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Mobilization of Toxic Elements from an Abandoned Manganese Mine in the Arid Metropolitan Las Vegas (NV, USA) Area

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Speciation of technetium in carbonate media under helium ions and γ radiation

Abstract: Technetium carbonates complexes produced by chemical, electrochemical and radiolytic methods have been studied by UV-Visible, X-ray Absorption Fine Structure (XAFS) and Density Functional Theory methods. The $(NH_4)_2TcCl_6$ salt was dissolved in 2 M $KHCO_3$. The resulting purple solution was analyzed by XAFS and UV-Visible spectroscopy. The UV-Visible spectra exhibits a band centered at 515 nm. The XAFS results were consistent with the presence of polymeric species containing the $[Tc_2(\mu - O)_2]^{4+}$ core coordinated to carbonate ligand. Concerning the electrochemical methods, the pertechnetate anion was electrochemically reduced in concentrated carbonate solution $[(CO_3^{2-}) = 5$ M and $(HCO_3^-) = 0.5$ M]. For the radiolytic reduction, the speciation of Tc under Helium ions particle beam and γ radiation was examined by UV-Visible and XAFS spectroscopy in high concentrated carbonate media. In concentrated carbonate solutions, pertechnetate as Tc(VII), was not reduced under irradiation due to the formation of carbonate radical which is a strong oxidant. Then, the solution proposed was the addition of formate to the solution which can scavenge hydroxyl radical 10 times faster than carbonate and prevent re-oxidation

of reduced technetium. The XANES and EXAFS spectroscopies, approved by theoretical methods, revealed that the final product of the radiolytic reduction of pertechnetate is in the +IV oxidation state. The final structure of the reduced product by He^{2+} radiolysis was the same as electrochemical reduction. From this complex determination and evolution vs. the dose, this study is reporting the solubility of the Tc(IV) complex.

Keywords: Technetium speciation, carbonate, X-ray absorption spectroscopies, α-radiation, γ-radiation.

1 Introduction

Technetium, element 43, is the lowest atomic number radioelements, it was discovered in 1937 during irradiation of a molybdenum plate with deuteron beam at the Berkeley cyclotron [1]. Different Tc isotopes with half-life varying from a couple of seconds to millions of years for ^{99}Tc [2] are reported. The most common isotopes are ^{99}Tc ($t_{1/2} = 2.11 \times 10^5$ years, $E_{\beta-max.} = 295.5$ keV [3]) and ^{99m}Tc ($t_{1/2} = 6.01$ h; $\gamma = 142.6$ keV). The isotope ^{99}Tc is a fission product of the nuclear industry (6% from fission of 235-U) while ^{99m}Tc is used as an imaging agent in medical applications.

In nuclear waste management, Tc species in the oxidation state (III) and (IV) can be produced by the chemical or radiolytic reduction of Tc(VII). These species can interact with the surrounding ligands, in a storage media containing carbonate and Tc(IV) and/or Tc (III)-carbonate complexes may be formed and control the mobility of Tc. Therefore, the understanding of the fundamental chemistry of Tc in the presence of carbonates is important to predict its behavior in storage conditions.

Previous studies in carbonate media have shown that Tc(IV) carbonate complexes can be produced by (i) electroreduction of TcO_4^- in 0.7 M HCO_3^- or (ii) dissolution of TcO_2 or $(NH_4)_2TcCl_6$ with CO_3^{2-}.

A previous electrochemical study [4] has suggested the carbonate complex of Tc(IV) [synthesized in 0.7 M (HCO_3^-)] to be mononuclear. The formula $Tc(CO_3)_q(OH)_n^{4-n-2q}$ and $Tc(CO_3)_q(OH)_{n+1}^{3-n+1-2q}$ were respectively proposed for Tc(IV) and Tc(III). Nevertheless, these formulas were never confirmed and supported by structural analysis.

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Further UV-Visible studies have shown that Tc(IV) spectra exhibits a band a 515 nm. Previous study on Tc(IV) chemistry in chloride, sulfate and triflate media indicate that this band to be characteristic to the $[Tc(\mu - O)_2Tc]^{4+}$ structure. Then it might be possible that Tc(IV) in carbonate media exhibits also the $[Tc(\mu - O)_2Tc]^{4+}$ structure.

X-ray Absorption Fine Structure (XAFS) spectroscopy has been shown to be a powerful technique for the determination of Tc polymer structure but it has never been performed on Tc carbonate species.

Due to the presence of high level waste, radiations (α, β, or γ) are likely to be encountered in storage conditions. For this reason, understanding the speciation of Tc carbonate under radiation is important. There are very few studies on the speciation of technetium in carbonate media. Also, its behavior has been studied only under γ irradiation [5] and no other types of ionizing radiation. Pertechnetate chemistry under irradiation has been studied [6, 7]. These works have reported that the major product of radiolysis of Tc(VII) in alkaline solutions (pH = 10.8) in presence of most of organic compounds is insoluble $TcO_2 \cdot xH_2O$. So, the radiolysis of aqueous solutions has induced the formation of Tc(IV) oxide colloids [8, 9].

