Redox behaviour of Tc(VII)/Tc(IV) couple in diluted NaCl solution and various reducing systems

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Introduction

Experimental

Results and discussion
- Tc(VII)/Tc(IV) redox behavior in each reducing system
- general trend of Tc(VII)/Tc(IV) redox behavior
- solubility of Tc(IV) hydrous oxides under reducing condition

Conclusion

Contents
Introduction - Safety assessment of radioactive waste disposal -

For the safety assessment of nuclear waste repositories,
- Analysis of isolation potential
- Assessment of the retention capabilities
- Assessment of radionuclide mobility
- Analysis of consequences

Migration behavior of radionuclide

For a reliable prediction of radionuclide solubility limits, understanding of the mechanism and thermodynamic data are needed.

Introduction - Tc migration behavior in geological system -

- Technetium-99 in nuclear waste repositories:
  - produced by the fission of $^{235}$U and $^{239}$Pu, included in radioactive waste.
  - long half life (2.1·10$^5$ y), potential environmental mobility.

- Tc migration behavior closely related to the Tc oxidation state:
  (in geological system, +IV, or +VII as stable state)
  - Tc(VII): as $\text{TcO}_4^-$ in aqueous system, highly soluble, mobile.
  - Tc(IV): precipitate as sparingly soluble Tc(IV) oxide ($\text{TcO}_2\times x\text{H}_2\text{O}(s)$), strong retention.

=> Reduction/Oxidation (Redox) behavior of Tc(VII) / Tc(IV) couple is decisive parameter for the migration behavior of Tc in relevant geological systems.
**Introduction - Redox behavior of Tc(VII)/Tc(IV) couple** -

- **Redox reaction of Tc(VII)/Tc(IV) \( (\text{TcO}_2\cdot x\text{H}_2\text{O}(s)) \)**

  \[
  \text{TcO}_4^- + 3\text{e}^- + 4\text{H}^+ \rightleftharpoons \text{TcO}_2\cdot x\text{H}_2\text{O}(s) + (2-x)\text{H}_2\text{O}
  \]

  \[ E^\circ = 0.746 \pm 0.012 \text{ V} \quad (\log K^\circ = 37.8 \pm 0.6) \quad \text{(NEA-TDB review, Rard et al. (1999))} \]

  Standard potential for reduction \( (E^\circ) \) (equilibrium constant: \( K^\circ \)) determined by electrochemical studies using well-defined \( \text{TcO}_4^- / \text{TcO}_2\cdot x\text{H}_2\text{O}(s) \) couple.

- **Redox behavior in laboratory/natural systems (homogeneous and heterogeneous systems)**

  - Reduction of Tc(VII) in the presence of iron (Fe(II)) minerals observed. (Bondietti et al. (1977))
  - Extremely slow reduction by Fe\(^{2+}\) depending on [Fe\(^{2+}\)], pH, [Tc(VII)]. (Ben Said et al. (1998))
  - Rapid reduction of Tc(VII) to a precipitated Fe/Tc(IV) form at pH 7, 8, while no reduction at pH 6. (Zachara et al. (2007))

  \[ \Rightarrow \text{Systematization of Tc redox behavior as a robust base in order to extend thermodynamics to various laboratory/natural systems.} \]

**Introduction - Objective of this study** -

Tc(VII)/Tc(IV) stability field calculated from

- **basic geochemical parameters** \((E_\mu, \text{pH})\).
- **thermodynamic constants** (solubility product, complex formation constant, etc).

This study:

Tc(VII)/Tc(IV) redox behavior in various reducing systems (various \( E_\mu, \text{pH} \) conditions, homogeneous, heterogeneous systems)

- to check applicability of \( E_\mu, \text{pH} \) concept.
- to compare with thermodynamic calculations.
- to confirm Tc(IV) stability fields and solubility.

Systematize Tc(VII)/Tc(IV) redox behavior with pH-\( E_\mu \) diagram.
Experimental - Sample preparation and measurement -

• Sample preparation
  TcO$_4^-$ stock solution added to 15 ml 0.1 M NaCl/NaOH pre-equibrated with various reducing systems under Ar atmosphere. Initial TcO$_4^-$ concentration was 10$^{-5}$ M.

