour and solubility of Tc(IV) in nitrate systems

The Tc(IV) solid phase used in the solubility experiments was pre pared and characterized in a previous study (Baumann et al., 2017). Briefly, a Tc(IV) stock solution was prepared by electrochemical re duction of Tc(VII) in 1 M HCl under Ar atmosphere in a glovebox used exclusively for Tc studies. The resulting Tc(IV) suspension was quan titatively precipitated in a strongly reducing solution (5 mM Na₂S₂O₄) at pH$_m$ ∼12.5 and aged for two months. The solid phase was char acterized as TcO₂·0.6H₂O(am) by means of X ray diffraction (XRD), scanning electron microscopy energy disperse spectrometry (SEM EDS), quantitative chemical analysis (Tc by LSC and Na by inductively coupled plasma optical emission spectroscopy, ICP OES) and thermo gravimetric analysis (TG DTA).

The solubility experiments with TcO₂·0.6H₂O(am) were performed from undersaturation conditions in 0.1 and 5.0 M NaCl NaNO₃ NaOH solutions with [NaNO₃] = 0.1 and 1 M, respectively. Each sample composition was prepared as a redox buffered (presence of 10 mg Fe powder (per sample), 2 mM Sn(II)[1] or 2 mM Na₂S₂O₄ as reducing agent) and an unbuffered (absence of reducing agent) sample. The samples of each ionic strength were divided into solutions with pH$_m$ values ranging from 8.5 to 14.5. The pH$_m$ values were adjusted using HCl NaCl and NaCl NaOH solutions under conservation of the corresponding ionic strengths. A second series of samples was prepared under the same boundary conditions (ionic strength, [NaNO₃], pH$_m$ and presence/ab sence of reducing agents) but in the absence of Tc. A third series of samples prepared in the absence of Tc was spiked with 5 10⁵ Bq ¹³⁷Cs (β emitter with $t_{1/2}$ = 30.17 years). Such activity is similar to the one resulting from the decay of ≈0.5 mg ⁹⁹Tc as used in the Tc solubility experiments. This series of samples aimed at evaluating the possible role of a β radiation dose in redox processes between nitrate and the reducing chemicals used in the present study, although it should be noted that the decay energy of ¹³⁷Cs is slightly higher than that of ⁹⁹Tc. This set of samples resulted in a total of 36 independent batch

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[1] Sn(II) forms sparingly soluble oxo-hydroxides and is characterized by an amphoteric behaviour (formation of cationic and anionic hydrolysis species in acidic and alkaline pH conditions, respectively). Although originally introduced in the system as SnCl₂, the presence of Sn(II) solid phase/s (possibly Sn(OH)₂(s) and/or Sn₆O₄(OH)₄(s)) was observed in all samples at pH$_m$ < 12. For these samples, the total concentration of Sn(II) in solution was clearly below than the original [SnCl₂], although [Sn]$_{aq}$ was not quantified experimentally.
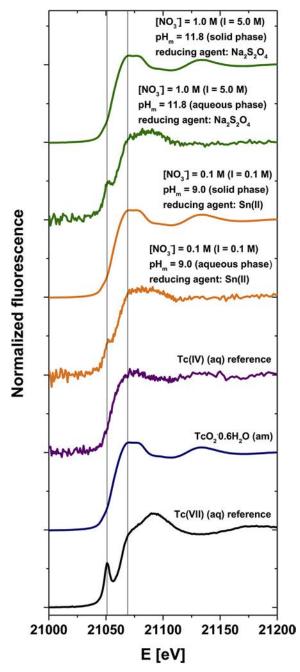
Fig. 7. Tc K-edge XANES spectra of Tc(VII)(aq) reference, original Tc(IV) solid phase (TcO$_2$·0.6H$_2$O(am)), Tc(IV)(aq) reference and 4 selected solubility samples (2 solid + 2 aqueous) in the presence of nitrate.