In this context, we decided to study to study the speciation of Tc carbonate in absence and presence of He^{2+} and γ radiations. Here, we prepared Tc carbonate complexes from (i) the electroreduction of TcO_4^-, (ii) the dissolution of $(NH_4)_2TcCl_6$ and (iii) the radiolytic reduction in carbonate media and perform their speciation by UV-Visible and XAFS spectroscopy. The structures of the complexes were also studied by density functional theory (DFT) methods in order to match the theoretical and the experimental results.

2 Materials and methods

2.1 Chemical

Techetium-99 is a weak beta emitter (E_{max} = 292 keV). All manipulations were performed in radiochemistry laboratories designed for chemical synthesis with radionuclides using efficient HEPA-filtered fume hoods and following locally approved radioisotope handling and monitoring procedures. The solution of ammonium pertechnetate in water (0.118 M) was obtained from LEA-CERCA laboratory and used to prepare the solution for radiolysis with a purity of 99.99 %.

All the chemicals were purchased from Sigma-Aldrich with analytical grade and used without further purification. TcO_4^- in liquid form with the concentration of 5×10^{-4} M was added in carbonate solution $[(K_2CO_3) = 5 M, (KHCO_3) = 0.5 M]$.

The ratio of carbonate/bicarbonate is resulting in a buffer solution with pH = 10.8. Radiometer PHM220 was used for pH measurement and it was checked that the pH value does not evolve after irradiation experiments. All the solutions and systems were purged with pure argon gas before irradiation experiments in order to avoid the N_2 effect from atmosphere. All the experiments were carried out in ambient conditions. The ultra-pure water with R > 18.5 MΩ was provided by Milli-Q Advantage A10 system.

2.2 Experiments

2.2.1 Electrochemistry

Electrochemistry experiments in galvanic mode were carried out for reduction of Tc(VII). The electrochemical set-up of a three electrodes system connected to a Radiometer VoltalabPGP201 Potentiostat and controlled by a computer. The working electrode was a platinum plate (30 mm × 10 mm). The counter electrode was a platinum plate and the reference electrode was a Ag/AgCl in 3 M KCl.

2.2.2 He²⁺ irradiation

The He^{2+} ions beam was provided by the ARRONAX cyclotron facility with E = 64.5 MeV and linear transfer energy (LET) = 22.7 keV · μm⁻¹. The dose rate was determined *in situ* according to the Super Fricke dosimetry [10] method using a CARY4000 (VARIAN) UV-Visible spectrophotometer and a HELLMA probe with an optical path of 10 mm. The super Fricke method was based on the oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) by water radiolysis. The variation of Fe^{3+} absorbance was recorded as a function of the irradiation time at 304 nm (ε = 2197 M⁻¹ cm⁻¹). Super Fricke solutions were prepared by dissolving the desired quantity of ferrous sulfate [H_2SO_4, (Fe^{2+}) = 10 mM] and sodium chloride NaCl (1 mM) in aerated aqueous 0.4 M sulfuric acid (H_2SO_4) solutions. Fricke dose rate was found around 3800 Gy · min⁻¹ using the ferric ion radiolytic yield for the high energetic Helium ions particle from the literature [G(Fe^{3+}) = 1.2 μmol · J⁻¹] [11]. The technique of in situ UV-Visible spectrophotometry can be broadened beyond dose rate determination. Indeed, it can also be used to quickly and accurately quantify the species which have a UV-Visible signature. The irradiation cell was made from Poly-Ether-Ether-Ketone (PEEK) like γ-ray irradiation except its entrance window (Borosilicate Glass of 150 μm). All the samples were homogenized by stirring and followed by UV-Visible spectroscopy.

2.2.3 γ-ray irradiation

Gamma-Service Medical, model GSM D1 with ^{137}Cs as radioactive source with LET = 0.23 keV · μm^{-1} was used for γ-ray irradiation into the ARRONAX facility lab. The source activity is up to 200 TBq with dose uniformity less than 10 % over a 300 mm[2]. The dose rate was determined for all irradiation positions at 3 Gy · min^{-1}. Fricke dosimetry method was used for dose rate determination [10]. Fe(III) concentration was measured by recording the UV-Vis absorption of solution after irradiation at λ = 304 nm. Cylindrical PEEK cells were used for irradiation.

2.2.4 Radiolytic chemical yields

The radiolytic yield was defined as the number of species formed or disappeared per unit of deposited energy. It is expressed in the international system by μmol · J[-1] and was calculated at a time t after transition of the ionizing irradiation according to the below equation:

$$G_t(X) = \frac{X_t}{\rho D}$$

where (X)t is the concentration of the species X at the time t (M), ρ is the density of the irradiated solution (kg · L^{-1}) and D the absorbed dose (J · kg^{-1}). Radiolytic yields were calculated by taking in account the high density (ρ = 1.54 kg · L^{-1}) of the highly concentrated carbonate solution (5 M).

