

TECHNETIUM METAL, TECHNETIUM CHLORIDES AND CHLORINE SPECIES IN PYROMETALLURGICALLY FORMED SEDIMENTS AND MELTS - SPECIATION BY Tc-99 AND Cl-35,36,37-NMR AND EXAFS / XANES

K.E. German¹, T. Reich², G.A. Kirakosyan¹, E.V. Johnstone,^{3,4} K.R. Czerwinski,³
F. Poineau,³ A.P. Sattelberger⁵

¹ A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia

² Johannes Gutenberg-Universität - Institut für Kernchemie, Mainz, Germany

³ University of Nevada – Las Vegas, Chem. and Biochemistry Departm., Las Vegas, NV, USA

⁴ Global Medical Isotope Systems (GMIS), Las Vegas, NV, USA

⁵ Argonne National Laboratory, Chemistry Division, Lemont, IL, USA

DOI: 10.13140/RG.2.2.35204.37769

EXAFS and NMR are being developed with respect to study and speciation of technetium-99 in course of pyrometallurgical reprocessing of spent nuclear fuel. Based on the set of standards including technetium metal, different technetium halogenides, oxohalogenides, oxides and pyrometallurgically formed sediments, Tc chemical forms responsible for Tc accumulation in fused salts, deposits or gas-off depending on the applied reprocessing conditions are studying by means of NMR and EXAFS. NMR spectrum of Tc metal powder obtained by FT of a free induction decay accumulated after excitation of the spin system by a sequence of high frequency pulses (0.8 μ s) with a dead time of 5.4 μ s and a repetition time of 1 μ s, provided with Knight shift $K(ppm) = 7305 - 1.52 \times T$; $\nu Q(^{99}Tc) = 230$ kHz at 293 K, $CQ(^{99}Tc) = 5.52$ MHz. EXAF spectra provided with excellent evidence for Tc(IV) halogenides, but need further development for lower oxidation states of technetium.

Introduction: EXAFS and NMR are promising methods to enable us with speciation of radioactive nuclides. It is important to use them for Tc speciation in pyrometallurgy which is now considered as the most probable alternative approach to reprocessing of spent nuclear fuel. Pyrometallurgy of uranium and plutonium in chloride and fluoride fused salts are now intensively studied while little attention is given to long lived fission product technetium which is one of the hazardous nuclear wastes. During pyrometallurgical spent fuel reprocessing, technetium can remain in the fused salt or enter (depending on the applied temperatures, reagents and potentials) either the sedimented phase contaminating Pu enriched phase, or electrodeposited U phase (Scheme 1). Neither in sediment nor in deposit Tc phase could be detected by means of X-ray diffraction, Tc phase being finely dispersed and X-ray amorphous. It is therefore very important to develop some other methods of analyses like EXAFS and NMR applicable to Tc speciation in such samples. Our preliminary results show that under such conditions Tc can also form several oxydes, oxychlorides and chlorides of different but rather high volatility, turning on an important polluting risk allied to gas-off.

EXAFS / XANES were registered at Eur. Synch. Rad. Facility, ROBL, Grenoble, France in our previous work [1].

The data on EXAF and NMR spectra of technetium being fragmentary and not presenting the whole of the species possible in the pyrometallurgy conditions, it is of high importance to carry synthetic work to supply a large set of technetium compounds in the closed containers which will meet the security and quality demands, radioactivity level, special requirements on sample size, thickness, sample homogeneity.

Some EXAFS measurements of technetium solutions applicable in some content to pyrometallurgical treatment of spent nuclear fuel were presented earlier by [1, 2]. It provided with EXAF data on technetium(IV) hexachloride in HCl solution. Recent studies however has given some indication on the presence of unknown Tc chloride complex [3] Tc metal and its binary alloys with vanadium have been studied earlier by ⁹⁹Tc NMR at ambient temperature [4, 5]. In

these early works, the measurements were made in relatively low magnetic fields ($B_0 = 1.4$ T) in the differential passing mode with field sweep, which made difficult the measurements of the anisotropic Knight shift (K_{an}). Moreover, the reported values of isotropic Knight shift (K) for metal Tc varied from $K = 6100$ ppm in [4] to $K = 7150$ ppm and $K_{an} = 1160$ ppm in [5].