The figure labels (from top to bottom):

[NO$_3$] = 1.0 M (I = 5.0 M)
pH$_m$ = 11.8 (solid phase)
reducing agent: Na$_2$S$_2$O$_4$

[NO$_3$] = 1.0 M (I = 5.0 M)
pH$_m$ = 11.8 (aqueous phase)
reducing agent: Na$_2$S$_2$O$_4$

[NO$_3$] = 0.1 M (I = 0.1 M)
pH$_m$ = 9.0 (solid phase)
reducing agent: Sn(II)

[NO$_3$] = 0.1 M (I = 0.1 M)
pH$_m$ = 9.0 (aqueous phase)
reducing agent: Sn(II)

Tc(IV) (aq) reference

TcO$_2$·0.6H$_2$O (am)

Tc(VII) (aq) reference

2.5. XANES measurements

XANES spectra were recorded at the ACT Beamline for Actinide Research (2.5 T superconducting wiggler source) at the 2.5 GeV KIT synchrotron radiation source, KIT Campus North (Zimina et al., 2017).

Both solid and aqueous phases were characterized by XANES to evaluate the redox state of Tc. Three reference samples were used in the XANES characterization: (i) 1 10^{-3} M TcO$_4^-$ solution, (ii) the original TcO$_2$·0.6H$_2$O(am) solid phase before contacting nitrate solutions and (iii) the corresponding Tc(IV) aqueous supernatant at pH$_m$ ≈ 12.5 (absence of nitrate, [Tc] ≈ 3.8 10^{-5} M). Two solid and two aqueous samples were selected for XANES measurements: (a) solid phase and corresponding supernatant solution equilibrated for 307 days in 0.1 M NaNO$_3$ with I = 0.1 M at pH$_m$ = 9 ([Tc] ≈ 6.9 10^{-5} M) in the presence of Sn(II), and (b) solid phase and corresponding supernatant solution equilibrated for 124 days in 1.0 M NaNO$_3$ with I = 5.0 M at pH$_m$ = 11.8 ([Tc] ≈ 5.9 10^{-5} M) in the presence of Na$_2$S$_2$O$_4$.

In all cases, approximately 300 µl of the suspension were transferred to a 400 µl polyethylene vial under 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 (polyimide) inside an Ar glovebox and transported to the ACT Beamline, where it was kept under continuous flow of Ar during the course of the measurements.

A pair of Si(311) crystals is used in the double crystal mono chromator (DCM, FMB Oxford, Oxford, United Kingdom). The mono chromatic radiation delivered by the DCM is focused by a Rh coated toroidal mirror into a spot size below 1 mm diameter at the sample position. The intensity of the beam is optimized at 21.5 keV. The in tensity of the incoming beam (I0) is monitored using an Ar filled io nization chamber at ambient pressure. A five pixel LEGe solid state detector (Canberra, Olen, Belgium) is used for collecting Tc K$_\alpha$ fluor escence radiation. The fluorescence signal emitted by the sample is analyzed and filtered by a digital X ray pulse processing system (XMAP DXP module, XIA LLC, Hayward (CA), USA). Tc K edge XAFS spectra of liquid samples are recorded in fluorescence detection mode by re gistering the Tc K$_{\alpha1,2}$ fluorescence yield (18.367 keV (K$_{\alpha1}$) and 18.251 keV (K$_{\alpha2}$)) as a function of the incident photon energy. For solid samples XAFS spectra are recorded simultaneously in fluorescence and transmission mode. The Tc K edge spectra (E(Tc^0 1s) = 21.044 keV) are calibrated against the first derivative X ray absorption near edge structure (XANES) spectrum of a molybdenum metal foil (energy of first inflection point set to E(Mo^0 1s) = 20.000 keV) recorded simulta neously. XAFS data analysis is based on standard procedures, normal izing energy calibrated XANES spectra to their edge jump as im plemented in the Demeter suit of programs version 0.9.26 (Ravel and Newville, 2005).