2.3 Structure determination

2.3.1 XAFS spectroscopy

X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements were performed at the SOLEIL synchrotron facility on the MARS beamline, which is dedicated to the study of radioactive samples in the hard X-ray range [12], and at the Advance Photon Source at Argonne National laboratory on the 12 BM beamline. The ring of SOLEIL synchrotron was operated at 2.75 GeV with an average intensity of 430 mA. Incoming X-ray beam energy selection and horizontal focusing was performed by using a Si(220) double crystal monochromator and high-energy rejection (harmonic part) and vertical collimation/focalization was performed by using two Pt coated large reflecting mirrors. The spectra were recorded around the Tc-K edge (21044 eV) at room temperature in fluorescence mode with a high-purity Ge multi-element solid state detector using specifically adapted cells for liquids. The concentration of Tc in the solutions was around 5×10^{-4} M. A molybdenum foil was used for the calibration of beam energy at 20,000 eV. EXAFS were recorded within the range 21,000–21,094 eV with variable energy steps depending on the scan region (5 eV at the pre-edge; 1 eV at the edge, increasing energy steps after the edge; k steps equal 0.05 Å^{-1}). ATHENA and ARTEMIS [13] software were used for the data analysis and fitting, respectively. The data normalization for XANES and EXAFS spectra extraction were performed using standard procedures. In particular, the EXAFS spectra have been k[3]-weighted and their Fourier transform performed in the k range (2.9–11.45) Å^{-1} with a Kaiser-Bessel window (dk = 1). The fits were performed in the R space (ranges specified in the tables) starting from the models obtained from DFT calculations (see below). Phases and amplitudes were calculated using the FEFF6 code [14] integrated in ARTEMIS. The amplitude reduction factor S_0^2 was fixed to one, the energy threshold E_0 was taken at the inflection point of the edge. The obtained data are presented in the k[3]-weighted EXAFS and Fourier transforms. The uncertainty determined by EXAFS on the distance is ±1 %.

2.3.2 Computational details

All structures were optimized using the DFT approach as implemented in the Gaussian09 package [15]. Calculations were performed using the hybrid B3LYP functional [16]. The 6-31++G** basis set for the Hydrogen, Carbon and O atoms were used as well as the Stuttgart/Dresden effective core potentials [17] (SDD ECPs) for the Tc metal atoms. To take into account part of the solvent effect, solvation was introduced using a dielectric continuum model of permittivity $\epsilon_0 = 80$. The conductor-like polarizable continuum model [18] implemented in Gaussian09 was used.

3 Results and discussion

3.1 Speciation of technetium in concentrated carbonate media without radiation

In absence of ionizing radiation, the Tc carbonate complex was synthesized by two different methods; (1) chemical reaction and (2) electrochemical reduction. In chemical reaction, $(NH_4)_2TcCl_6$ is dissolved in $KHCO_3$ solution. The concentration of $(NH_4)_2TcCl_6$ and $KHCO_3$ were 10^{-3} M and 2 M, respectively. The violet solution of technetium chloride moves to a pink solution with absorption
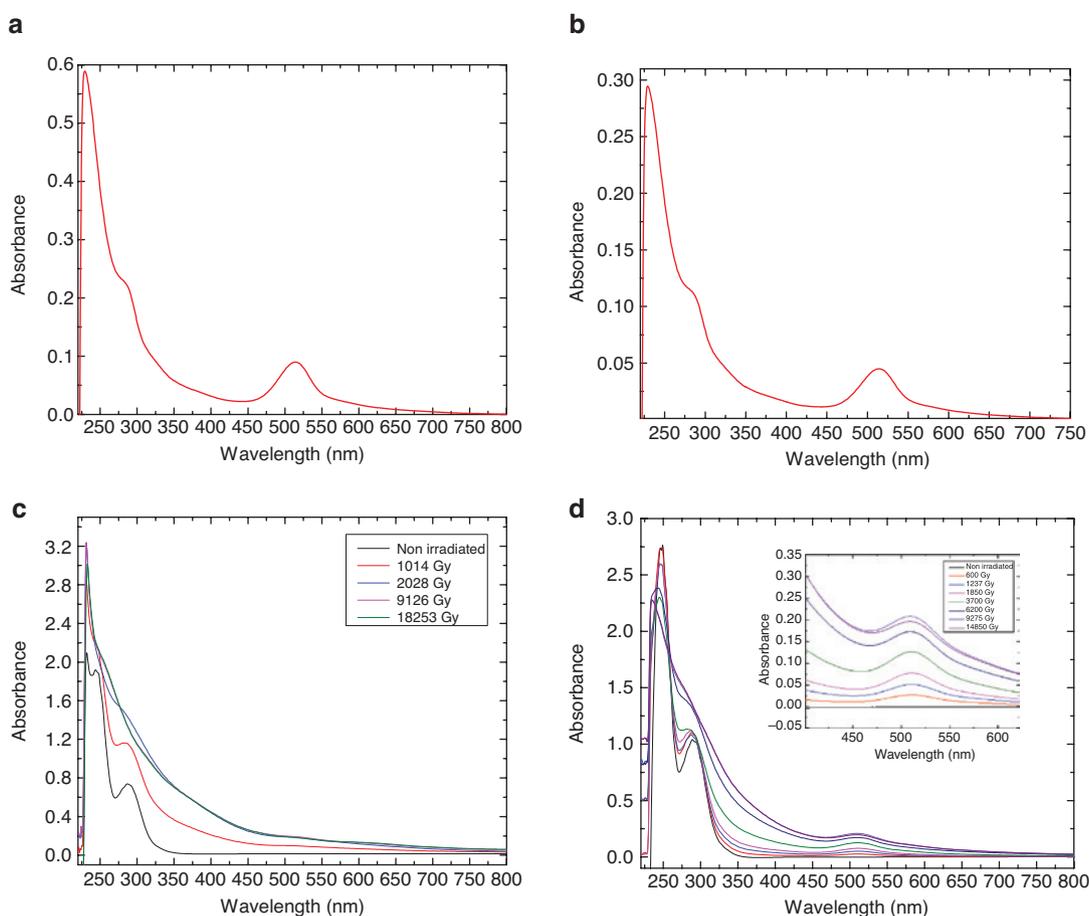
Figure 1: The figures a and b have been obtained after the chemical or electrochemical reductions TcVII/TcIV while in figures c and d, the evolution of the spectrum have been followed as a function of the dose.