Experimental : In this work EXAFS measurements are made at Radiochemical Hutch of ROBL/ ESRF: beamsize of 3×20 mm², integrated flux at sample 6×10^{11} /s 200mA@ 20keV, spectral range 5 - 35 keV; 2/3 filling mode. Beam line control carried out with VME, SUN workstation, SPEC Hot cells are used for sample positioning.

⁹⁹Tc NMR spectra of Tc metal powder at 120-400 K, technetium foil and some preliminary results on the $K(^{99}\text{Tc})$ shifts in the alloy samples were recorded on a Bruker MSL-300 radiospectrometer in 7.04T magnetic field at 67.55 MHz resonance frequency.

Spectra NMR were obtained by FT of a free induction decay accumulated after excitation of the spin system by a sequence of high frequency pulses (0.8 μ s) with a dead time of 5.4 μ s and a repetition time of 1 μ s. The Knight shifts were measured relative to the external standard 0.1M KTcO_4 aqueous solution.

Chemical preparations: All reagents were chemically pure grade. Technetium was purchased as NH_4TcO_4 from Amersham Co. and as KTcO_4 from V/O ISOTOP, RF and converted to HTcO_4 by cation exchange. $\text{N}(\text{CH}_3)_4\text{TcO}_4$ was prepared as described in [6] Tc metal was prepared by reduction of tetramethylammonium pertechnetate $\text{N}(\text{CH}_3)_4\text{TcO}_4$ (99.9% purity) in a flow of nonexplosive gas mixture 6% H_2 in Ar in a quartz tube at 1150 K. Samples were cooled, crashed and the 80-150 μ m fraction was sieved of for NMR measurements. Same method was used for preparation of the dispersed metal on metal oxide supports MgO , Al_2O_3 , modified for evaporation of NH_4TcO_4 at the later surface. To improve the resolution and accumulation NMR mode minimizing the electric contacts, some technetium metal samples were dispersed in dodecane : apiezon (20 : 1) mixture and then air-dried.

Tc halogenides and oxides were prepared as described in [7, 8]. Reference technetium compounds prepared for EXAFS study : chlorides (M_2TcCl_6 , $\text{M} = \text{Li, Na, K, R}_4\text{N}$); fluorides, (M_2TcF_6 , $\text{M} = \text{H, Na, K}$); bromides ($\text{M} = \text{Na, K, R}_4\text{N}$); oxides TcO_2 , Tc_4O_5 and pertechnetates MTcO_4 ($\text{M} = \text{Na, K, Cs}$); Samples of simulated pyrometallurgically reprocessed nuclear fuel (to be prepared): Tc hexachlorides in fused salts (chlorides and fluorides); Tc sublimated fraction; Tc precipitated/deposit fraction (*all with Tc-99 as the only radionuclide*)