3. Results and discussion

3.1. Redox behaviour and solubility of Tc(IV) in nitrate systems

In the absence of reducing chemicals, thermodynamic calculations suggest that all nitrate containing samples should feature E_h conditions above the Tc(VII)/Tc(IV) borderline in the pH$_m$ region investigated, considering the redox couple NO$_3^-$/NO$_2^-$. Redox borderlines shown in the following Pourbaix diagrams represent a 1:1 distribution of the respective redox partner (e.g. Tc(VII)/Tc(IV) or NO$_3^-$/NO$_2^-$). As shown in Fig. 1 a, this is true for all systems investigated both in the presence and absence of TcO$_2$·0.6H$_2$O(am). Subsequently and due to the partial oxidation of Tc(IV) to Tc(VII)O$_4^-$, the solubility of technetium (IV) in the presence of nitrate is strongly increased relative to the low solubility expected for Tc(IV) systems in the absence of nitrate (see Fig. 1 b). We note however that a (smaller) fraction of solid phase re mained in all solubility experiments, thus indicating that the oxidation of TcO$_2$·0.6H$_2$O(am) to Tc(VII) was incomplete. The maximum

experiments (see Table 1). pH$_m$ and E_h values of prepared background electrolytes were measured after 2 days to ensure stable pH$_m$ conditions and, in the case of buffered samples, that the targeted reducing starting conditions for Tc(IV) samples had been reached. After confirming that all solutions met the necessary requirements, 1 2 mg of Tc(IV) solid were washed three times with 1 ml of the respective background elec trolyte solution and then added to 20 ml of matrix solution in 50 ml screw cap centrifuge vials (Nalgene™, Thermo Scientific) to form the final active Tc(IV) samples. pH$_m$, E_h and Tc concentrations in the so lubility samples were measured at regular time intervals for up to 460 days.

concentration of Tc in solution is estimated as $5 \cdot 10^{-4}$ M, assuming the complete dissolution of 1–2 mg ^{99}Tc(IV) solid in 20 ml of solution.

Previous studies have shown that reducing agents such as Sn(II), $Na_2S_2O_4$ or Fe powder are able to retain technetium as Tc(IV) for prolonged periods of time (Baumann et al., 2017; Kobayashi et al., 2013b; Liu et al., 2005; Liu et al., 2007; Steigman and Eckelman, 1992; Steigman et al., 1975; Warwick et al., 2007; World Nuclear Association (WNA), 2014; Yalçıntaş et al., 2016; Yalçıntaş et al., 2015). In a recent study on the redox behaviour of Tc(IV)/Tc(VII), long term stable reducing conditions were observed in 0.5 and 5.0 M NaCl solutions containing Fe powder and $pH_m \leq 9$ (see red triangles in Fig. 2a) (Yalçıntaş et al., 2015). In the present work, Fe powder was not able to retain persistent reducing conditions at $pH_m \sim 9$ in the presence of 0.1–1.0 M $NaNO_3$. Within hours of adding $NaNO_3$ to the Fe(0) systems, E_h increased towards the Tc(IV)/Tc(VII) redox borderline and subsequently established more oxidizing conditions (compared to nitrate free systems in the presence of Fe powder) during the course of the experiments (see Fig. 2 a and b). Note that a fast reaction between nitrate and Fe(0) under near neutral pH conditions has been previously described in the literature (Alowitz and Scherer, 2002).

$Na_2S_2O_4$ has been reported to buffer strongly reducing conditions under hyperalkaline pH_m conditions (Riedel and Janiak, 2015; Wiberg and Hollemann, 2008). The impact of nitrate in $Na_2S_2O_4$ buffered systems is shown in Fig. 3 a (pH_m and pe values) and Fig. 3 b (solubility of Tc). Because of the known decomposition of $Na_2S_2O_4$ in weakly alkaline and acidic pH_m conditions (with consequent increase in E_h) (Lem and Wayman, 1970; Wayman and Lem, 1970), only samples with $pH_m \geq 11.5$ were considered in the present study.