UV-Vis spectrum of obtained pink solution with $\lambda Tc^{IV} = 515$ nm by (a) dissolving $(NH_4)TcCl_6$ [(KHCO_3) = 2 M]; (b) electrochemical reduction of TcO_4^- [$(CO_3^{2-}) = 5$ M, $(HCO_3^-) = 0.5$ M], E = −0.78 V; (c) γ radiolysis of [Tc(VII)] = 5 × 10^{-4} M in the solution of carbonate [$(CO_3^{2-}) = 5$ M, $(HCO_3^-) = 0.5$ M, $(HCO_2^-) = 1$ M], dose rate = 3 Gy · min^{-1}; (d) He^{2+} radiolysis of [Tc(VII)] = 5 × 10^{-4} M in carbonate solution [$(CO_3^{2-}) = 5$ M, $(HCO_3^-) = 0.5$ M, $(HCO_2^-) = 0.7$ M], dose rate = 1000 Gy · min^{-1}.

at 515 nm. In the electrochemical reduction experiments, pertechnetate (TcO_4^-) with a concentration of 5×10^{-4} M was reduced by electrochemistry (reduction potential, E = −0.78 V in highly carbonate solution [$(CO_3^{2-}) = 5$ M and $(HCO_3^-) = 0.5$ M]. The transparent solution of Tc(VII) becomes pink. The product obtained by electrochemistry shows the same UV-Visible spectrum (Figure 1b) as the one obtained by chemical reaction (Figure 1a), which implies that the final products obtained from both methods should be the same. To confirm this observation and to try to unravel the structure of the possible Tc complex that was formed, XANES and EXAFS spectroscopy are used for determination of oxidation state and structural definition, respectively. As shown in Figure 2a, the XANES spectrum of the final product obtained by chemical reaction indicates that the oxidation state is +IV, thus considering the UV-Vis results, it can be assumed that the final product is in both cases a carbonate complex of Tc(IV).

The EXAFS spectrum and the corresponding Fourier transform of the final product from the chemical reaction are given in Figure 3a together with the associated theoretical best fit signals. Between the different structures determined by calculations using DFT, the best fit results are obtained by starting with the structure of $(OH_2)_2(CO_3)_2Tc$-O_2-$Tc(CO_3)_2(OH_2)_2$ (Figure 4), which is a dimer of technetium with the core of $Tc_2(\mu - O)_2$. EXAFS parameters (Table 1) obtained for the best fit indicate that the local environment of the Tc absorbing atoms is constituted by 4 O atoms at 2.03(2) Å, 2 O atoms at 2.48(2) Å, 1 Tc atoms at 2.32(2) Å, 2 C atoms at 3.13(3) Å and 8 O atoms at 3.89(4) Å. The important latter contribution is probably partially to be ascribed to the multiple scattering signals from the O-Tc-O atomic paths.

Previous study in carbonate solution [4] [$(HCO_3^-) = 0.7$ M] suggested the Tc(IV) carbonate to be a mononuclear species. In our experimental conditions [$(CO_3^{2-}) = 5$ M,

a

b

c
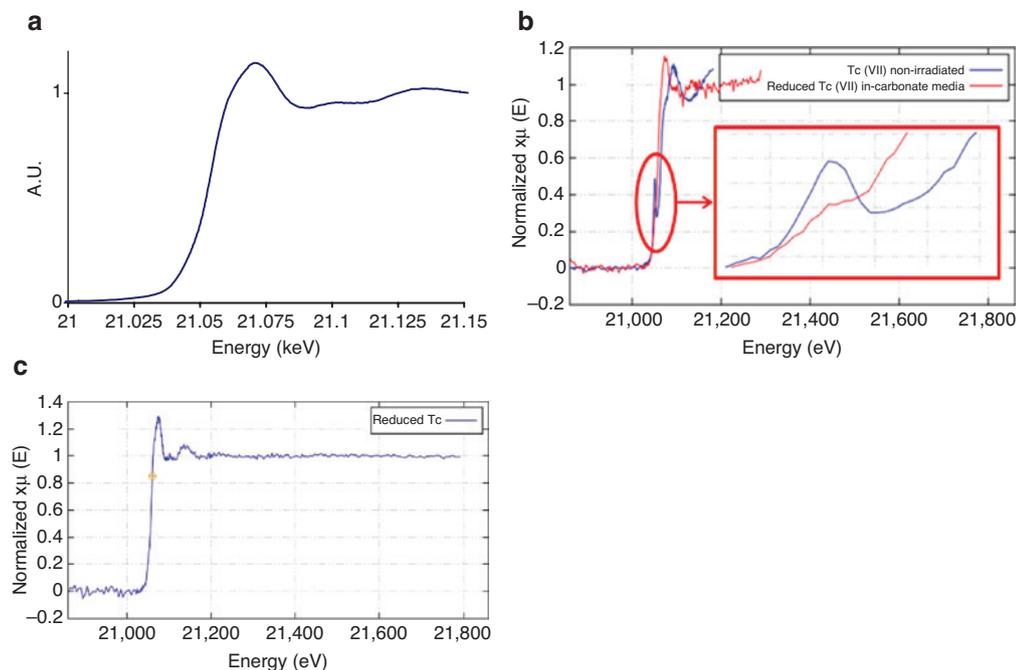
Figure 2: The figures a and c show the XANES spectrum of the TcIV while the figure b shows the XANES spectrum of TcVII before and after the irradiation experiment.