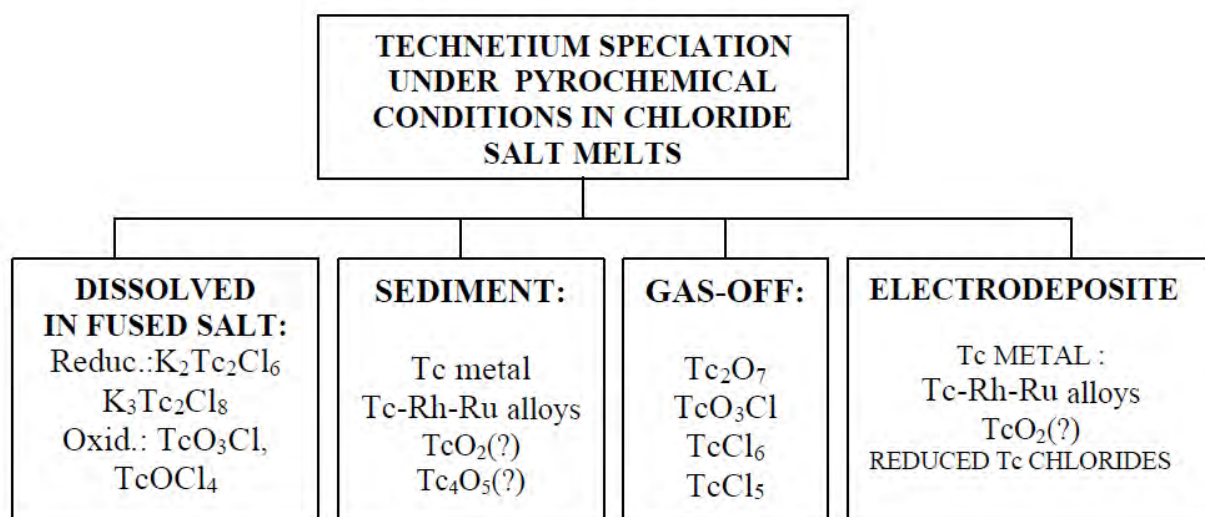


Fig. 1. Technetium speciation under pyrochemical conditions in chloride salt melt

Results and discussion: The ⁹⁹Tc-NMR spectrum of polycrystalline metallic Tc comprises 8 symmetrically arranged satellites and the central component whose shape is governed by the Knight shift anisotropy (Fig 2). The distance in KHz between the first inner satellites is the lowest frequency of a quadruple transition ν_Q . The line width of the central component at half-maximum

was ~ 22 kHz at 293 K thus having masked the effects of shift-anisotropy on the lineshape of the central transition ($-1/2 \rightarrow +1/2$). At 400 K the line width is reduced and shows the axially symmetric line shape with $K_{||} - K_{\perp} = -809 \pm 30$ ppm.

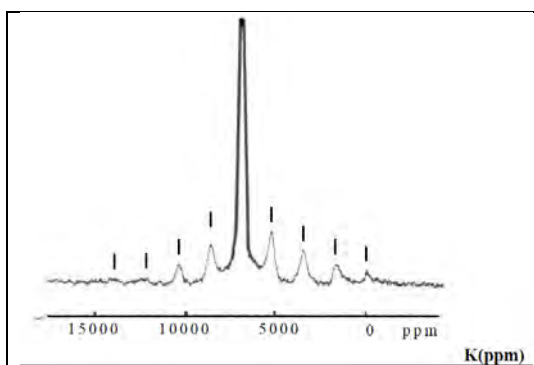


Fig 2. NMR-⁹⁹Tc spectrum of Tc metal powder (Ø 80-150 μm)

Fig. 2 presents the temperature dependence of the isotropic Knight shift for technetium metal powder,

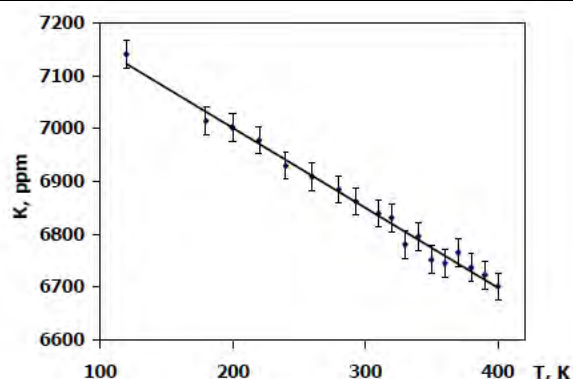


Fig.3. Temperature dependence of isotropic Knight shift (K) for Tc metal powder

Fig. 3 presents the temperature independence of the νQ for the same sample. This study provided with $K(\text{ppm}) = 7305 - 1.52 \times T$; $R^2 = 0.99$. Experimental $\nu Q(^{99}\text{Tc})$ is 230 kHz at 293 K which gives $CQ(^{99}\text{Tc}) = 5.52$ MHz. The latter is related to electric field gradient EFG (q_{exp}) by the equation:

$$q_{\text{exp}} [\text{cm}^{-3}] = 2.873 \cdot 10^{22} CQ[\text{MHz}]/Q[\text{barn}] = 52.86 \cdot 10^{22} \text{ cm}^{-3}, \text{ where } Q = 0.3 \text{ barn.}$$

In general, the total EFG at a nuclear site in a noncubic metal results from the addition of two EFG parts, one being due to the lattice of the ionic core (enhanced by the Sternheimer antishielding effect) and the other being due to the non-s-character of the conducting electrons: $q_{\text{exp}} = (1-\tilde{\alpha})q_{\text{lat}} + q_{\text{el}}$.

