

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



7th International Symposium on Technetium and Rhenium – Science and Utilization  
July 4 - 8, 2011, Moscow, Russia

**Kobayashi, T.<sup>1</sup>, Gaona, X.<sup>1</sup>, Fellhauer, D.<sup>1,2</sup>, Altmaier, M.<sup>1</sup>**

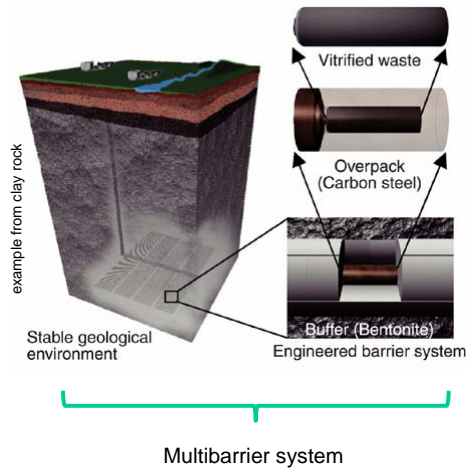
<sup>1</sup> Institut für Nukleare Entsorgung (INE), Karlsruhe Institute of Technology, Germany

<sup>2</sup> Institute for Transuranium Elements (ITU), Joint Research Centre, European Commission, Germany

## Contents

- 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

### Geological disposal of radioactive waste



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.

### • Technetium-99 in nuclear waste repositories:

- produced by the fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ , included in radioactive waste.
- long half life ( $2.1 \cdot 10^5$  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** ( $\text{TcO}_2 \cdot x\text{H}_2\text{O(s)}$ ), 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) ( $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ )



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

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

### • Redox behavior in laboratory/natural systems (homogeneous and heterogeneous systems)

- Reduction of Tc(VII) in the presence of iron (Fe(II)) minerals observed. (Bondiotti et al. (1977))
- Extremely slow reduction by  $\text{Fe}^{2+}$  depending on  $[\text{Fe}^{2+}]$ , pH,  $[\text{Tc(VII)}]$ . (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))

...

=> 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

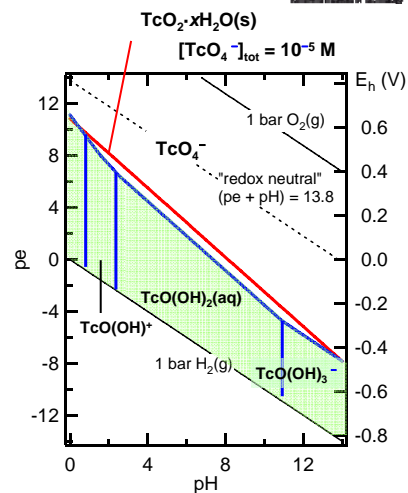
- **basic geochemical parameters** ( $E_h$ , pH).
- **thermodynamic constants** (solubility product, complex formation constant, etc).

This study:

Tc(VII)/Tc(IV) redox behavior in various reducing systems (various  $E_h$ -pH conditions, homogeneous, heterogeneous systems)

- to check applicability of  $E_h$ /pH concept.
- to compare with thermodynamic calculations.
- to confirm Tc(IV) stability fields and solubility.

Systematize Tc(VII)/Tc(IV) redox behavior with pH- $E_h$  diagram.



Tc(VII)/Tc(IV) stability fields calculated from thermodynamic data (NEA-TDB)

## Experimental - Sample preparation and measurement -



### •Sample preparation

TcO<sub>4</sub><sup>-</sup> stock solution added to 15 ml 0.1 M NaCl/NaOH pre-equibrated with various reducing systems under Ar atmosphere. Initial TcO<sub>4</sub><sup>-</sup> concentration was 10<sup>-5</sup> M.