• Reducing systems (homogeneous and heterogeneous)
  - 3.10 mM hydroquinone (HQ)
  - 3 mM sodium anthraquinone / anthrahydroquinone disulfonate; AQDS / AH$_2$QDS = 1:3
  - 1.6 mM 2-hydroxy-1,4-naphthoquinone (Lawsone); oxidized form / reduced form = 1:3
  - 1 mM Sn(II) dissolved (acidic, alkaline pH) / suspension of Sn(II) hydroxide (neutral pH)
  - 1 mM sodium dithionite (Na$_2$S$_2$O$_4$)
  - Fe(II) / Fe(III) dissolved (acidic pH) / suspension (alkaline pH) (Fe(II) / Fe(III) = 1 mM / 0.1 mM)
  - 1 mg / 15 ml Fe powder suspensions

• Measurement
  After given periods, pH and E$_h$ of the systems measured, supernatants ultra-filtrated (10kD membrane).
  - Total Tc concentration in the solutions
    Tc concentration in the filtrate was determined by LSC.
  - Tc(VII) concentration in the solutions; solvent extraction
    TcO$_4^-$ was extracted to chloroform using 1 mM tetraphosphonylchloride (TPPC).

Redox behavior in quinone systems:
• Hydroquinone (HQ)
• Anthraquinone / anthrahydroquinone disulfonate (AQDS / AH$_2$QDS)
• 2-hydroxy-1,4-naphthoquinone (Lawsone); oxidized form / reduced form
Results and discussion - Hydroquinone solutions -

Hydroquinone solutions (3 mM, 10 mM)

Calculated equilibrium line from NEA-TDB
\[
\text{TcO}_4^- + 4H^+ + 3e^- \rightleftharpoons \text{TcO}_2\cdot x\text{H}_2\text{O(s)} + (2-x)\text{H}_2\text{O}
\]
\[
\log K = 37.8, [\text{Tc}]_{\text{tot}} = 10^{-5} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>pH</th>
<th>log [Tc] aqueous</th>
<th>log [Tc] organic</th>
<th>Tc(VII) / [Tc]tot %</th>
</tr>
</thead>
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<tr>
<td>A2-2</td>
<td>3.89</td>
<td>-7.28</td>
<td>-5.14</td>
<td>99.3</td>
</tr>
<tr>
<td>A2-4</td>
<td>8.48</td>
<td>-7.40</td>
<td>-5.09</td>
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<tr>
<td>A2-6</td>
<td>12.25</td>
<td>-7.22</td>
<td>-5.12</td>
<td>99.2</td>
</tr>
</tbody>
</table>

No reduction
Results and discussion - AQDS/AH2QDS redox buffer solutions -

AQDS / AH2QDS redox buffer solutions (0.75 mM : 2.25 mM)

Results and discussion - Lawsone (oxidized form / reduced form) redox buffer solutions -

Lawsone redox buffer solutions (oxidized form : reduced form = 0.4 mM : 1.2 mM)
Results and discussion - Kinetic effect -

**AQDS/AH₂QDS buffer solutions:**
- Slow reduction at pH 10.5.
- No reduction at pH > 11.3.

**Lawsone buffer solutions:**
- Extremely slow reduction at neutral and alkaline pH.

![Kinetic behavior in AQDS / AH₂QDS = 1 : 3 system](image1)

![Kinetic behavior in Lawsone redox buffer solutions (oxidized form / reduced form = 1:3) system](image2)

Redox behavior in strongly reducing systems:
- Sn(II) dissolved (acidic, alkaline pH) / suspension of Sn(II) hydroxide (neutral pH)
- Sodium dithionite (Na₂S₂O₄)
Results and discussion - Sn(II) solutions and suspensions of Sn(II) hydroxide -

**Sn(II) solutions and suspensions of Sn(II) hydroxide (1 mM)**

Calculated equilibrium line from NEA-TDB

\[
\text{TCO}_4^- + 4H^+ + 3e^- \rightleftharpoons \text{TCO}_2 \cdot x \text{H}_2\text{O(s)} + (2-x)\text{H}_2\text{O}
\]

\[
\log K = 37.8, [\text{TC}]_{\text{eq}} = 10^{-5} \text{ M}
\]