In case of Tc, the contribution arising from the ionic core lattice may be interpolated from de Wette's [9] results for $\tilde{\alpha} = c/a = 1.604$. We find that $(1-\tilde{\alpha})q_{\text{lat}} = 27.57 \cdot 10^{22} \text{ cm}^{-3}$ (at $\tilde{\alpha} = -5$ [10]). This value is 52% of the experimental value obtained in the present work. This proportion is typical of the most metals in which the $(1-\tilde{\alpha})q_{\text{lat}}$ contribution is usually lower (in magnitude) than the observed one.

NMR and EXAFS studies of dispersed Tc (supported on oxide matrix of MgO and Al₂O₃) and of Tc-Ru and Tc-Rh alloys are in progress. NMR spectrum of the sample, sedimented from K₂TcCl₆ in NaCl-KCl melt at 550° C under reducing conditions formed by Ar-1% H₂ bubbling, gave evidence for some metal state (9884 ppm) but also some to 30% of Tc(VII) (31 ppm). Three main aspects under consideration with respect to EXAFS/XANES studies are the following: 1) the ligand influence on the technetium EXAF spectra within the same Tc oxidation state (F, Cl, Br, I and OH, H₂O being the ligands of interest with respect to pyrometallurgy as a reprocessing method), 2) the oxidation state including the lower and mixed oxidation states as well as Tc cluster formation on the technetium EXAF spectra 3) cations on the Tc EXAF spectrum within the same Tc oxidation state (Li, Na, K, Rb, Cs, Me₄N, Et₄N, Pr₄N, Bu₄N could be the cations of interest, while TcO₄⁻ and TcX₆²⁻ would be the anions under study (some preliminary results are given in Fig. 6 and 7).

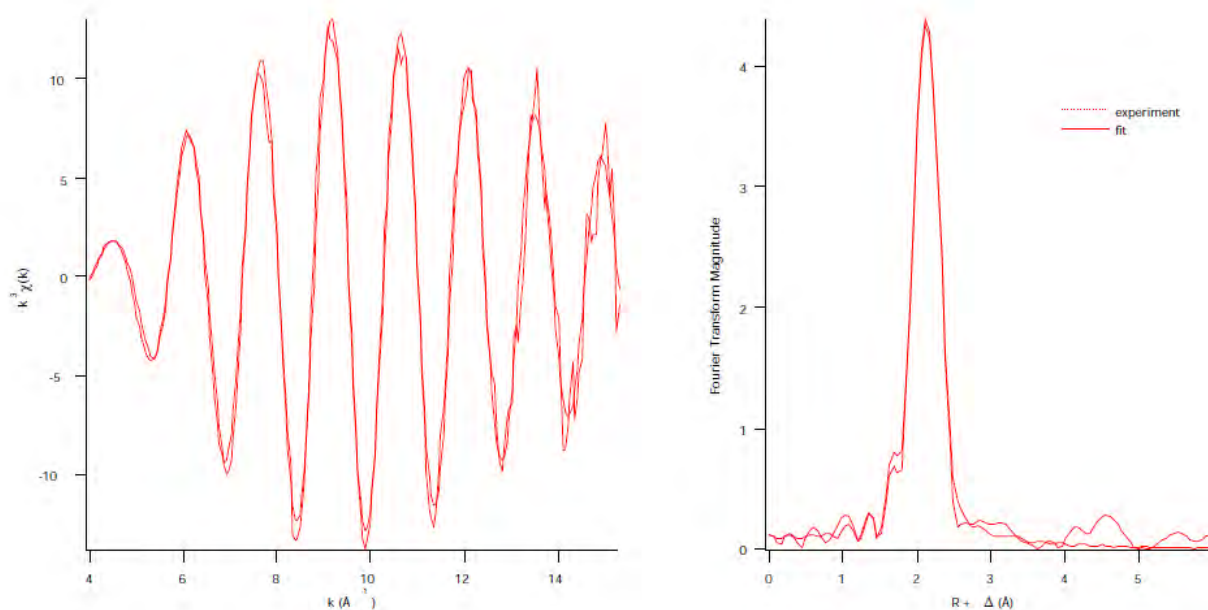


Fig. 6. Tc K-edge k^3 -weighted EXAFS and corresponding Fourier transform of sample $(\text{Me}_4\text{N})_2\text{TcBr}_6$: EXAFS structural parameters: Tc-Br $N=5.8(2)$ $R=2.51(2)$ Å $\sigma^2=0.0040$ Å² $\Delta E_0=-16.9(5)$ eV