Normalized XANES spectrum of the Tc species obtained by (a) dissolving $(NH_4)TcCl_6$ [$(KHCO_3) = 2$ M]; (b) γ radiolysis of $[Tc(VII)] = 5 \times 10^{-4}$ M in the solution of carbonate [$(CO_3^{2-}) = 5$ M, $(HCO_3^-) = 0.5$ M, $(HCO_2^-) = 1$ M], dose rate = 3 Gy · min^{-1}; (c) He^{2+} radiolysis of $[Tc(VII)] = 5 \times 10^{-4}$ M in carbonate solution [$(CO_3^{2-}) = 5$ M, $(HCO_3^-) = 0.5$ M, $(HCO_2^-) = 0.7$ M], dose rate = 1000 Gy · min^{-1}.

a

b
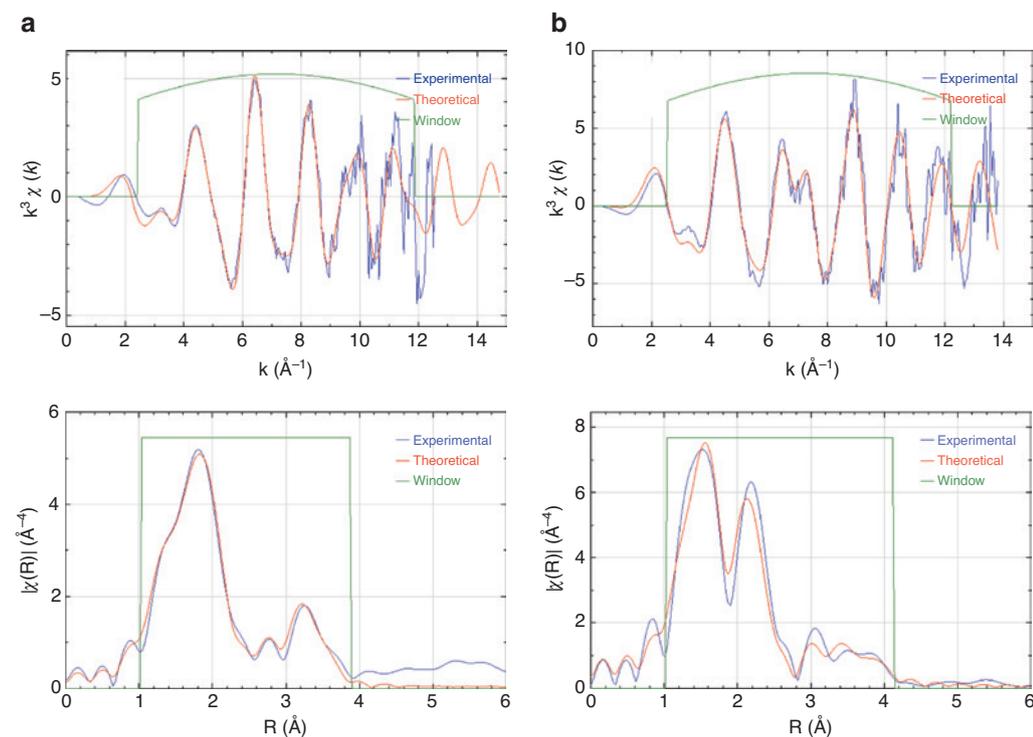
Figure 3: Figure a shows the EXAFS spectrum of the TcIV obtained by the chemical reduction while the figure b shows the EXAFS spectrum of TcIV obtained by the radiolytic one.

k^3- EXAFS spectra (top) and Fourier Transform (bottom) of the Tc species obtained by (a) dissolving $(NH_4)TcCl_6$ [$(KHCO_3) = 2$ M]; (b) He^{2+} radiolysis of $[Tc(VII)] = 5 \times 10^{-4}$ M in carbonate solution [$(CO_3^{2-}) = 5$ M, $(HCO_3^-) = 0.5$ M, $(HCO_2^-) = 0.7$ M], dose rate = 1000 Gy · min^{-1}.
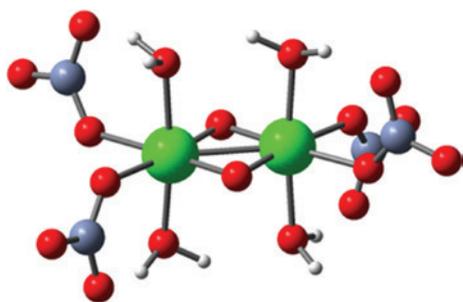
Figure 4: Calculated structure by DFT simulation of the technetium carbonate complex; technetium, oxygen, carbon and hydrogen atoms in green, red, gray and white colors; hydrogen bonds are showing in dotted mode with formula $Tc_2(\mu-O)_2(CO_3)_4(OH_2)_4$.

