IST-2008 , Port-Elizabeth
7-10 Oct. 2008, South Africa

ISTR-2011 , Moscow
4-8 July 2011, Russia

TECHNETIUM: NEW TRENDS IN INVESTIGATION AND APPLICATION

KONSTANTIN GERMAN AND FREDERIC POINEAU

The chalenges of Technetium Thermodynamics - NEA_TDB

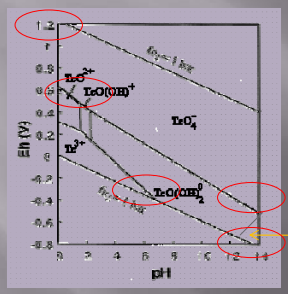
Rard J.A. and the delegates IST2005

- At IST1993 a draft project on Tc Thermodynamics project was first presented.
- 12 years ago an excellent review of NEA-TDB summed up the chemical thermodynamics of Tc : Rard J.A., Rand M.H., Anderegg G., Wanner H., Chemical thermodynamic of technetium. Eds. Sandino Amalia M., Osthols E. NEA (1999) Elsiever Publ. Amsterdam. - Axes for studies
- Time passed being characterized with the controversy of nuclear industry present and future status, drastic for Tc-99 originating mostly as the uranium fission product.
- The definite stop in nuclear development would fix Tc further accumulation but now is clearly not the case and we appreciate the authors who were continuing efforts in Tc focused sciences.

Recent steps

- In Port Elizabeth at the ISTR-2008 we reexamined the gaps in Tc thermodynamics data, having seen that most of the problems lightened by Joe Rard remained .
- All the gaps should be closed - we know - so indeed one may see : among the gaps named 3 years ago – some are thoroughly studied and important answers were obtained: Tc(VII) in strong acids – closed thanks to our collaboration with F. Poineau and his colleagues from UNLV
- Chemical medium for stabilisation and Instrumental and methodology breakthroughs

Eh-pH *Pourbaix* diagram for Tc

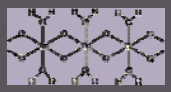


- The solubility of Tc(IV) remains independent of pH until around 13.5, when a small increase can be seen which continues to increase linearly with pH.
- Modelling suggests that this increase occurs as the species $TcO(OH)_3^-$ is formed. The formation constant was estimated with data from this study and was found to be $\log K_2 = -21.6 \pm 0.3$.
- **Authors:** Peter Warwick | S. Aldridge | Nick Evans | Sarah Vines - Rad. Acta 2007

E. Breynaert, D. Dom, J. Vancluysen,A. Maes 2007-8

Tc-O			Tc-Tc		
C.N.	R	σ^2	C.N.	R	σ^2
6	2.03	0.006	1.5	2.56	0.005

$Tc(OH)_4(H_2O)_2$ and



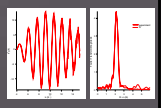
Tc speciation in solutions & melts by XAFS

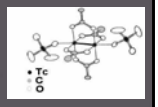
ROBL_ESRF
Grenoble

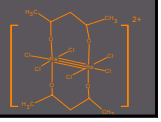
Advanced Photon
Source inst. & UNLV

Kurchatov Institute
(KI) MOSCOW

- TcO_4^- - is highly environmental migrating species
- Radiolyse in presence of organic components lead to the reduction of Tc(VII) to Tc(V, IV, III)
- In chloride melts Tc could be examined (German, Simonoff, Reich, 2000, Grenoble)
- Acetate complexes Tc(V, IV, III) exist but the data are scattered and the structure not systematically studied (the one presented at IST1993 by Prof. Grigoriev) Acetate complexes of Tc(III) could co-exist withTc(VII)
- Re acetates structure by XAFS to be present at ISTR2011 by Murzin and co-workers).

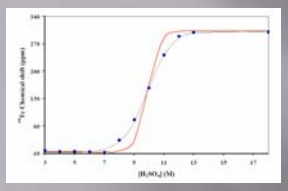


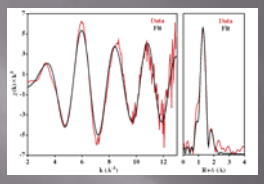


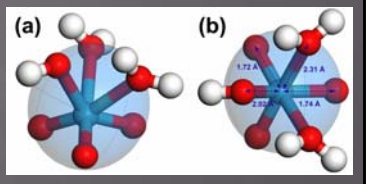


Ga-DTPA – PET A.Maruk

Tc(VII) in strong acids







The speciation of Tc(VII) in 12 M sulfuric acid was studied last year by NMR, UV-vis and XAFS spectroscopy, experimental results were supported by DFT calculation and were in agreement with the formation of $TcO_3OH(H_2O)_2$.

