

Chemical Behaviour of Tc(IV) Complexes under Alpha Irradiation in Chloride Media

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In order to study the stability of Tc(IV) complexes in chloride media under alpha radiation produced by a cyclotron, an electrochemical cell was developed. In this cell, the stability of TcCl_6^{2-} , $\text{TcCl}_5(\text{H}_2\text{O})^-$, $\text{Tc}_2\text{OCl}_{10}^{4-}$, $\text{Tc}_n\text{O}_y^{(4n-2y)+}$ and $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ were studied in 3 M chloride media with a pH range from 0.3 to 2.5. The stability of a ($\text{TcCl}_6^{2-}/\text{TcCl}_5(\text{H}_2\text{O})^-/\text{Tc}_2\text{OCl}_{10}^{4-}$) mixture was also investigated during alpha irradiation under a constant current. These studies showed that TcCl_6^{2-} is a very stable compound whereas chloro-oxygenated compounds were oxidized to Tc(VII). Consequently, the relative stabilities of the Tc(IV) complexes in 3 M chloride media under alpha irradiation was determined.

1. Introduction

One option retained for management of nuclear waste is storage in deep underground which presents naturally reducing conditions (absence of oxygen and reducing potential). Nevertheless, the presence of nuclear waste and its radiation associated may lead to the radiolysis of the surrounding media and to the formation of radiolytic compounds. Among these nuclear wastes, ^{99}Tc is considered as one of the most important fission products: it represents 10% of the mass of fission product and has an important toxicity ($T_{1/2} = 2.01 \times 10^5$ y, β^- emitter). That is why studies on the behaviour of technetium are of great importance.

In the storage media, Tc could be present in Tc(IV) or even Tc(III) forms. The behaviour of Tc under radiation depends on the radiolytic species formed: in presence of organic compounds (formate,¹ EDTA,² alcohol t-butyl^{3,4}) radiolysis leads to the reduction of Tc(VII) to Tc(IV) and formation of colloids or polymers whereas in non organic media, oxidation of Tc(IV) to Tc(VII) is observed.^{5,6}

After 10 000 years of deposit, alpha emitters will be the preponderant radioactive elements in the spent fuel. Then alpha radiolysis will be the dominant radiolytic process. After this period, ^{99}Tc will also be present in the spent fuel and in the case of an alteration of the confinement barrier, the Tc species could be in contact with the water radiolysis products. In this context, the stability of Tc(IV) complexes under alpha radiation was studied in aqueous media.

Many researches on the speciation of Tc(IV) were carried out in chloride media. Recent studies^{7,8} have shown that speciation of Tc(IV) between pH = 0 and pH = 2.5 is dominated by polymeric species. For this reason, in our work, the stability of Tc(IV) complexes was studied in 3 M chloride. These studies were carried out under alpha radiation produced by a cyclotron. Furthermore, an electrochemical cell was specially developed: it was used to study the stability of Tc(IV) complex under alpha radiation. It has also been used in other works to study influence of alpha radiolysis on the stability of UO_2 (Ref. 9) and nuclear glass.¹⁰

In this work, we present the effects of alpha radiation on Tc(IV) stability in chloride media in absence and presence of an electrochemical potential.

2. Experimental

2.1. Electrochemical cell and experimental set-up. Alpha irradiation by a cyclotron has already been used to study the influence of alpha radiolysis on stabilities of radio-elements.¹¹ The experimental set-up was composed of electrochemical cells which presented a reduced volume in order to minimize dilution of radiolytic product. Those cells have an optical window with a thickness < 500 μm that allowed the transmission of alpha particles.

The cell developed for our studies, presents a volume of 30 ml and an optical window made of silica with a thickness of $130 \pm 10 \mu\text{m}$. The cell (Figure 1) consists of: a reactional block for solution, a cover used to maintain the electrochemical system and a collimator.

The collimator (\varnothing 6 mm) was designed in order to focus alpha beam through solution. It also permits to maintain the optical window whose tightness is assured by an O-ring. The solutions were homogenized by a magnetic stirrer and permanently purged by Argon bubbling during irradiation.