### •Reducing systems (homogeneous and heterogeneous)

- 3, 10 mM hydroquinone (HQ)
- 3 mM sodium anthraquinone / anthrahydroquinone disulfonate; AQDS / AH<sub>2</sub>QDS = 1:3
- 1.6 mM 2-hydroxy-1,4-naphthoquinone (Lawsonite); 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<sub>2</sub>S<sub>2</sub>O<sub>4</sub>)
- Fe(II) / Fe(III) dissolved (acidic pH) / suspension (alkaline pH) (Fe(II) / Fe(III) = 1 mM / 0.1 mM)
- 1mg / 15 ml Fe powder suspensions

### •Measurement

After given periods, pH and E<sub>h</sub> 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<sub>4</sub><sup>-</sup> was extracted to chloroform using 1 mM tetraphosphonylchloride (TPPC).



### Redox behavior in quinone systems:

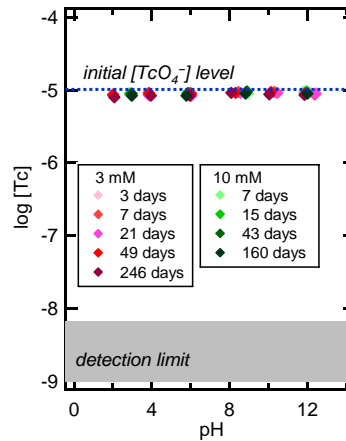
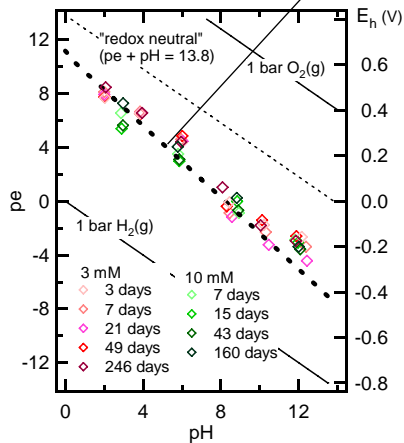
- Hydroquinone (HQ)
- Anthraquinone / anthrahydroquinone disulfonate (AQDS / AH<sub>2</sub>QDS)
- 2-hydroxy-1,4-naphthoquinone (Lawsonite); oxidized form / reduced form

## Results and discussion - Hydroquinone solutions -



### Hydroquinone solutions (3 mM, 10 mM)

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

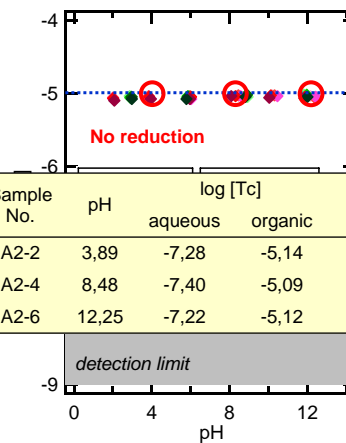
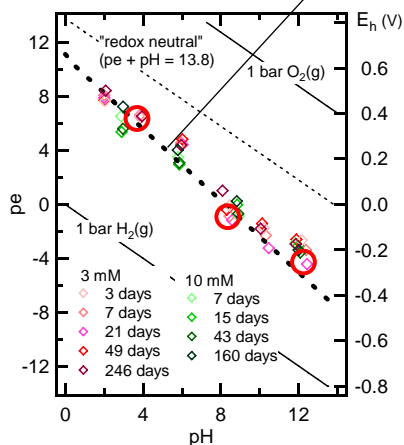