F. Poineau, Ph. Weck, K. German, A. Maruk, G. Kirakosyan, W. Lukens, D. Rego, A. Sattelberger, K. Czerwinski , Dalton Trans. 2010

The speciation of Tc(VII) in $HClO_4$ is being reported at this Symposium and supports the TcO_4^- conversion to new Tc(VII) species in strong acids

Tc oxides & hydroxides

	Tc Oxide	Parameters for inner electrons ($Tc3d_{3/2,5/2}$)	
		E(Tc)	Half-width
1	Tc_2O_5	256,6	1,8
2	$Tc_2O_5*nH_2O$	256,0	1,7
3	TcO_2	255,2	1,8
4	$TcO_2*1.6H_2O$	255,4	2
5	Tc_2O_3	-	-
6	$Tc_4O_5*14H_2O$	255,9	1,8
7	Tc_4O_5	255,0 (0,4) 253,6 (0,4) (I1:I2=1:1.3)	3.5

Preparation and Characterization of Phosphine Complexes of Technetium Possessing a Metal-Metal Bond Order of 3.5. F. A. Cotton, S.C. Haefner and A. P. Sattelberger *Inorg. Chem. 1996, 35, 1831.*

Tc_2O_5- decomposition of $Tc_2O_5*nH_2O$ at 100°C

$Tc_2O_5*nH_2O$ – gamma in NaOH + i-BuOH

$Tc_4O_5*14H_2O$ hydrolisis of $K_3Tc_2Cl_8$

Tc_4O_5 - thermolisis of $Tc_4O_5*14H_2O$

- Mazzi, 1974 - Tc_2O_3

Inorganica Chimica Acta, Volume 9, 1974, Pages 263-268 G. A. Mazzocchin, F. Magno, U. Mazzi, R. Portanova

Possible fractional reduction of polymers

Haefner - Sattelberger $[Mo_3O_4(DMF)_9]^{4+}$

Study of Tc(IV) uptake with *FeOOH* under reducing conditions

- Reducing agent: 0.02M FeSO4, T = 60°C, time = 3 h
- Precipitate : $FeOOH/Fe_2O_3/Tc_{reduced}$

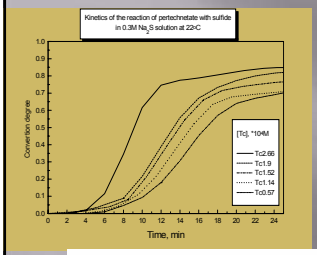
Precipitation test:		Leaching test (t=18 °C, d = days):				
NaOH M	Tc in solid phase, %	Leaching agent:	Leaching yield ,Tc, %			
			1 d	10 d	29 d	105d
0.6	97	0.1M NaOH	1.0	9.8	14.9	24
2.0	88.0	1M NaOH	2.9	16.5	40.2	58
4.0	90	2M NaOH	0.8	2	3	8.2

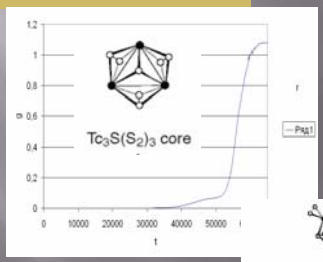
Though Tc adsorbed better on iron hydroxide from 0.5–2.0 M NaOH relative to 3.0-4.0 M NaOH, the precipitates formed at lower NaOH concentration were more easily leached by the NaOH leachant,

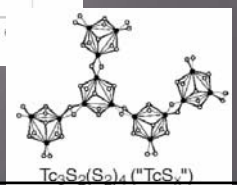
The precipitate should be examined by XAFS