The electrochemical system is composed of 3 electrodes purchased from Radiometer Analytical, S.A. The working electrode

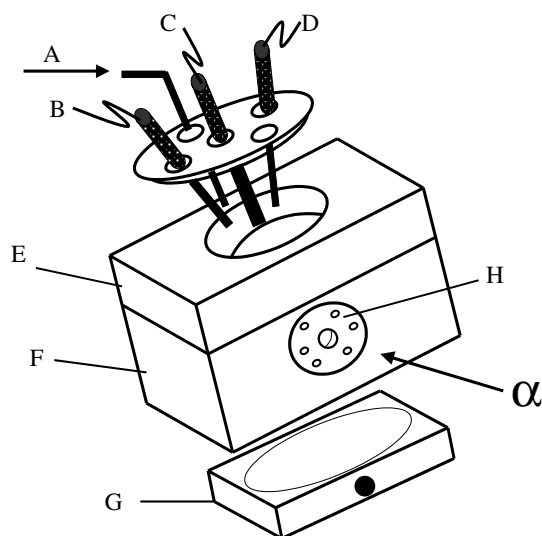


Figure 1. Set-up used for alpha radiolysis experiment. A: argon bubbling, B: auxiliary electrode, C: working electrode, D: reference electrode, E: cover, F: reactional block, G: magnetic stirrer and H: collimator.

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(XR 140) is made of a platinum plate (1 cm × 4 cm). The auxiliary electrode (XR 110) is constituted of a platinum plate (5 mm × 5 mm). This electrode is installed in a lounge (Al 120) in order to isolate oxidation products that may form at this electrode during reactions. The reference electrode is an Ag/AgCl electrode (XR 300), $E = 248 \text{ mV/ENH}$.

These electrodes were installed on a glass cover CP 4R which was settled and screwed on the cell cover. This electrochemical system was connected to a PGP 201 potentiometer equipped with voltmaster 4, which allows to work under constant current or potential and provides analyses by cyclic voltammetry. This experimental set-up was then settled on an ionisation chamber and controlled from the outside of the cyclotron alveolus through large coaxial cables.

Alpha irradiation was performed at the CERI cyclotron (CNRS-Orleans). This cyclotron generates alpha particles ($^4\text{He}^{2+}$) in an energy range from 5 MeV to 45 MeV. Energy of 28 MeV was chosen for all the Tc experiments. The calculations from SRIM2000 code indicated that $^4\text{He}^{2+}$ (28 MeV) passed into the cell carrying energy of 5–6 MeV and a penetration depth in solution about 45 μm . The rest of energy was absorbed by the cell window and by the titanium windows of the ionization chamber. The alpha beam was monitored during the experiments as a function of the measured $^4\text{He}^{2+}$ current on the ionisation chamber. During all the experiments, the current of $^4\text{He}^{2+}$ flux in solution was fixed in the range from 10 nA to 50 nA. The irradiation time depending of experience, vary between 5 mn to 40 mn. The duration of an experiment is around 1h30.

2.2. Dosimetry and H_2O_2 measurement. Doses were measured using the Fricke's dosimetry¹² which is based on the oxidation of Fe(II) to Fe(III) by water radiolysis products. The Fe(II) solution used was 1 mM FeSO_4 prepared in a 0.4 M H_2SO_4 solution. The concentration of Fe(III) was then determined by UV-Vis measurement at 304 nm ($\epsilon = 2197 \text{ M}^{-1}\text{cm}^{-1}$). The radiolytic yield G (Fe(III)) used for the dose calculations was $1.06 \cdot 10^{-6} \text{ mol. J}^{-1}$.

The concentrations of H_2O_2 produced during the irradiation were measured using the Ghormley's method¹³ which is based on oxidation of I^- to I_3^- by H_2O_2 . The 1 mM iodide solution, used in this work, was prepared by dissolving KI in a 0.1 M NaOH solution. The measurement protocol is showed as follows: 1) A phthalate buffer solution (pH = 6) was added to the KI solution. 2) The $[\text{I}_3^-]$ was then determined by UV-Vis measurement at 350 nm ($\epsilon = 28000 \text{ M}^{-1}\text{cm}^{-1}$). 3) The concentration of H_2O_2 in solution was finally determined from the concentration of I_3^- .

2.3. Chemical and Sample preparation. The NaTcO_4 solution used for all syntheses was purchased from Cerca, Co France. All chemicals used are of analytical purity and all solutions were prepared with Milli-Q water.