Fig. 3 a shows that (within the time frame investigated for this system, $t \leq 260$ days) nitrate induces only a slight increase in E_h for those $Na_2S_2O_4$ buffered systems in the absence of $TcO_2 \cdot 0.6H_2O$(am). On the contrary, all samples containing $TcO_2 \cdot 0.6H_2O$(am) show a significant increase in E_h above the Tc(IV)/Tc(VII) redox borderline independent of nitrate concentration or ionic strength. This observation is consistent with experimental solubility data shown in Fig. 3 b, where the significant increase in [Tc] (compared to the solubility of Tc(IV) in the absence of nitrate) can be attributed to an oxidative dissolution of $TcO_2 \cdot 0.6H_2O$(am) with the corresponding formation of Tc(VII) in the aqueous phase. Colorimetric tests to distinguish nitrate from reduced nitrite performed in selected samples of both systems (absence/presence of $TcO_2 \cdot 0.6H_2O$(am)) show the presence of nitrite only in those systems containing $TcO_2 \cdot 0.6H_2O$(am), thus confirming that the observed oxidation of Tc(IV) is induced by the reduction of nitrate to nitrite.

Fig. 4 a and 4 b show the experimental pe values as a function of time for NaCl–$NaNO_3$–NaOH systems in the presence of $Na_2S_2O_4$, both in the absence and presence of $TcO_2 \cdot 0.6H_2O$(am). Both figures show that the significant increase in pe observed in the presence of $TcO_2 \cdot 0.6H_2O$(am) (6–10 pe units) occurs within the first 20 days of contact time, whereas a far smaller increase in pe (< 1 pe unit) is observed in the absence of $TcO_2 \cdot 0.6H_2O$(am) within 270 days. These results suggest a catalytic effect of $TcO_2 \cdot 0.6H_2O$(am) on the redox process occurring under these conditions. Many transition metals (e.g. Fe, Pt, Pd, Rh, among others) are known to catalyse both inorganic and organic reactions (Appl, 2000; Brückner, 2004; Carey and Sundberg, 2007a; b; Ostwald, 1907). Technetium itself has also been reported to exhibit catalytic behaviour e.g. in hydrocarbon reforming but is also known to accelerate the oxidation of hydrazine by nitric acid which in the absence of technetium is very slow except at increased temperatures and acidities (Blackham and Palmer, 1973; Garraway and Wilson, 1984).

Sn(II) is known to be a strong reducing agent (close to the border of water reduction to H_2) in a broad pH_m range extending from very acidic to hyperalkaline conditions (Riedel and Janiak, 2015; Wiberg and Hollemann, 2008). The impact of nitrate in Sn(II) buffered systems is shown in Fig. 5 a (pH_m and pe values) and Fig. 5 b (solubility of Tc).

Fig. 5 a shows that nitrate promotes an increase of E_h in Sn(II) buffered systems, both in the absence and presence of $TcO_2 \cdot 0.6H_2O$ (am). Fig. 5 b confirms that, for the samples containing Tc, this increase in E_h is correlated with a significant increase in the concentration of Tc as expected for the oxidative dissolution of $TcO_2 \cdot 0.6H_2O$(am) to Tc(VII). The colorimetric nitrate/nitrite test shows the presence of nitrite in these samples, thus supporting that oxidation is triggered by the reduction of nitrate. Fig. 6 a–6 c show the experimental pe values as a function of time for NaCl–$NaNO_3$–NaOH systems in the presence of Sn (II), both in the absence and presence of $TcO_2 \cdot 0.6H_2O$(am). These figures confirm that the increase in E_h is significantly accelerated in the presence of $TcO_2 \cdot 0.6H_2O$(am), again underpinning the role of this solid phase in catalysing the redox reaction between nitrate and the reduced species in the system. The precise mechanism for the technetium case is not fully known yet, but heterogeneous catalysis is generally considered to proceed by surface adsorption processes (Riedel and Janiak, 2015; Wiberg and Hollemann, 2008). Amorphous surfaces, due to their increased overall surface area, are known to exhibit increased catalytic properties compared to more crystalline structures(Wiberg and Hollemann, 2008). Fig. 6 a–6 c also show that E_h values reach the stability field of Tc(VII) faster with increasing pH_m. This can be qualitatively rationalised by the known stabilisation of higher oxidation states with increasing pH_m, and further quantitatively assessed with the chemical reaction (1) and corresponding chemical equation (2) describing the oxidative dissolution of $TcO_2 \cdot 0.6H_2O$(am):

$$TcO_2 \cdot 0.6H_2O(am) + 1.4H_2O(l) \rightleftharpoons TcO_4^- + 4H^+ + 3e^- \qquad (1)$$

$$\log K^\circ_{IVs-VII} = \log a(TcO_4^-) - 4 pH - 3 pe - 1.4 \log a_w \qquad (2)$$

