

## Introduction

Technetium-99 is one of the main fission products of  $^{235}\text{U}$  and  $^{239}\text{Pu}$  in nuclear reactors. Due to its long half-life ( $2.1 \cdot 10^5$  a) and redox-sensitive character,  $^{99}\text{Tc}$  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, only +VII and +IV are long-term stable in the absence of complexing ligands. Tc(IV) forms sparingly soluble hydroxides ( $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ ) 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.

## Outlook of Diploma Thesis

Main activities within this diploma work  
(November 2013 – May 2014)

1) Assessment of pH measurements in dilute to concentrated KCl solutions. Determination of empirical A-values

2) Tc(IV) solubility studies in dilute (0.1 m) to concentrated (4.58 m) KCl solutions under acidic to hyperalkaline pH conditions in the absence of carbonate and complexing ligands

3) Determination of chemical, thermodynamic and activity models for the system  $\text{Tc}^{4+}\text{-K}^+\text{-H}^+\text{-Cl}^-\text{-OH}^-\text{-H}_2\text{O}$

4) Thermodynamic calculations and experimental solubility of Tc(IV) in "real systems": assessment of cementitious and saline systems

## Experimental

### Sample preparation [KCl experiments]

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

### Measurements

- Empirical determination of A-values for KCl systems
- pH measurements:  $\text{pH}_m = -\log m_{\text{H}^+} = \text{pH}_{\text{exp}} + A_m$
- $E_h$  measurements
- [Tc] by LSC
- Solid phase characterization (foreseen): XRD, CA

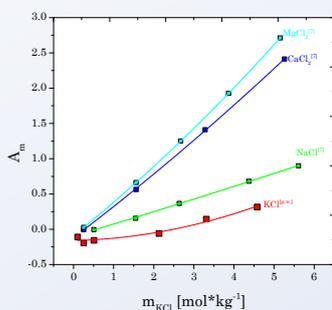
Solubility of Tc(IV) in "real systems":

Original Source	[KCl] [mol·l <sup>-1</sup> ]	[KOH] [mol·l <sup>-1</sup> ]	[NaCl] [mol·l <sup>-1</sup> ]	[NaOH] [mol·l <sup>-1</sup> ]	[MgCl <sub>2</sub> ] [mol·l <sup>-1</sup> ]	[CaCl <sub>2</sub> ] [mol·l <sup>-1</sup> ]	pH <sub>c</sub>
Artificial cement porewater (ACW) <sup>[2]</sup>		0.182		0.114			13.41
Cement L/ILW simulates exposed to NaCl brine <sup>[3]</sup>	0.603		5.215	(0.027)*			13.46
Cement L/ILW simulates exposed to NaCl brine <sup>[3]</sup>	0.237		4.450	(0.021)*			12.98
GWB simulated WIPP brine <sup>[4]</sup>	0.414		2.723		0.903		7.47
Canadian reference groundwater <sup>[5]</sup>	0.303		2.065		0.320	0.756	6.71

\* Calculated from experimentally reported pH<sub>exp</sub>

## Results and Discussion: Redox Measurements and Solubility

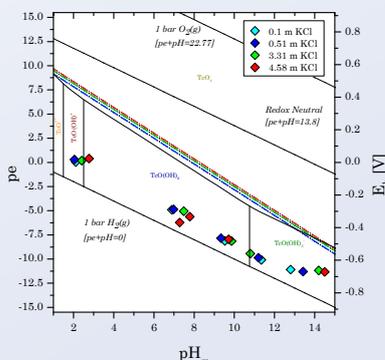
### Determination of empirical A values



$$A_{\text{KCl}} = -0.160 + 0.0132 m_{\text{KCl}} + 0.0204 (m_{\text{KCl}})^2$$

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

### Redox measurements

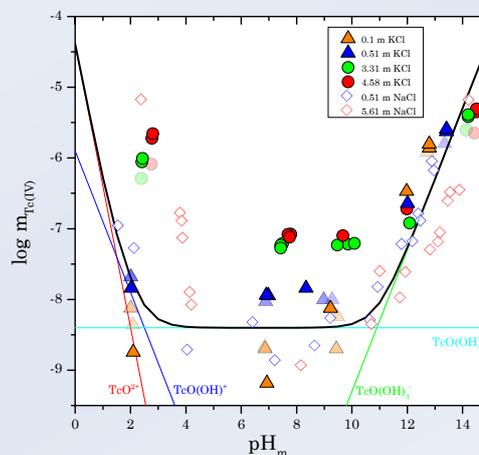


Tc(VII)/Tc(IV) redox borderline calculated for the chemical reaction:



- Aqueous speciation calculated at  $I = 0$  using NEA-TDB<sup>[1]</sup>
- All measured  $E_h$  values fall well below the Tc(VII)/Tc(IV) borderline  $\Rightarrow$  predominance of Tc(IV) in the solubility experiments

### Solubility of Tc(IV) in KCl solutions



- Tc(IV) solubility data in dilute KCl solutions is in very good agreement with hydrolysis scheme reported by NEA-TDB<sup>[1]</sup> and similar to solubility of Tc(IV) in dilute NaCl solutions<sup>[6]</sup>.
- Very significant increase of solubility with  $m_{\text{KCl}}$  at  $\text{pH}_m \leq 6 \rightarrow$  strong ion interaction processes also observed for NaCl
- Increase of solubility observed at  $\text{pH}_m \geq 11 \rightarrow$  system not yet in equilibrium
- Solid phase characterization (XRD, chemical analysis) will be performed for selected samples after attaining equilibrium conditions

## Conclusion

- Tc(IV) solubility data in KCl solutions agree well with the current hydrolysis scheme selected in the NEA-TDB<sup>[1]</sup>, as well as with previous observations for NaCl<sup>[6]</sup>
- Thermodynamic equilibrium has not been attained yet for those samples in hyperalkaline conditions
- Thermodynamic and activity models will be derived after attaining equilibrium conditions

## References

- [1] R. Guillaumont et al., *Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc*, Vol.5 of Chemical Thermodynamics, Elsevier, Amsterdam, 2003.
- [2] E. Wieland et al., *PSI Bericht* **06**, 2003, 6-9.
- [3] C. Bube et al., *Physics and Chemistry of the Earth* **64**, 2013, 87-94.
- [4] J.-F. Lucchini et al., *Journal of Alloys and Compounds*, **2007**, 506-511.
- [5] L. Duro et al., *NWMO TR-2010-02*, 2010, 15-19.
- [6] Poster of Yalcintas et al., 2014.
- [7] M. Altmaier et al., *Geochimica et Cosmochimica Acta Supplement* **67**, 2003, 3595-3601.