The stock solution of TcCl_6^{2-} (0.02 M, 6 M HCl) was prepared by heating TcO_4^- at 90 °C in concentrated HCl. The stock solution was kept in the dark at an inert gas glove box.

The stock solution of $\text{Tc}_2\text{OCl}_{10}^{4-}$ (8.8 mM) in $[\text{Cl}^-] = 3 \text{ M}$, pH = 0.3 was synthesised by using the method recently developed.⁸ The $\text{TcCl}_6^{2-}/\text{Tc}_2\text{OCl}_{10}^{4-}$ mixture in 3 M chloride solution (pH = 0.3, $[\text{Tc}] = 10.95 \cdot 10^{-5} \text{ M}$) was prepared from $\text{Tc}_2\text{OCl}_{10}^{4-}$ and TcCl_6^{2-} stock solutions.

The $\text{Tc}_n\text{O}_y^{(4n-2y)+}/\text{TcO}_2 \cdot x\text{H}_2\text{O}$ solution was prepared by diluting TcCl_6^{2-} in a medium of $[\text{Cl}^-] = 3 \text{ M}$ and pH = 1. The pH was adjusted to 2.5 by NaOH. The solution was kept in an inert gas glove box, sealed and carried to Orleans cyclotron facility under inert atmosphere to avoid oxidation.

The mixture $\text{TcCl}_6^{2-}/\text{TcCl}_5(\text{H}_2\text{O})^-/\text{Tc}_2\text{OCl}_{10}^{4-}$ used for experiment under constant current was synthesised by reduction ($i = -500 \mu\text{A}$) of TcO_4^- in the electrochemical cell in 3 M chloride solution (pH = 1).

2.4. Other techniques. ⁹⁹Tc analysis was performed using liquid scintillation counting: Packard 2550 TR/AB Liquid

Scintillation analyzer). The scintillation cocktail used was ULTIMA GOLD ABTM (Packard). UV-Vis spectra between each irradiation were recorded on a Shimadzu 2401 double beam spectrometer in 1 cm cell. Ultra pure water was used as the reference.

3. Results

All experiments were performed in the aim of describing the behaviour of Tc(IV) complexes under alpha irradiation. In this work, our studies were focused on 3 M chloride media with a pH range from 0.3 to 2.5 since the speciation of Tc(IV) in this domain is well documented.^{7,8} According to their results, $\text{Tc}_2\text{OCl}_{10}^{4-}$ is dominant in a pH range from 0 to 1 and $\text{Tc}_n\text{O}_y^{(4n-2y)+}$ over pH = 1.3. At $[\text{Tc}] = 10^{-4} \text{ M}$, $\text{Tc}_n\text{O}_y^{(4n-2y)+}$ begin to precipitate in $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ at pH = 2.2⁷. Thus, irradiations of TcCl_6^{2-} and $\text{Tc}_2\text{OCl}_{10}^{4-}$ were carried out at pH = 0.3 and those of a $\text{Tc}_n\text{O}_y^{(4n-2y)+}/\text{TcO}_2 \cdot x\text{H}_2\text{O}$ mixture at pH = 2.5. The stability of a $\text{TcCl}_6^{2-}/\text{TcCl}_5(\text{H}_2\text{O})^-/\text{Tc}_2\text{OCl}_{10}^{4-}$ mixture in $[\text{Cl}^-] = 3 \text{ M}$, pH = 1 was also studied under a constant current ($i = -500 \mu\text{A}$).

3.1. Irradiation of TcCl_6^{2-} . TcCl_6^{2-} ($\text{Tc} = 9.85 \cdot 10^{-5} \text{ M}$) was irradiated in a 3 M chloride medium (pH = 0.3), with a dose rate of $117.43 \text{ Gy} \cdot \text{min}^{-1}$. Changes of absorption spectra during irradiations are presented in Figure 2.

Figure 2 reveals that TcCl_6^{2-} is practically stable under alpha irradiation. After irradiation with a dose of 11700 Gy, only 4 % of TcCl_6^{2-} was transformed. Thus, the initial radiolytic yield was found to be $-(3.40 \pm 1.13) \cdot 10^{-10} \text{ mol} \cdot \text{J}^{-1}$, which is 1000 lower than that of Fattahi et al⁵ under gamma radiation in the same medium.