Table 1: Results of EXAFS spectra fits for the technetium carbonate complex obtained by dissolving $(NH_4)TcCl_6$ [$(KHCO_3)=2$ M].

Scattering	# C.N	R (Å)	σ^2 (Å^2)
Tc-O	4	2.03(2)	0.0089
Tc-O	2	2.48(2)	0.0090
Tc-Tc	1	2.32(2)	0.0054
Tc-C	2	3.13(3)	0.0040
Tc-O	8	3.89(4)	0.0042

$S_0^2=1$, $\Delta E_0=-7.9$ eV, fit in R space (range $=1.01-3.89$ Å), $K_w=3$, R-factor $=0.0002$ and reduced $\chi^2=2.32$

C.N, number of neighboring at distance R; # fixed value.

$(HCO_3^-)=0.5$ M] the XAFS analysis indicate the Tc(IV) carbonate complex to be a dimer. According to the other studies [19], the reduction of Tc(VII) in sulfato-chloride media leads to a $[Tc^{IV}(\mu-O)_2Tc^{III}]$ complex and the reduction of Tc(IV) in EDTA media leads in a first step to $[Tc^{IV}(\mu-O)_2Tc^{III}]$ and in a second step to $(Tc^{III}-O-Tc^{III})$ but reduction of Tc(VII) in concentrated carbonate media leads only to the $[Tc^{IV}(\mu-O)_2Tc^{IV}]$ dimer.

Another study [20] has suggested that the carbonate stabilize the Tc(IV). In this study the pink carbonate complex of Tc(IV) was kept in contact with air and also in glove box with controlled atmosphere ($O_2 < 2$ ppm). In air, the pink Tc(IV)-carbonate solution was oxidized to transparent solution of Tc(VII) while its was stable for 6 months in glove box under inert atmosphere.

As the complex has a dimeric $[Tc_2(\mu-O)_2]^{4+}$ core, the concentration of the complex at the end of reduction will be half of the initial concentration of Tc(VII) before reduction. Considering that $(Tc)_{initial}=5\times10^{-4}$ M, the concentration of the complex can be calculated at the end of the reaction and was equal to 2.5×10^{-4} M. Its absorption coefficient was determined to 200 $M^{-1}\cdot cm^{-1}$.

3.2 Speciation of technetium in concentrated carbonate media in presence of radiation

Irradiation of carbonate solutions forms the carbonate radical which is a powerful oxidant [21]. In order to understand the mechanism of technetium radiolysis in carbonate solutions, it is mandatory to know the effect of direct radiolysis on the carbonate radical formation. To this purpose, we have performed a pico-second pulse radiolysis study of concentrated carbonate solutions [22], it was shown that carbonate radicals are formed from the direct effect decay in 500 ns after absorption of the radiation. It was observed that only those carbonate radicals, produced by scavenging of hydroxyl radical, which can react with technetium, were obtained.
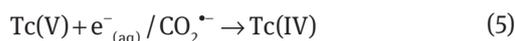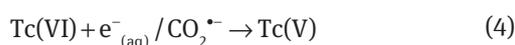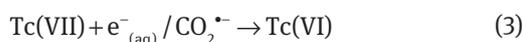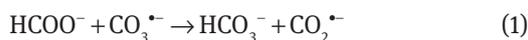
3.2.1 γ radiolysis of technetium in carbonate solution

Pertechnetate with a concentration of 5×10^{-4} M was added to the carbonate solution (5 M). It was observed that pertechnetate ion was not reduced under irradiation it due to its redox potential (E = 0.78 V) in presence of carbonate radical as a powerful oxidant. That is the reason why it was concluded that the formate ion must be added also in this case to the carbonate solution in order to reduce Tc(VII). The formate ion scavenges the hydroxyl radical 10-fold faster than carbonate [23] and so the produced formate radical is a reductant species but weaker than $e^-_{(aq)}$.

In a first step, the formate was added with the concentration of 1 M to the carbonate solution (5 M) and after irradiation of Tc(VII) was reduced to the pink solution associated previously to the Tc(IV) complex. XANES spectroscopy indicates the presence of Tc(IV) in the final product (Figure 2b).
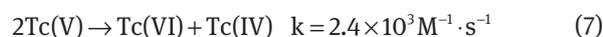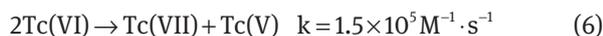
The evolution of the UV-Visible spectra of the Tc(VII) solution in carbonate during the γ-irradiation is presented in Figure 1c. The time evaluation by irradiation of spectra implies that Tc(VI) and Tc(V) are reduced rapidly through disproportionation or radiolysis. It can be concluded that Tc(VII) was reduced directly to Tc(IV). The UV-Visible spectrum of the irradiation product differs from those obtained by chemical and electrochemical reduction. It implies that the final product of γ radiolysis has a different structure. The same solution is irradiated only with lower formate concentration (0.7 M) in order to prevent the direct effect on the formate radiolysis but the result and final product have not changed.