E_h measurements performed for up to 100 days in Sn(II) and $Na_2S_2O_4$ systems in the presence of ^{137}Cs showed no significant changes in the initial redox conditions (see Figs. 4 and 6). This observation is in line with E_h measurements in "inactive" systems, and thus indicates that the β^- radiation dose in these samples (as well as in presence of ^{99}Tc) does not play a relevant role in the redox processes on going in the investigated systems.

3.2. Tc redox speciation

The results of liquid–liquid extraction in the supernatant solution are shown in Table 2 as the fraction of Tc(VII) present in the supernatant of selected solubility samples. In most cases, liquid–liquid extraction confirms the predominance of Tc(VII) in solution. This observation is in line with E_h and solubility measurements, as well as with thermodynamic calculations considering the excess of nitrate in the system.

3.3. XANES measurements

Fig. 7 shows the XANES spectra of the selected 3 reference systems and 4 solubility samples (2 solid + 2 aqueous) in the presence of nitrate. The shape of the individual XANES spectra and the presence of the characteristic Tc(VII) pre peak (transition 1s→4d signature) unequivocally prove the predominance of Tc(VII) in the supernatant solution of the samples investigated (Allen et al., 1997; Lukens et al., 2004; Saslow et al., 2017). The shape of the individual XANES spectra and the energy position of the respective inflection points of the solid phases measured show the sole presence of Tc(IV) above the detection limit of the technique (< 10% in mol fraction) in all solid phases and thereby suggest that there was no solid phase transformation during the course of the experiments. These results are in line with the predominance of Tc(VII) expected in the aqueous phase according to (pe + pH_m) values measured experimentally and the redox speciation data obtained by liquid–liquid extraction.

4. Conclusions

The impact of nitrate on the redox potential of different reducing systems (Fe powder, $Na_2S_2O_4$, Sn(II)) and the corresponding effect on the Tc redox and solubility were investigated in alkaline, dilute to concentrated NaCl systems.

Nitrate induces an increase in E_h in most of the evaluated systems. This increase is especially important (6 10 pe units) and faster (5 50 days) in the presence of a Tc(IV) solid phase, $TcO_2 \cdot 0.6H_2O$(am). This observation hints towards a catalytic role of the Tc(IV) solid phase in the redox processes between nitrate and the reducing systems in vestigated. Nitrate also promotes a very significant increase in the Tc solubility in samples with a Tc(IV) solid phase (1 6 log units, de pending upon pH_m and ionic strength). Liquid liquid extraction and XANES confirm that technetium is predominantly found as Tc(VII) in the aqueous phase, thus supporting that the increase in solubility is due to the oxidative dissolution of $TcO_2 \cdot 0.6H_2O$(am). The identification of nitrite in solution by a colorimetric test confirms that nitrate is the redox counterpart responsible of the oxidation of Tc(IV). The evolution of E_h in nitrate containing systems with [137]Cs (and absence of ^{99}Tc) is analogous to that of inactive systems, thus indicating that the catalytic role of technetium is not driven by the β radiation dose of ^{99}Tc in the solubility experiments with $TcO_2 \cdot 0.6H_2O$(am).

Our new experimental observations indicate that nitrate is able to oxidize Tc(IV) if present in excess over reducing agents. Such conditions are also conceivable in a repository for low and intermediate level waste. Our data clearly show that the role of nitrate as oxidant is fa cilitated by the presence of a Tc(IV) solid phase, although kinetically hindered. This catalytic effect possibly extends to other transition me tals available in the repository (e.g. Fe). Further experiments are on going at KIT INE to evaluate the effect of nitrate on other redox sen sitive systems of relevance in the context of nuclear waste disposal. Such investigations are of relevance for correctly assessing the source term of specific ILW/LLW wastes featuring large nitrate inventories.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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