Under the same experimental conditions, the alpha irradiation of a 3 M chloride solution (pH = 0.3) without Tc led to the apparition of a specie characterized by an absorption band at 230 nm. According to literature data [14] this band is characteristic of the radiolytic product Cl_3^- .

3.2. Irradiation of a $\text{TcCl}_6^{2-}/\text{Tc}_2\text{OCl}_{10}^{4-}$ mixture. A $\text{TcCl}_6^{2-}/\text{Tc}_2\text{OCl}_{10}^{4-}$ mixture ($\text{Tc} = 10.95 \cdot 10^{-5} \text{ M}$) was irradiated in a 3 M chloride solution (pH = 0.3) with a dose rate of $117.43 \text{ Gy} \cdot \text{min}^{-1}$. Changes of absorption spectra during irradiations are presented in Figure 3 and the evolution of Tc species in Figure 4.

Figure 3 and 4 confirm the stability of TcCl_6^{2-} and revealed that irradiation of $\text{Tc}_2\text{OCl}_{10}^{4-}$ leads to its oxidation to TcO_4^- . This reaction is characterized by disappearance of the band at 354 nm ($\epsilon = 9307 \text{ M}^{-1}\text{cm}^{-1}$) of $\text{Tc}_2\text{OCl}_{10}^{4-}$ and the apparition at 287 nm ($\epsilon = 2316 \text{ M}^{-1}\text{cm}^{-1}$) of the band characteristic of TcO_4^- . Consequently, the hypothesis that irradiation of $\text{Tc}_2\text{OCl}_{10}^{4-}$ leads to its oxidation to Tc(VII) was proved. The initial radiolytic yields of the Tc species are presented in Table 1.

3.3. Irradiation of a $\text{Tc}_n\text{O}_y^{(4n-2y)+}/\text{TcO}_2 \cdot x\text{H}_2\text{O}$ mixture. A $\text{Tc}_n\text{O}_y^{(4n-2y)+}/\text{TcO}_2 \cdot x\text{H}_2\text{O}$ mixture ($\text{Tc} = 9.9 \cdot 10^{-5} \text{ M}$) was irradiated in a medium of $[\text{Cl}^-] = 3 \text{ M}$ and pH = 2.5, with a dose rate

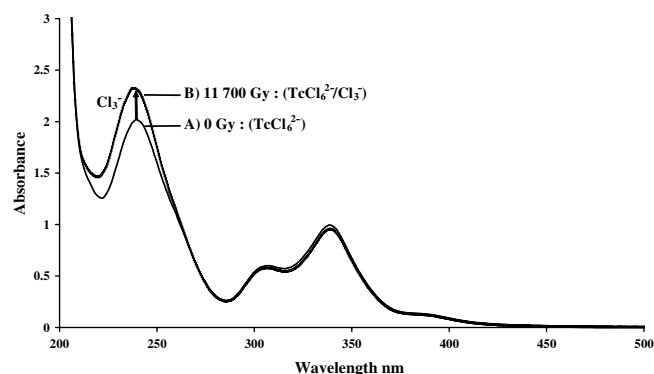


Figure 2. Change of absorption spectra of TcCl_6^{2-} during alpha irradiation. Operating conditions: dose rate: $117.43 \text{ Gy} \cdot \text{min}^{-1}$; atmosphere argon; $[\text{Tc}] = 9.85 \cdot 10^{-5} \text{ M}$, $[\text{Cl}^-] = 3 \text{ M}$, pH = 0.3.