Tc K-edge k^3 -weighted EXAFS and corresponding Fourier transform of the sample of standard Tc(IV) halogenide $(\text{Me}_4\text{N})_2\text{TcBr}_6$ is present at Fig. 6. It resulted in the following EXAFS structural parameters: Tc-Br $N=5.8(2)$; $R=2.51(2)$ Å ; $\sigma^2 = 0.0040$ Å² ; $\Delta E_0 = -16.9(5)$ eV. The six halogenide atoms and the distance found correspond well to the same parameters known for similar compounds based on X-ray monocrystal analyses.

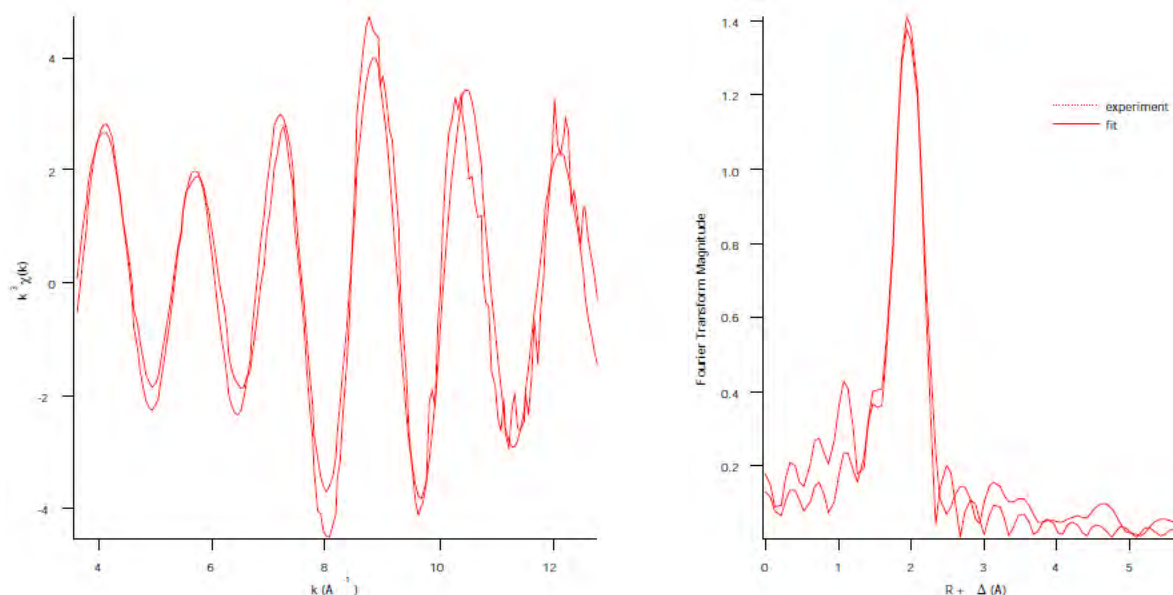


Fig. 7. Tc K-edge k^3 -weighted EXAFS and corresponding Fourier transform of sample $\text{K}_3\text{Tc}_2\text{Cl}_8$ EXAFS structural parameters for $\text{K}_3\text{Tc}_2\text{Cl}_8$: Tc-Tc $N=1.6(3)$ $R=2.20(2)$ Å $\sigma^2=0.0069$ Å² $\Delta E_0=-1.1(9)$ eV and Tc-Cl $N=2.2(4)$ $R=2.46(2)$ Å $\sigma^2=0.0107$ Å².