## Results and discussion - Hydroquinone solutions -



### Hydroquinone solutions (3 mM, 10 mM)

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

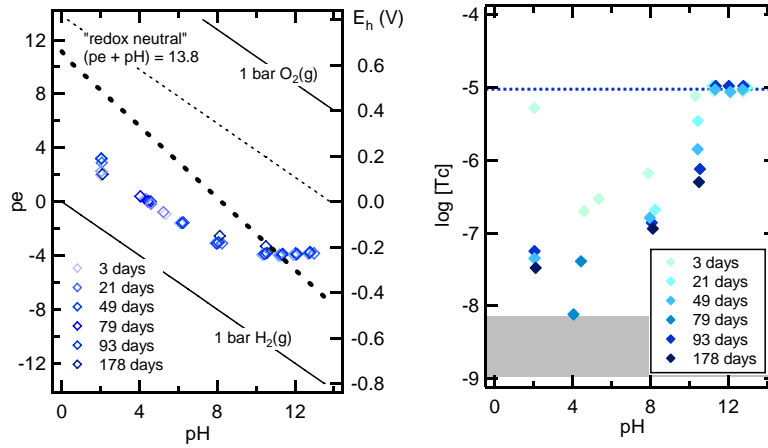


Sample No.	pH	log [Tc]		Tc(VII) / Tc <sub>tot</sub> %
		aqueous	organic	
A2-2	3,89	-7,28	-5,14	99,3
A2-4	8,48	-7,40	-5,09	99,5
A2-6	12,25	-7,22	-5,12	99,2

Results and discussion - AQDS/AH<sub>2</sub>QDS redox buffer solutions -



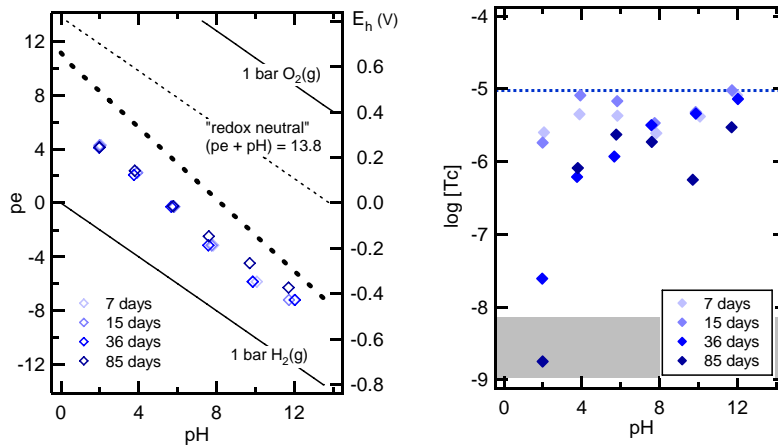
AQDS / AH<sub>2</sub>QDS redox buffer solutions (0.75 mM : 2.25 mM)



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)

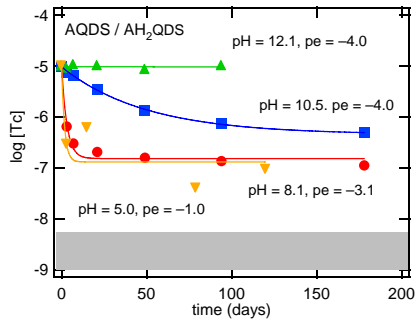


## Results and discussion - Kinetic effect -



### AQDS/AH<sub>2</sub>QDS buffer solutions:

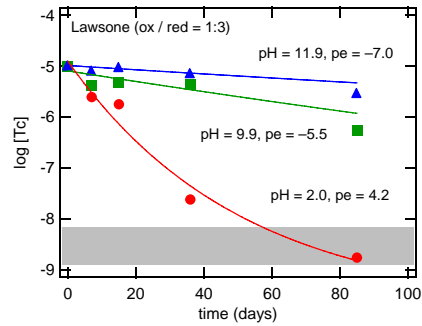
- Slow reduction at pH 10.5,
- no reduction at pH > 11.3.



Kinetic behavior in AQDS / AH<sub>2</sub>QDS = 1 : 3 system

### Lawsonite buffer solutions:

- Extremely slow reduction at neutral and alkaline pH.



Kinetic behavior in Lawsonite redox buffer solutions (oxidized form / reduced form = 1:3) system