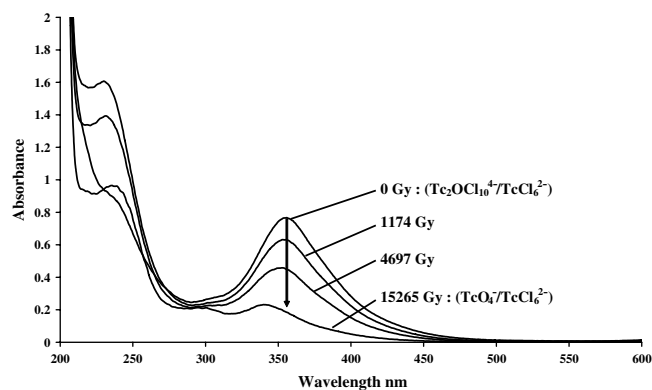


Figure 3. Change of absorption spectra of a $\text{Tc}_2\text{OCl}_{10}^{4-}/\text{TcCl}_6^{2-}$ mixture during alpha irradiation. Operating conditions: dose rate: $117.43 \text{ Gy}\cdot\text{min}^{-1}$; atmosphere argon; $[\text{Tc}] = 10.95 \cdot 10^{-5} \text{ M}$, $[\text{Cl}^-] = 3 \text{ M}$, $\text{pH} = 0.3$; doses: 0 Gy, 1174 Gy, 4697 Gy and 15365 Gy.

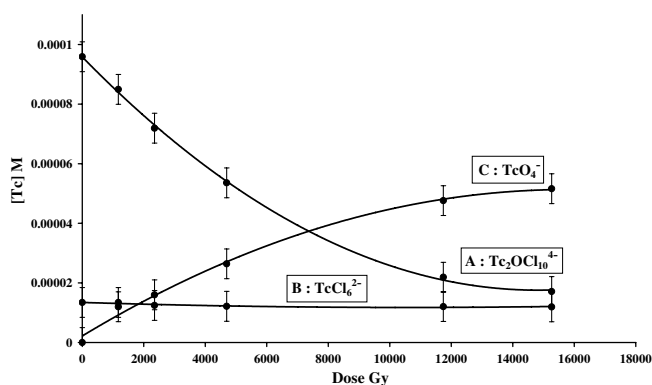


Figure 4. Concentration of Tc species as a function of dose during alpha irradiation of a $\text{Tc}_2\text{OCl}_{10}^{4-}/\text{TcCl}_6^{2-}$ mixture. Operating conditions: $[\text{Cl}^-] = 3 \text{ M}$, $\text{pH} = 0.3$; atmosphere argon. Dose rate: $117.43 \text{ Gy}\cdot\text{min}^{-1}$. A: $\text{Tc}_2\text{OCl}_{10}^{4-}$, B: TcCl_6^{2-} and C: TcO_4^{2-} .

TABLE 1: G Values for TcO_4^{2-} , TcCl_6^{2-} and $\text{Tc}_2\text{OCl}_{10}^{4-}$ in 3 M Chloride, $\text{pH} = 0.3$ Under Alpha Radiation

Compound	G ($\text{mol}\cdot\text{J}^{-1}$)
$\text{Tc}_2\text{OCl}_{10}^{4-}$	$-9.05 \cdot 10^{-9}$
TcCl_6^{2-}	$-2.70 \cdot 10^{-10}$
TcO_4^{2-}	$1.02 \cdot 10^{-8}$

Dose rate: $117.43 \text{ Gy}\cdot\text{min}^{-1}$, argon atmosphere

of $28.55 \text{ Gy}\cdot\text{min}^{-1}$. During this experiment, the Tc concentration was measured using liquid scintillation after filtration through a $0.2 \mu\text{m}$ membrane filter. The changes of absorption spectra during irradiations are presented in Figure 5 and the evolution of Tc species in Figure 6.

These figures reveal the complete oxidation of Tc(IV) species to Tc(VII) after a dose of 1713 Gy. The initial radiolytic yield for the soluble Tc species are presented in Table 2.

During this experiment the concentration of H_2O_2 was determined using Ghormley's method (Figure 7). The value of $[\text{H}_2\text{O}_2]$ produced in presence of Tc(IV) was compared to the value obtained without Tc. The initial radiolytic yield of H_2O_2 without Tc was then determined: $G(\text{H}_2\text{O}_2) = 1.23 \cdot 10^{-7} \text{ mol}\cdot\text{J}^{-1}$. Meanwhile, in presence of Tc(IV), H_2O_2 or OH. radicals were completely consumed in a dose range from 0 Gy to 400 Gy.