Solubility increase with increasing pH

\[
\text{TCO}_2 \cdot x \text{H}_2\text{O(s)} + \text{OH}^- \rightleftharpoons \text{TCO(OH)}_{3-x}^- + (x-1)\text{H}_2\text{O}
\]

Formation of anionic Tc(IV) complex
Results and discussion - Sodium dithionite solutions -

Na$_2$S$_2$O$_4$ solutions (1 mM)

Rather fast reduction in Na$_2$S$_2$O$_4$ solutions, but slower than in Sn(II) system.

Redox behavior in iron systems:
- Fe(II) / Fe(III) dissolved (acidic pH) / suspension (alkaline pH)
- Fe powder suspensions
Results and discussion - Fe(II)/Fe(III) solutions and precipitates -

Fe(II) / Fe(III) dissolved / suspension (Fe(II) / Fe(III) = 1 mM / 0.1 mM)

No reduction below pH 6

Results and discussion - Fe powder suspensions -

Fe powder suspensions (1 mg / 15 ml)

Calculated equilibrium line from NEA-TDB

\[ \text{TcO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{TcO}_2\\cdot x\text{H}_2\text{O(s)} + (2-x)\text{H}_2\text{O} \]

\[ \log K = 37.8, [\text{Tc}]_{\text{tot}} = 10^{-5} \text{ M} \]
Results and discussion - Kinetic effect -

Fe(II)/Fe(III) solutions and precipitates:
- No reduction in the acidic pH range (pH < 6).
- Fast reduction (within 3 days) at pH 6 and 8, where Fe(II)/Fe(III) precipitates formed.

Fe powder suspensions:
- At pH 6 < 10, considerably fast reduction (within 3 days).
- At pH > 10, no reduction of Tc(VII).

Discussion - General interpretations of the redox behavior -

1. Experimental borderline for Tc(VII) reduction independent of reducing systems.
   pH, Eₚ values are decisive parameters for reduction.

2. Kinetics related to Eh values (mostly in homogeneous solutions.)

Reduction rate correlating pe values.

Redox behaviour of Tc(VII) in 0.1 M NaCl/NaOH. Open symbols: reduced, filled symbols: not reduced.
Discussion - Comparison with thermodynamic calculation -

Calculated equilibrium line from NEA-TDB
\[ \text{TcO}_4^- + 4H^+ + 3e^- \rightleftarrows \text{TcO}_2\cdot xH_2O(s) + (2-x)H_2O \]
\[ \log K = 37.8, \ [\text{TcO}_4^-] = 10^{-5} \text{ M} \]

\( pe = \frac{-1}{3}(4 \cdot pH + \log K \cdot [\text{TcO}_4^-]) \)

3. Experimental borderline slightly lower than the calculated equilibrium line of \( \text{TcO}_2\cdot xH_2O(s) \) from NEA-TDB.

\( \Rightarrow \) more soluble solids: \( \text{TcO}_2\cdot xH_2O \) (coll, hyd).

(related to particle size effect...)

Redox behaviour of Tc(VII) in 0.1 M NaCl/NaOH. Open symbols: reduced, filled symbols: not reduced.

Discussion - OUTLOOK: Solubility of Tc(IV) oxide -

Comparison of Tc(IV) solubility data obtained under reducing conditions with literature data and calculated lines.

Further studies on...
- Tc(IV) solubility at low ionic strength.
- Tc(IV) solubility in the absence and presence of CO\(_2\).
- Tc(IV) solubility at high ionic strength (Na, Mg, Ca): relevant to waste disposal in rock salt mine.
Conclusion

• The reduction of Tc(VII) occurred both in heterogeneous suspensions and in homogeneous solutions (without solids). A reduction borderline independent of reducing systems.

• Under the borderline, the reduction rate was correlated to the pe values in general, but also may be correlated to the existence of solid.

• The experimental borderline for the reduction was observed to be lower than the calculated equilibrium line of TcO₂·xH₂O(s). This may suggest another solid phase with different solubility. Further confirmation of solids is needed.