### Redox behavior in strongly reducing systems:

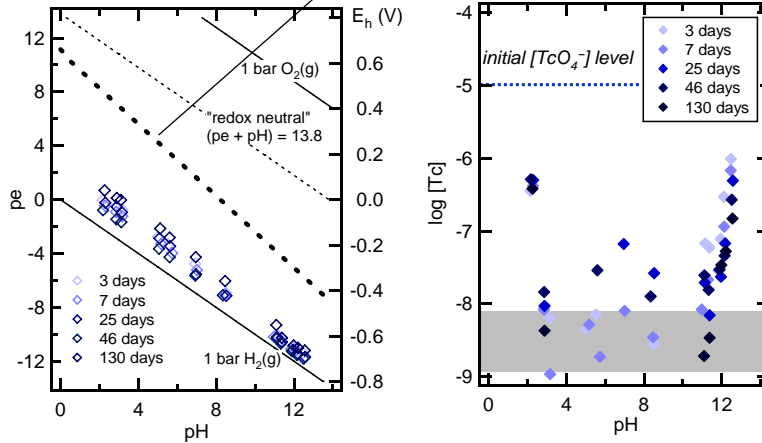
- Sn(II) dissolved (acidic, alkaline pH) / suspension of Sn(II) hydroxide (neutral pH)
- Sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>)

Results and discussion - Sn(II) solutions and suspensions of Sn(II) hydroxide -



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

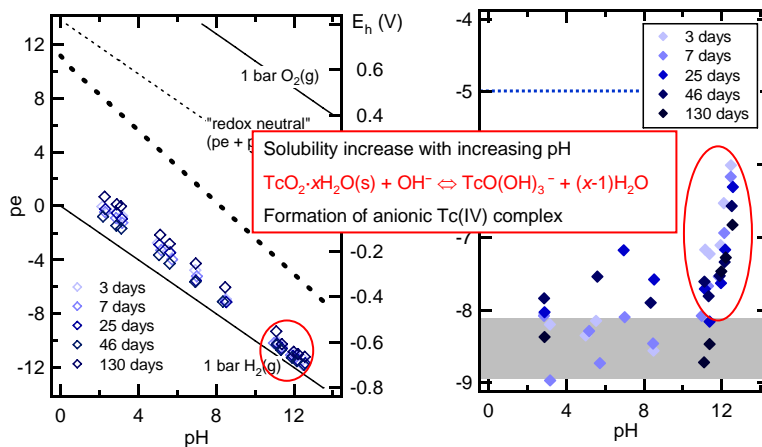
Calculated equilibrium line from NEA-TDB  
 $\text{TcO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s}) + (2-x)\text{H}_2\text{O}$   
 $\log K = 37.8; [\text{Tc}]_{\text{tot}} = 10^{-5} \text{ M}$