3.4. Irradiation of a $\text{TcCl}_6^{2-}/\text{TcCl}_5(\text{H}_2\text{O})^-/\text{Tc}_2\text{OCl}_{10}^{4-}$ mixture under constant current. Aim of this experiment is to study the behaviour of Tc(IV) complexes during alpha irradiation under reducing potential: a mixture $\text{TcCl}_6^{2-}/\text{TcCl}_5(\text{H}_2\text{O})^-/\text{Tc}_2\text{OCl}_{10}^{4-}$ was irradiated in a 3 M chloride solution ($\text{pH} = 1$) with a dose yield of $34.40 \text{ Gy}\cdot\text{min}^{-1}$ under a constant current ($i = -500 \mu\text{A}$). During irradiation, the electrochemical potential fluctuated between -420 mV and $-450 \text{ mV}/(\text{Ag}/\text{AgCl})$. The

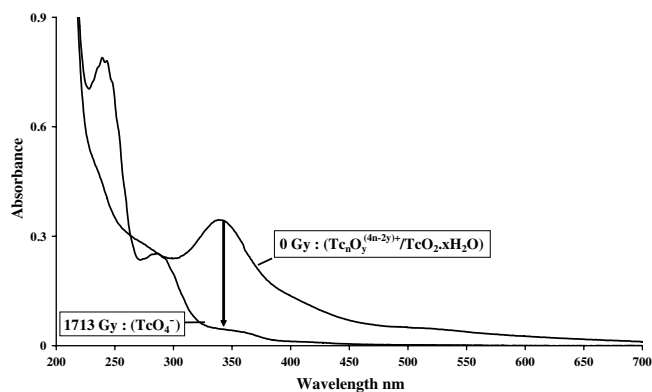


Figure 5. Change of absorption spectra of a $\text{TcO}_2 \cdot x\text{H}_2\text{O}/\text{Tc}_n\text{O}_y^{(4n-2y)+}$ mixture during alpha irradiation. Operating conditions: dose rate: $28.55 \text{ Gy}\cdot\text{min}^{-1}$; atmosphere argon; $[\text{Tc}] = 9.9 \cdot 10^{-5} \text{ M}$, $[\text{Cl}^-] = 3 \text{ M}$, $\text{pH} = 2.5$; doses: 0 Gy and 1713 Gy.

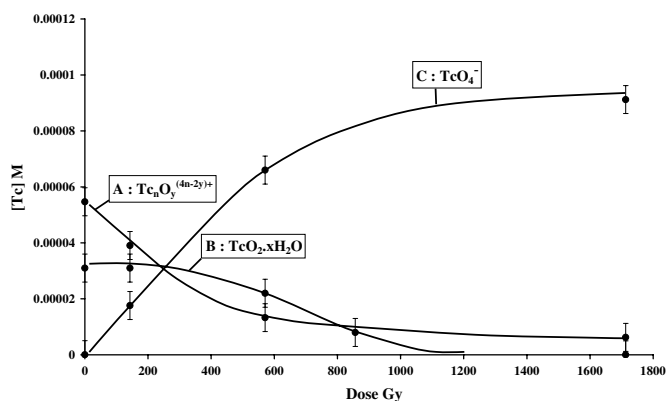


Figure 6. Concentration of Tc species as a function of dose during alpha irradiation of a $\text{TcO}_2 \cdot x\text{H}_2\text{O}/\text{Tc}_n\text{O}_y^{(4n-2y)+}$ mixture. Operating conditions: $[\text{Cl}^-] = 3 \text{ M}$, $\text{pH} = 2.5$; atmosphere argon. Dose rate: $28.55 \text{ Gy}\cdot\text{min}^{-1}$. A: $\text{Tc}_n\text{O}_y^{(4n-2y)+}$, B: $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ and C: TcO_4^{2-} .

TABLE 2: G Values for TcO_4^{2-} and $\text{Tc}_n\text{O}_y^{(4n-2y)+}$ in 3 M Chloride ($\text{pH} = 2.5$) Under Alpha Radiation

Compound	G ($\text{mol}\cdot\text{J}^{-1}$)
$\text{Tc}_n\text{O}_y^{(4n-2y)+}$	$-1.09 \cdot 10^{-7}$
TcO_4^{2-}	$1.12 \cdot 10^{-7}$