Tc K-edge k^3 -weighted EXAFS and corresponding Fourier transform of the standard Tc(2,5+) halogenide sample $\text{K}_3\text{Tc}_2\text{Cl}_8$ is present in Fig. 7. The first coordination sphere of Tc in this compound includes one Tc atom and four Cl atoms. EXAFS structural parameters for $\text{K}_3\text{Tc}_2\text{Cl}_8$ (in such preliminary approximation) resulted in the following values: Tc-Tc $N=1.6(3)$ $R=2.20(2)$ Å $\sigma^2=0.0069$ Å² $\Delta E_0=-1.1(9)$ eV and Tc-Cl $N=2.2(4)$ $R=2.46(2)$ Å $\sigma^2=0.0107$ Å². The

overestimation of Tc-Tc intervention is evidently due to neglect of the four Cl atoms bound to the second Tc atom. This correction of the model will be made in the near future.

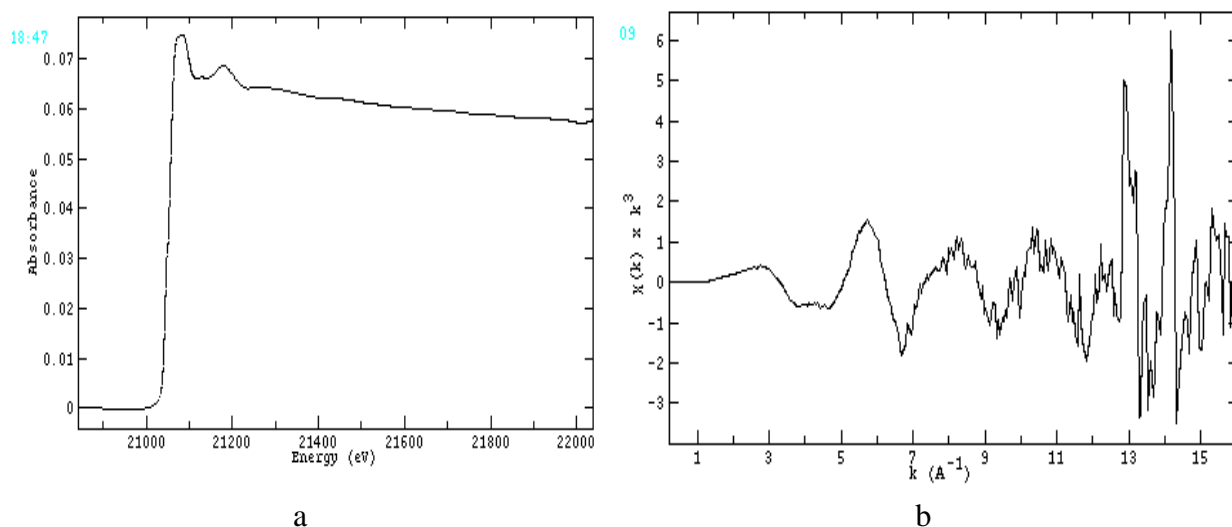


Fig. 6. Original EXAFS spectrum of prismatic hexanuclear chloride cluster $(\text{Me}_4\text{N})_3[\text{Tc}_6(\mu\text{-Cl})_6\text{Cl}_6]\text{Cl}_2$ (a) and its Tc K-edge k^3 -weighted EXAFS part (b).

No reliable Fourier transform leading to unambiguous atomic distances could be driven within the actual calculation code. This is most probably due to the very complicated scattering system of Tc and Cl atoms see Fig. 7.