Results and discussion - Sn(II) solutions and suspensions of Sn(II) hydroxide -



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

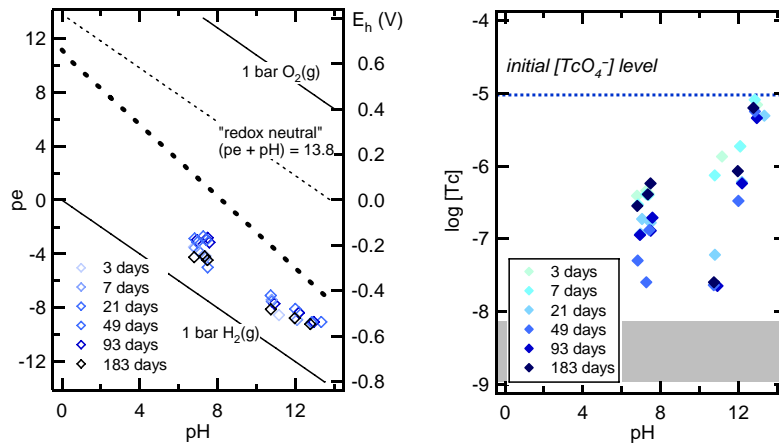




## Results and discussion - Sodium dithionite solutions -



### $\text{Na}_2\text{S}_2\text{O}_4$ solutions (1 mM)



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



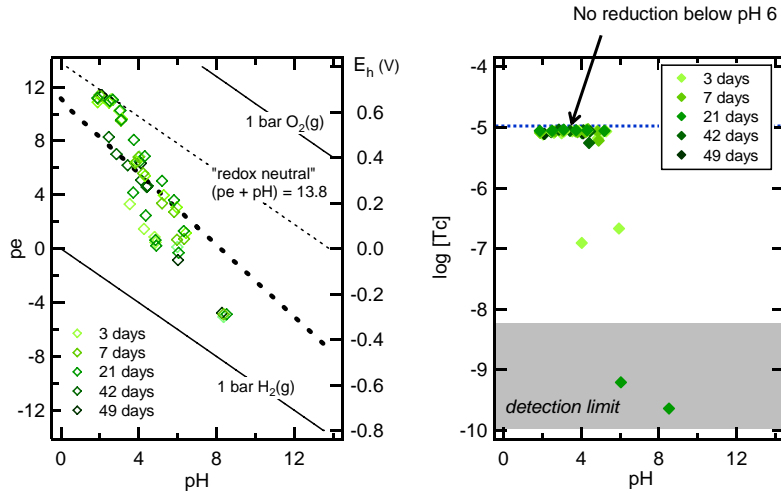
### Redox behavior in iron systems:

- 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)**

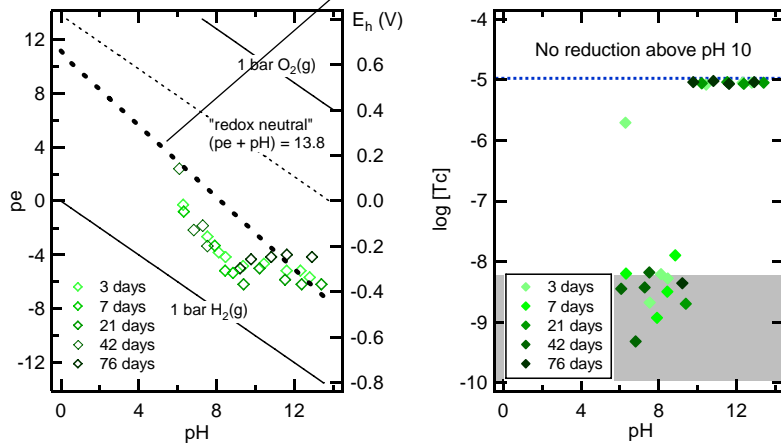


## Results and discussion - Fe powder suspensions -



**Fe powder suspensions (1 mg / 15 ml)**

Calculated equilibrium line from NEA-TDB  
 $\text{TcO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s}) + (2-x)\text{H}_2\text{O}$   
 $\log K = 37.8, [\text{Tc}]_{\text{tot}} = 10^{-9} \text{ M}$



## Results and discussion - Kinetic effect -

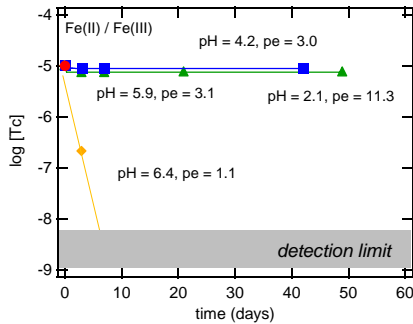


### Fe(II)/Fe(III) solutions and precipitates:

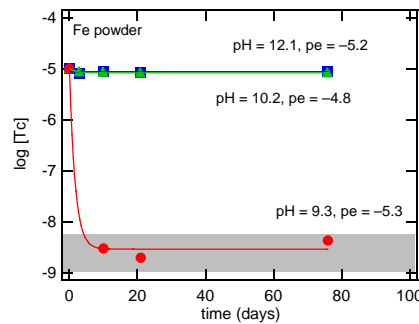
- No reduction in the acidic pH range ( $pH < 6$ ).
- Fast reduction (within 3 days) at  $pH 6$  and  $8$ , where Fe(II)/Fe(III) precipitates formed.