Tc leaching with H_2O_2 was 20 % and with $Na_2S_2O_8$ was70-100% in 100 days

Tc(VII) + S^{2-}





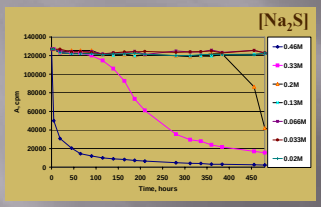


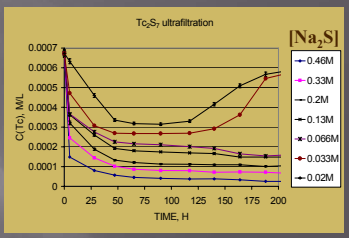
- Induction period of the reaction of pertechnetate with Na_2S varies from 4 to 100 minutes depending on the concentration of reagents, pH and T
- Reaction of Tc(VII) with Na_2S is completed within 1 to 10 hours depending on the concentration of reagents, pH and T
- Reaction *is fast if compared to slow* Tc_2S_7 ($TcS_{3,33}$) *sedimentation (under most conditions) - colloid formation*
- D. Shuh, W. Lukens, C. Burns, Final report on Project Number: EMSP-73778, 2004

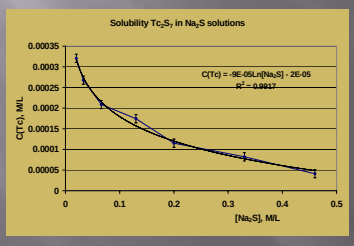
Reviewed : ISTR2011- July 5 by German K. E., Peretrukhin V. F, Tsivadze A.Yu.

Separation of Tc_2S_7 colloides from Na_2S solution by Microfilterfuge (RAININ Instr. Co) with ultrafiltration membranes - 30000 NMWL

Sedimentation of colloides Tc_2S_7

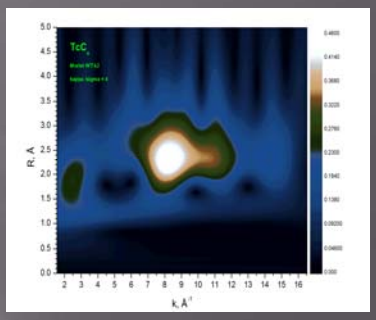


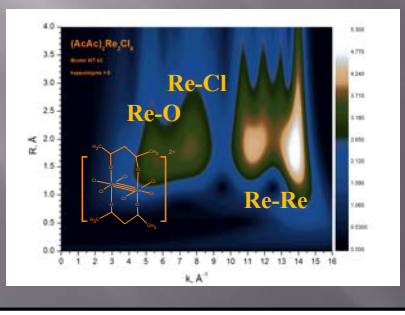


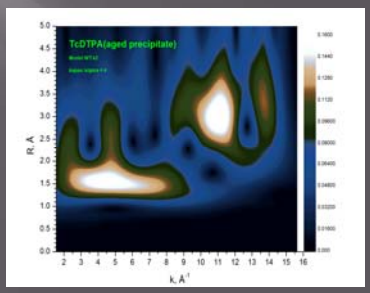


- Formation of colloides Tc_2S_7 is completed in 50 hours under these conditions
- [Tc] in the solutions at times from 50 to 150 hours corresponds to true solubility of Tc_2S_7

New Wavelet based structure analyses of X-ray amorphous complexes and solutions (Re polynuclear Tc-DTPA and Tc&Re nanoparticles (Zubavichus –plen.lect. Murzin – oral pres., ISTR2011 – Nanosession - July7)





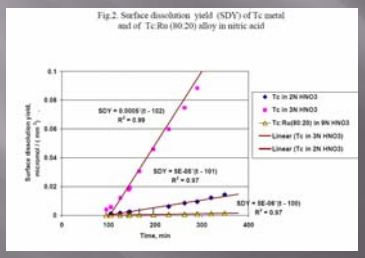


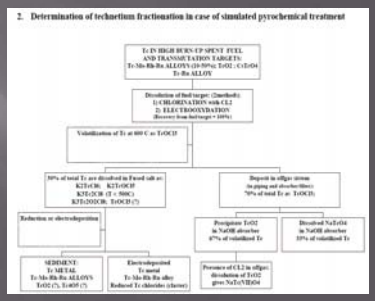
Nanoscale DTA and DSC measurements (Mettler-Toledo)

FG	• ghj
Kk	• ghj
RUSNANO	• ghj
RFBR	• Strange – this was not a prepaid annaucement – but just my personal oppinion

Transmutation target : Tc/Ru recovery

- Tc-Ru acidic and pyrochemical solubilization problem





N. Schroeder approach : homogeneous transmutation

Applications

- RICS : 1 barrel of Tc is capable to guarantee 1W thermal (0.5 W electr.) during 100000 years
- Medicine – Back to Tc from PET , but at the new resolution abilities and new deseases to be treated
- Some about 50 g of pure Ru-100 have been obtained by Tc transmutation