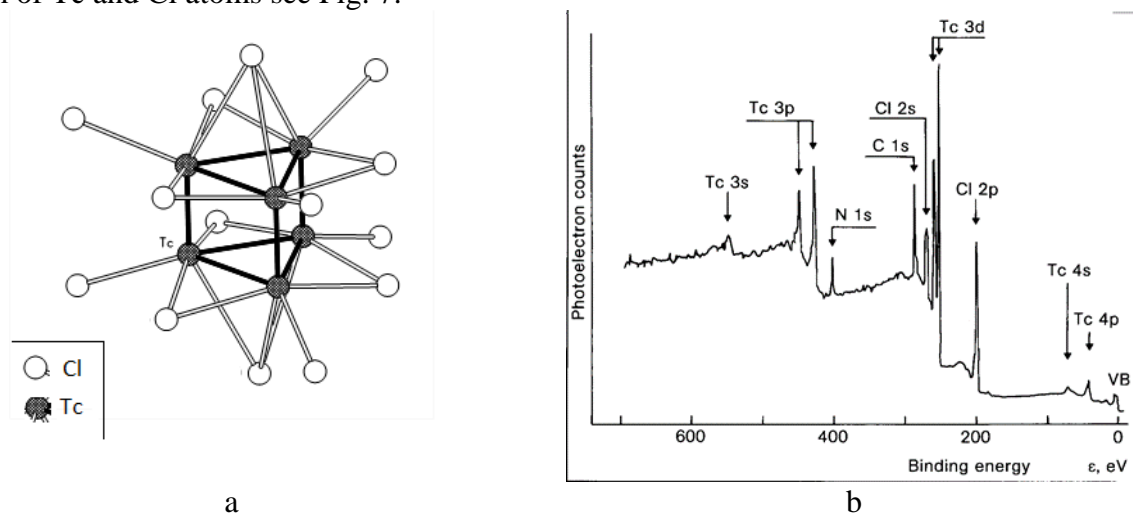


Fig.7. Structure of prismatic hexanuclear chloride cluster $(\text{Me}_4\text{N})_3[\text{Tc}_6(\mu\text{-Cl})_6\text{Cl}_6]\text{Cl}_2$ and its ESCA spectrum

The results show excellent agreement in case of the octahedral Tc(IV) bromide, while for the Tc cluster compound an important difference between the experimental and the fit suppose that some more Br atoms, but not only the first coordination sphere Br, are influencing the EXAF spectrum.

On the issue of the disproportionation of Tc(V): it is believed that it always disproportionates, but not in HCl medium. In 1984 P. Jordan, K. May, and K. Girgenrath unilaterally showed that if Cl_2 is removed with a nitrogen current, then Tc(V) is formed in HCl directly from Tc(VII), and without disproportionation, the same HCl is restored further to Tc(IV) [11]. These data were lost, not finding reflection in the book of Rard [12].

Chlorine-36 is one of long-lived, β -active isotopes with a half-life of 3.105 years and a rare nuclear structure – its odd-odd nuclei contain 19 neutrons and 17 protons. Being an artificial

isotope, ^{36}Cl is not an environmental hazard today because of its low abundance. However, some of the scenarios for the development of atomic power, i.e., involving the use of molten chloride reactor systems for destruction of weapons plutonium and pyrochemical reprocessing of spent nuclear fuel, may result in accumulation of ^{36}Cl due to the $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ reaction ($\sigma = 100$ barn) in amounts that cannot be ignored as radioactive waste. Either U and Pu nuclear fission in molten reactor or $^{23}\text{Na}(\alpha,n)^{26m}\text{Al}$ ($\sigma = 50$ mbarn) at the fuel reprocessing step, could be the sources of neutrons to provide with such an accumulation of ^{36}Cl . Thus, methods for analytical control of ^{36}Cl will be required with ^{36}Cl -NMR being one of the candidates [13].

The initial 30% HCl containing ca. 0.4% ^{36}Cl was reacted with KOH to produce an alkaline solution of KCl, which was subjected to electrolysis (current density on a platinum electrode was 0.2 A/cm^2) in the presence of the catalyst K_2CrO_4 at 70°C for several days, followed by electrolysis at $10\text{--}15^\circ\text{C}$ and 0.8 A/cm^2 [1]. The resulting sample was a solution of KCl and KClO_4 mixture, which was 0.1 M in the overall salt (sample 1). A portion of it was exhaustively electrolyzed to produce KClO_4 , followed by the reaction with Bu_4NOH . The isolated solid salt Bu_4NClO_4 was used to prepare a 3.3 M solution in acetonitrile (sample 2). The solid anhydrous Bu_4NClO_4 was also studied (sample 3). The isotope contents of the samples were determined by mass spectrometry of the solid salt Bu_4NClO_4 pressed into a bismuth target [2]. The isotope composition of the salt found by mass spectrometry: $^{35}\text{Cl} : ^{36}\text{Cl} : ^{37}\text{Cl} = 75.08 : 0.28 : 24.64$. The independent determination of the ^{36}Cl content by measuring the specific β -activity of Bu_4NClO_4 by liquid scintillation counting in 'Ready-Gel' cocktail on Beckman 6500 LS gave the ^{36}Cl abundance of 0.4 wt-Cl %.