It is known that the reductant $CO_2^{\bullet-}$ species is produced by carbonate radiolysis [22]. However, $e^-_{(aq)}$, which comes

from water radiolysis, can be considered a more powerful reducing species. It can be concluded that the formate radical ($CO_2^{\bullet-}$) was involved in the reduction process of Tc(VII). The experimental conditions were chosen in order to enhance reduction process by decreasing oxidative species ($OH^{\bullet}$, $H^{\bullet}$) contribution. It can be considered that Tc(VII) was reduced mostly by $e^-_{(aq)}$ and partly by the formate radicals. Then, among the classical water radiolytic species ($OH^{\bullet}$, $H^{\bullet}$, $e^-_{(aq)}$, H_2, H_2O_2) we take into account for the $e^-_{(aq)}$ as the main agent involved into Tc(VII) the reduction. Therefore, the proposed reduction mechanism of Tc(VII) were proposed:

$$HCOO^- + CO_3^{\bullet-} \rightarrow HCO_3^- + CO_2^{\bullet-} \tag{1}$$

$$HCOO^- + OH^{\bullet} \rightarrow H_2O + CO_2^{\bullet-} \tag{2}$$

$$Tc(VII) + e^-_{(aq)}/CO_2^{\bullet-} \rightarrow Tc(VI) \tag{3}$$

$$Tc(VI) + e^-_{(aq)}/CO_2^{\bullet-} \rightarrow Tc(V) \tag{4}$$

$$Tc(V) + e^-_{(aq)}/CO_2^{\bullet-} \rightarrow Tc(IV) \tag{5}$$

The mechanisms of TcO_4^- reduction by $e^-_{(aq)}$ and of disproportionation have been discussed [6] and the rate constant for disproportionation of Tc(VI) and Tc(V) were determined:

$$2Tc(VI) \rightarrow Tc(VII) + Tc(V) \quad k = 1.5 \times 10^5 \, M^{-1} \cdot s^{-1} \tag{6}$$

$$2Tc(V) \rightarrow Tc(VI) + Tc(IV) \quad k = 2.4 \times 10^3 \, M^{-1} \cdot s^{-1} \tag{7}$$

These rates constants are relatively lower. Moreover, without the radiolytic yield of formation of Tc(IV), it is not possible to check if there is any disproportionation in reduction mechanism or not.

In order to study the effect of carbonate concentration on formation of technetium complexes, another radiolysis experiment is carried out under γ-ray irradiation of Tc(VII) with concentration of 5×10^{-4} M in solution with carbonate concentration of 10^{-2} M, bicarbonate 10^{-3} M and formate 10^{-2} M. The UV-Visible studies of the final product of radiolysis is consistent with the presence of small TcO_2 particles as described in the literature [8]. This result indicates that carbonate plays role as ligand only at high concentrations (>2 M).

3.2.2 Speciation of Tc in carbonate media under Helium ions particle beam

A solution of Tc(VII) (5×10^{-4} M) in 5 M carbonate/0.7 M formate was irradiated with a dose rate of 1000 Gy $\cdot$ min^{-1}. The UV-Visible spectra for He^{2+} radiolysis of Tc(VII) are

presented in Figure 1d. The UV-Visible spectra are similar to those obtained by electrochemistry this implies that the final product of reduction of Tc(VII) is Tc(IV) with the $Tc_2(\mu-O)_2$ center. XANES spectroscopy is consistent with the presence of Tc(IV) (Figure 2c). The EXAFS spectrum and the corresponding Fourier transform show that some differences are present in the local structure around the Tc centers compared to the chemical reaction product (Figure 3b). The EXAFS fitting parameters of the best fit obtained from the same initial DFT structure (Table 2) indicate that the local environment of the Tc absorbing atoms is constituted by 6 O atoms at 2.01(2) Å, 1 Tc atom at 2.51(3) Å, 2 C atoms at 3.09(3) Å and 8 O atoms at 4.35(4) Å, validated by the average values of these distances determined by DFT calculations (Table 3). In addition, in this case we managed to explicitly add a contribution at 4.03 Å (with a degeneracy of eight) due to the multiple scattering from the O-Tc-O path. These results show that also the complex obtained by He^{2+} radiolysis has a $Tc_2(\mu-O)_2$ center similarly to the structure obtained for the complex resulting by chemical synthesis (Figure 4), however, the fact that only one average short distance is obtained for the six neighboring oxygen atoms, implies that probably for this complex the formula might be written as $(H_2O)_2(CO_3)_2Tc-O_2-Tc(CO_3)_2(H_2O)_2$.

