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

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ABSTRACT

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 $t \leq 450$ 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 chemical 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 underground 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 process) 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	$Na_2S_2O_4$	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	$Na_2S_2O_4$	11.8, 14.2
	5.0	1.0	Sn(II)	≈ 9, 11.8, 14.2
1–2 mg $^{99}TcO_2$·0.6H_2O(am) "active"	0.1	0.1, 0.09[a]	none	≈ 9, 11.8
	0.1	0.1	Fe powder	≈ 9
	0.1	0.09	$Na_2S_2O_4$	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	$Na_2S_2O_4$	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	$Na_2S_2O_4$	11.8
	0.1	0.09	Sn(II)	11.8
	5.0	1.0	none	11.8
	5.0	1.0	$Na_2S_2O_4$	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).

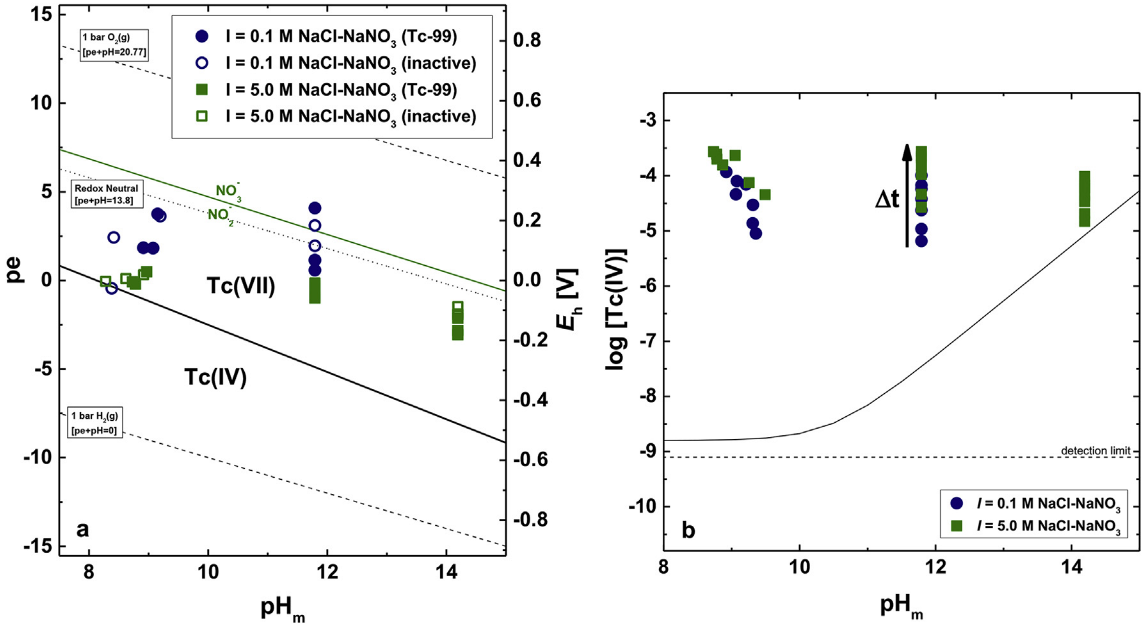

Fig. 1. (a) Pourbaix diagram of Tc calculated for $[Tc]_{tot} = 10^{-5}$ M and $I = 0$, and experimental pH_m and pe values determined in 0.1 and 5.0 M NaCl–$NaNO_3$–NaOH systems with [$NaNO_3$] = 0.1 and 1.0 M. Samples marked as "inactive" do not contain Tc; (b) Experimental solubility data of Tc(IV) (added as 1–2 mg of TcO_2·0.6H_2O(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), $Na_2S_2O_4$, hydrazine, Eu(II) or Fe powder), Tc is characterized by a very low solubility (controlled by TcO_2·xH_2O(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;