Spin-lattice relaxation times (T1) and NMR spectra for three Cl nuclides were measured on Bruker AC-200 and MSL-300 FT radiospectrometers at 300.0 ± 0.1 and $292 \pm 2 \text{ K}$, respectively. The resonance frequencies and nuclear characteristics of the isotopes are listed in Table 1. Spin-lattice relaxation times T1 were measured with the use of the inversion-recovery pulse sequence, $(180^\circ - \tau - 90^\circ) - 5T1$. The 90° pulse width was determined based on the greatest signal intensity and constituted 14 (12), 12 (11.2), and 15 (13) μs for ^{35}Cl , ^{36}Cl , and ^{37}Cl , respectively, at resonance frequencies corresponding to the field of 7.042 T (4.6975 T). At a field of 7.042 T, free induction decays in T1 measurement were accumulated in 8 K memories. The spectral width was 1 kHz. In each of T1 experiments, 12 to 14 time delays τ were specified. The number of transients accumulated was 100 for ^{36}Cl and 10 for ^{35}Cl and ^{37}Cl . NMR spectra were recorded using one-pulse excitation with a varied dead time. At a field of 4.6975 T, experiments were carried out at 300 K with both external and internal deuterium locks. Spectral widths of 100 to 500 Hz were employed with 8 K to 32 K data points.

References

1. K. Ben Said, M. Fattahi, Cl. Musikas, R.Revel , Speciation de Tc(IV) dans les solutions chlorées determine par spectroscopie d'absorption X (EXAFS). Comptes-rendus de Journées PRACTICE 1998, Villeneuve-les-Avignon, 25-26 Fev. 1999.
2. D. Revel, C. Auwer. Spectroscopie d'absorption X. Comptes-rendus de Journées PRACTICE 1998, Villeneuve-les-Avignon, 25-26 Fev. 1999.
3. L.Vichot, M.M. Fattahi, C. Musikas, B. Grambov. Etude des formes reduites du technetium en milieu sulfatochlore. Comptes-rendus de Journées PRACTICE 1999, Villeneuve-les-Avignon, 17-18 Fev. 2000.
4. D.O. Van Ostenburg, D. Lamm, H.D. Trapp, D.E. MacLead / Phys. Rev. (1962) V128, N 4, p.1550.
5. D.O. Van Ostenburg, H.D. Trapp, D. Lamm / Phys.Rev. (1962) V126, N 3, p. 938.
6. K.E. German, A.F. Kuzina, M.S. Grigoriev, B.G. Gulev, V.I. Spitzyn / Proc. Acad. Sci.Russ (1986) V 287, N 3, P. 650-653.

7. K.E. German, M.S. Grigor'ev, A.F. Kuzina, V.I. Spitsyn / Russ. Journ. Inorg. Chem. (1987) V 32, N 5, p. 667 – 670.
8. V.N. Gerasimov, S.V. Kryutchkov, K.E. German, V.M. Kulakov, A.F. Kuzina X-ray photoelectron study of structure of technetium compounds. In: Technetium and rhenium in chemistry and nuclear medicine. V.3. Ed. by Nicolini M., Bandoly G., Mazzi U. New York: Raven Press, 1990. P.231-252.
9. F.W. De Wette / Phys. Rev. (1961) v.123, N 1, p.103.
10. V.P. Tarasov, S.A. Petrushin, V.I. Privalov et all. / Koord. Khim. (1986) V12, N 9, p.713.
11. P. Jordan, K. May, K. Girgenrath. Abstracts of International Conference on Nuclear and Radiochemistry. Lindau, FRG. Oct. 8-12, 1984, p. 247.
12. J.A. Rard, M.H. Rand, G. Anderegg, H. Wanner. Chemical Thermodynamics of Technetium – Amsterdam: Elsevier, 1999. – 544 p.

The work was carried out with partial funding by the Ministry of Science and Higher Education of the Russian Federation (subject No. AAAA-A16-116110910010-3)



Thomas Gerber and Konstantin German