Nevertheless, the UV-Visible spectrum of the final product seems similar to the $Tc_2(\mu-O)_2$ center product obtained by electrochemistry. Then, the same absorption coefficient is used for the obtained product by He^{2+} radiolysis at 515 nm. Figure 5 displays the concentration

Table 2: Results of fitting of experimental and theoretical EXAFS spectra of technetium carbonate complex obtained by He^{2+} radiolysis of Tc(VII) in carbonate solution.
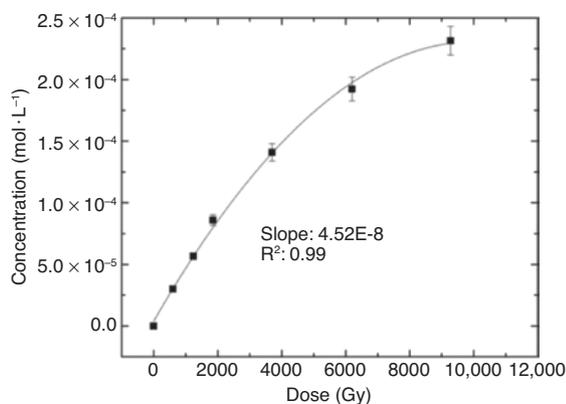
Scattering	# C.N	R (Å)	σ^2 (Å^2)
Tc-O	6	2.01(2)	0.0069
Tc-Tc	1	2.51(3)	0.00254
Tc-C	2	3.09(3)	0.0050
O-Tc-O	8	4.03(4)	0.0045
Tc-O	8	4.35(4)	0.0055

$S_0^2 = 1$, $\Delta E_0 = -2.69$ eV, fit in R space (range $= 1.02–4.11$ Å), $K_w = 3$, R-factor $= 0.0016$ and reduced $\chi^2 = 30.7$

C.N, number of neighboring at distance R; # fixed value.

Table 3: Interatomic distances (Å) in $Tc_2(\mu-O)_2(CO_3)_4(OH_2)_4$ found by DFT calculations.

Bond	Tc-O	Tc-Tc	Tc-C
Distance	2.04	2.52	3.07

Figure 5: Concentration of obtained $Tc_2(\mu - O)_2$ center product vs. dose obtained by He^{2+} radiolysis of $[Tc(VII)] = 5 \times 10^{-4}$ M in carbonate solution $[(CO_3^{2-}) = 5$ M, $(HCO_3^-) = 0.5$ M, $(HCO_2^-) = 0.7$ M], dose rate = 1000 Gy.min^{-1}.

of the $Tc_2(\mu - O)_2$ center product as a function of absorbed dose. Therefore, the $G[Tc_2(\mu - O)_2]$ value is determined as 3.0×10^{-8} mol · J^{-1}.

3.2.3 Discussion

A structural difference occurs between electrochemical and radiolytic reduction. It is due to the reduction mechanism because in radiolysis there are different types of radicals $[CO_2^{\bullet-}, e^-_{(aq)}, H^\bullet, CO_3^{\bullet-}]$ vs. the electrochemical where only e^- are involved. Moreover, the difference between the two radiations is the particle, and so the energetic deposition, pathway.

(i)   For γ-ray experiment, $G[e^-_{(aq)}]$ value (0.26 µmol · J^{-1}) [24] was higher and the Tc(VII) reduction occurs mainly by this strong reductant, then the UV-Visible analysis could not measure the complete $Tc_2(\mu - O)_2$ complex spectrum. In this case, more long is the experiment time more close are the Tc(IV) to react each other in the global system which improves the production of the Tc polymeric species assigned to the broad spectral background detected in the Figure 1c. For He^{2+} irradiation experiment, the $G(e^-_{(aq)})$ decreased (0.04 µmol · J^{-1}) [24] by the intra-track mechanisms and the Tc(VII) reduction occurs slowly mainly by the $CO_2^{\bullet-}$ formate radical species. In this case, the short time of the experiment (a few minutes) and the local irradiation of the solution induces lower reductant species and lower Tc(IV) improve Tc dimeric species and not polymeric one (see Figure 1d). Finally, it can be noticed that in this latter case the reduction by He^{2+} irradiation is close to the electrochemical one with the same UV-Visible spectrum of the final $Tc_2(\mu - O)_2$ complex.

4 Conclusion

In summary, technetium carbonate complexes were prepared from the dissolution of $(NH_4)_2TcCl_6$ in 2 M $KHCO_3$ and by the electroreduction of TcO_4^- in 5 M CO_3^{2-}. Both methods gave a pink solution with similar UV-Visible spectrum (band at 515 nm). Results indicate the pink species to be a Tc(IV) polynuclear species and consists of a $(Tc_2O_2)^{4+}$ core coordinated to carbonate ligand in monodentate mode; the formula $[Tc_2(\mu - O)_2(CO_3)_4(H_2O)_4]^{4-}$ was proposed. The radiation experiments have determined that the soluble Tc(IV) can be synthesized in the concentrated carbonate media. The electrochemical and chemical reactions give the products with the same molecular structure determined by XANES and EXAFS. Formate scavenge hydroxyl radical faster than carbonate thus the Tc(VII) can be reduced inside the concentrated carbonate solution under irradiation. This study reveals new insights on Tc chemistry: (i) the carbonate complex of Tc(IV) has a dimeric form and is not a mononuclear species as it was previously stated. (ii) Tc(IV) carbonate complex of is soluble at concentration of 5×10^{-4} M while in literature its solubility was suggested around 10^{-7} M within an high impact onto its migration into environment.

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