Solubility and hydrolysis of Tc(IV) in KCl solutions

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Introduction

Technetium-99 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 character, ^{99}Tc is a very relevant radionuclide in Performance Assessment exercises (PA) of repositories for radioactive waste. Although several oxidation states of technetium have been reported in literature, +VII and +IV are the most stable in the absence of complexing ligands. Tc(IV) forms sparingly soluble hydrous oxides (TcO$_2$·xH$_2$O(s)) under reducing conditions as those expected in deep underground repositories. Potassium is an abundant cation in different types of groundwaters, but can also be found in high concentrations (up to 0.4 M) in cementitious environments as those considered in several concepts for the disposal of low and intermediate level (L/ILW) and high level waste (HLW). In this context, an appropriate understanding of the Tc(IV) solubility and hydrolysis in dilute to concentrated KCl solutions is required for assessing the behaviour of technetium in cement-bearing underground repositories for radioactive waste disposal.

Experimental

Sample preparation

- Batch experiments in Ar atmosphere
- Undersaturation approach in 0.1–4.58 m KCl
- 1–2 mg ^{99}TcO$_2$·xH$_2$O per batch sample
- 2 ≤ pH$_m$ ≤ 14.5
- Reducing chemicals: Na$_2$S$_2$O$_4$ and Sn(II)

Measurements

- Empirical determination of A-values for KCl systems
- pH measurements: pH$_m$ = -log m$_{H^+}$ = pH$_{exp}$ + A$_m$
- E_h measurements
- [Tc] by LSC; [Tc(IV)] by solvent extraction
- Solid phase characterization: XRD, SEM-EDS, chemical analysis

## Results and Discussion: Redox Measurements and Solubility

Determination of empirical A values
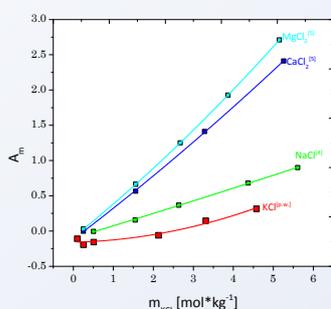
$$A_{KCl} = -0.160 + 0.0132\ m_{KCl} + 0.0204\ (m_{KCl})^2$$

- $A_m(I)$ = -log m$_{H^+}$ - pH$_{exp}$
- I = 0.10, 0.25, 0.51, 2.13, 3.31, 4.58 m KCl
- 2.0*10^{-2} m ≤ m$_{H^+}$ ≤ 6.25*10^{-4} m

Redox measurements
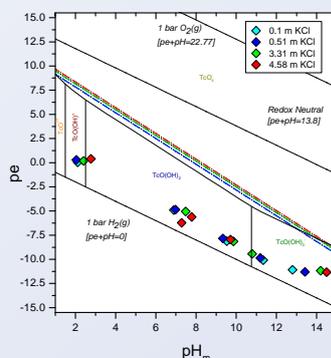
- Tc(VII)/Tc(IV) redox borderline calculated for the chemical reaction:

$$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO_2 \cdot xH_2O(s) + (2-x)H_2O$$

- Aqueous speciation calculated at I = 0 using NEA-TDB[1]

- *All measured E_h values fall well below the Tc(VII)/Tc(IV) borderline ⇒ predominance of Tc(IV) in the solubility experiments*

Solubility of Tc(IV) in KCl solutions
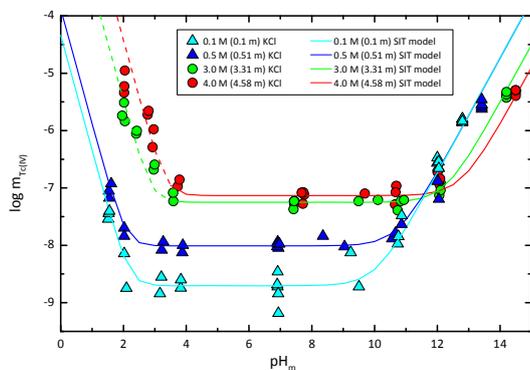
- **Acidic pH region:** a steep increase in solubility observed with increasing the ionic strength agrees well with NaCl system [2].
- **Near-neutral pH region:** significant increase in Tc(IV) solubility observed with increasing [KCl]. Unexpected effect if assuming the predominance of neutral species TcO(OH)$_2$(aq) [1]. Effect not observed in concentrated NaCl systems [2]. Further experiments in KCl–NaCl mixtures and NaNO$_3$-KNO$_3$ systems confirmed the single effect of K$^+$.
- **Hyper-alkaline pH region:** solubility of Tc(IV) increases with a well-defined slope of +1 in this pH region, indicating the predominance of the anionic hydrolysis species TcO(OH)$_3^-$. With increasing [KCl], the solubility of Tc(IV) slightly decreases.
- Solid and aqueous phase characterization confirmed the predominance of Tc(IV) in the aqueous phase and TcO$_2$.xH$_2$O(am) controlling the solubility.