### Fe powder suspensions:

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



Kinetic behavior in Fe(II)/Fe(III) dissolved / suspension system

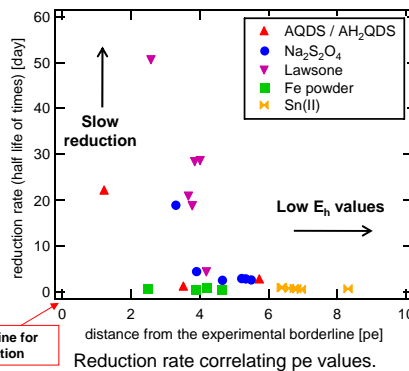


Kinetic behavior in Fe powder suspensions system

## Discussion - General interpretations of the redox behavior -

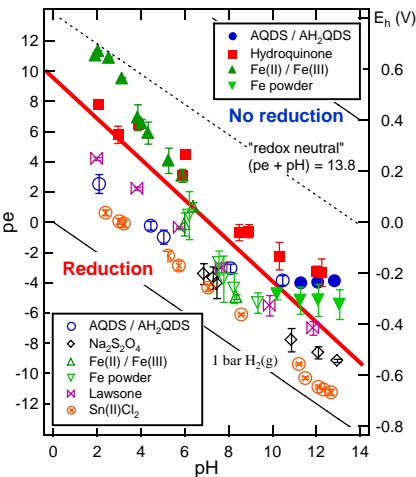


1. Experimental borderline for Tc(VII) reduction independent of reducing systems  
pH,  $E_h$  values are decisive parameters for reduction.
2. Kinetics related to Eh values (mostly in homogeneous solutions.)



Borderline for reduction

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 -

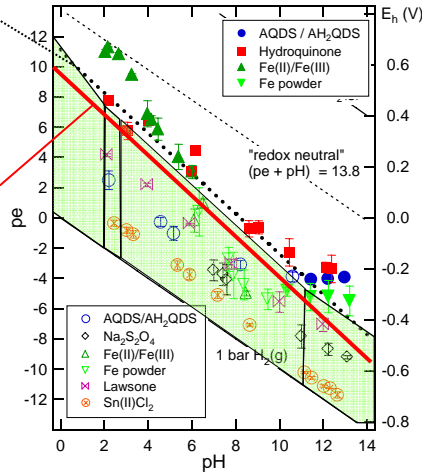


Calculated equilibrium line from NEA-TDB  
 $\text{TcO}_4^- + 4\text{H}^+ + 3\text{e}^- \leftrightarrow \text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s}) + (2-x)\text{H}_2\text{O}$   
 $\log K = 37.8, [\text{Tc}]_{\text{tot}} = 10^{-5} \text{ M}$   
 $\text{pe} = -1/3 (4 \cdot \text{pH} + \log K + [\text{TcO}_4^-])$

Experimental borderline

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

=> more soluble solids:  $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{coll, hyd})$ .  
 (related to particle size effect...)

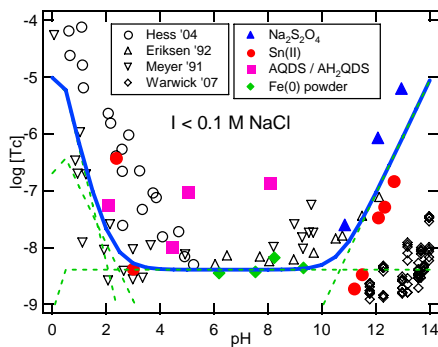


Redox behaviour of Tc(VII) in 0.1 M NaCl/NaOH. Open symbols: reduced, filled symbols: not reduced.

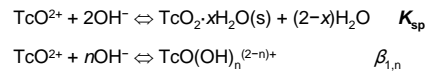
## Discussion - OUTLOOK: Solubility of Tc(IV) oxide -



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



Species	log $K^{\circ}_{\text{sp}}$	Reference
$\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$	-32.4	NEA-TDB
$\text{TcOOH}^+$	$\log \beta^{\circ}_{1,1}$	12.5
$\text{TcO}(\text{OH})_2(\text{aq})$	$\log \beta^{\circ}_{1,2}$	24
$\text{TcO}(\text{OH})_3^-$	$\log \beta^{\circ}_{1,3}$	27.1



Further studies on...

- Tc(IV) solubility at low ionic strength.
- Tc(IV) solubility in the absence and presence of  $\text{CO}_2$ .
- 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  $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ . This may suggest another solid phase with different solubility. Further confirmation of solids is needed.