SIT Model for Tc^{4+}–H$^+$–K$^+$–OH$^-$–Cl$^-$–H$_2$O system

Acidic pH region (pH$_m$ ≤3-4 , depending upon ionic strength):

- Slope of −2
- TcO$_2$·1.6H$_2$O(s) + 2H$^+$ ⇌ TcO^{2+} + 2.6 H$_2$O(l)   log$^*K^0_{s,(1,0)}$ ≤ -4.4 [1]
- ε(TcO^{2+},Cl$^-$) = -0.5 (unrealistic value) => estimated as ε(M^{2+},X$^-$)~0.15 [3]
- Tc$_n$O$_p^{(4n-2p)+}$ and/or Tc$_n$O$_p$Cl$_m^{(4n-2p-m)-}$ species suspected!! [4]

Near- neutral pH region (4 ≤ pH$_m$ ≤ 11):

- pH-independent region
- TcO$_2$·1.6H$_2$O(s) ⇌ TcO(OH)$_2$(aq) + 0.6 H$_2$O   log$^*K^0_{s,(1,2)}$ = -8.4 ± 0.9 [1]
- ε(TcO(OH)$_2$(aq),K$^+$) = -0.3 (unrealistic value) => new species proposed
- TcO$_2$ ·1.6H$_2$O(s) + K$^+$ ⇌ KTcO(OH)$_2^+$ + 0.6H$_2$O
- log$^*K^0_{s,(1,1,2)}$ = -7.7±0.01 (p.w.) ε(KTcO(OH)$_2^+$, Cl$^-$) = 0.03±0.00 (p.w.)
- log$^*K^0_{s,(1,2)}$ < -8.8 (p.w.)   ε(TcO(OH)$_2$(aq),K$^+$) = 0 (SIT definition)

Hyper-alkaline pH region (pH$_m$ ≳ 11):

- Slope of +1
- TcO$_2$·1.6H$_2$O(s) + 0.4 H$_2$O(l) ⇌ TcO(OH)$_3^-$ + H$^+$ log$^*K^0_{s,(1,3)}$ = 19.3 ± 0.9 [1]
- log$^*K^0_{s,(1,3)}$ = -19.2 ± 0.4 (p.w.) ε(TcO(OH)$_3^-$, K$^+$) = 0.20±0.06 (p.w.)

[Pitzer model on-going]

Conclusions

- Experimental Tc(IV) solubility data in dilute KCl systems can be properly explained with the current NEA–TDB hydrolysis scheme.
- New species need to be defined to adequately explain Tc(IV) solubility in acidic systems with high [Cl$^-$]. In agreement with previous spectroscopic evidence, species of the type Tc$_n$O$_p^{4n-2p}$ and Tc$_n$O$_p$Cl$_m^{4n-2p-m}$ are under evaluation in the thermodynamic model.
- The formation of the species KTcO(OH)$_2^+$ is proposed to explain the significant increase in solubility observed in the near-neutral pH.
- Thermodynamic and activity models (SIT, Pitzer) for the system Tc^{4+}–H$^+$–K$^+$–OH$^-$–Cl$^-$–H$_2$O are derived based on the newly generated experimental solubility data.

References

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[4] Vichot L, Fattahi M., Musikas Cl., Grambow B., Radiochim. Acta, 91, **2003**, 263-271.

[5] M. Altmaier et al., Geochimica et Cosmochimica Acta Supplement 67, **2003**, 3595-3601.