Dose rate: $28.55 \text{ Gy}\cdot\text{min}^{-1}$, argon atmosphere

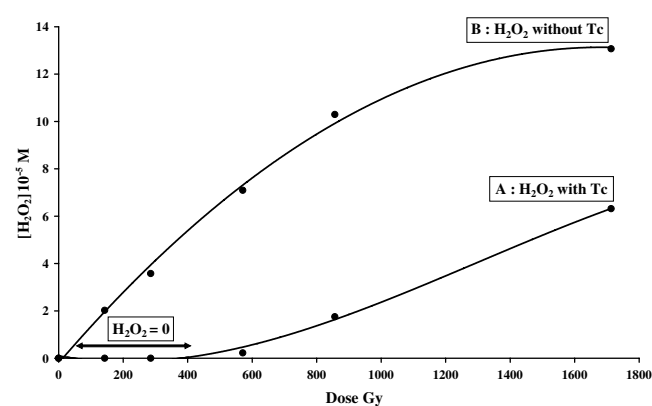


Figure 7. Concentration of produced H_2O_2 with A) and B) for in absence and in presence of Tc(IV) during irradiation of a 3 M chloride solution ($\text{pH} = 2.5$); atmosphere argon. Dose rate $28.55 \text{ Gy}\cdot\text{min}^{-1}$.

changes of absorption spectra during irradiations are presented in Figure 8 and the evolution of Tc species in Figure 9. Analyses of Figure 8 and 9 reveal that the electrochemical potential can not impede the oxidation of Tc(IV) to Tc(VII). The experimental yields of Tc species are presented in Table 3.

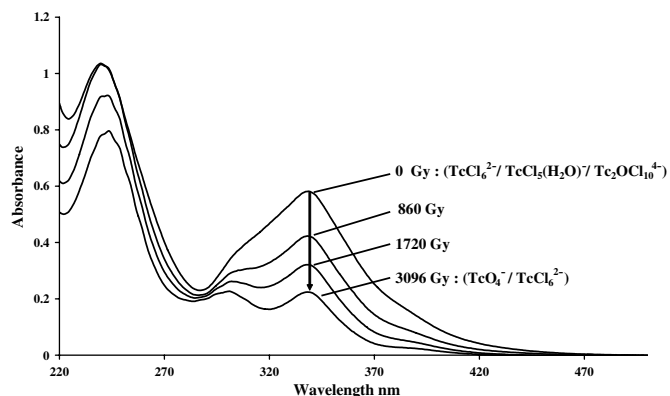


Figure 8. Change of absorption spectra of a $\text{TcCl}_6^{2-}/\text{TcCl}_5(\text{H}_2\text{O})^-/\text{Tc}_2\text{OCl}_{10}^{4-}$ mixture during alpha radiation under a constant current ($i = -500 \mu\text{A}$). Operating conditions: dose rate: $34.40 \text{ Gy}\cdot\text{min}^{-1}$; atmosphere argon; $[\text{Tc}] = 8.10 \cdot 10^{-3} \text{ M}$, $[\text{Cl}^-] = 3 \text{ M}$, $\text{pH} = 1$; doses: 0 Gy, 860 Gy, 1720 Gy and 3096 Gy.

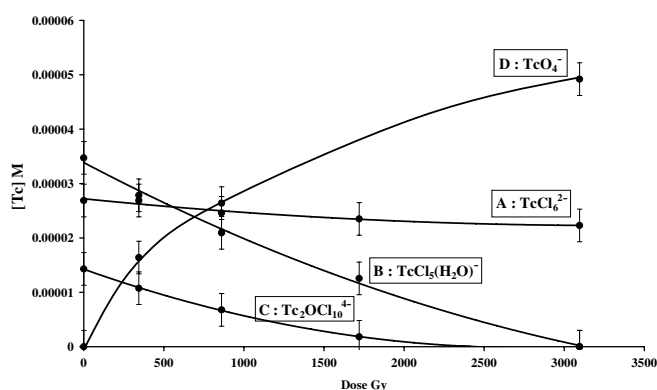


Figure 9. Concentration of Tc species as a function of dose during alpha irradiation of a $\text{TcCl}_6^{2-}/\text{TcCl}_5(\text{H}_2\text{O})^-/\text{Tc}_2\text{OCl}_{10}^{4-}$ mixture under a constant current ($i = -500 \mu\text{A}$). Operating conditions: $[\text{Cl}^-] = 3 \text{ M}$, $\text{pH} = 1$; atmosphere argon. Dose rate: $34.40 \text{ Gy}\cdot\text{min}^{-1}$. A: TcCl_6^{2-} , B: $\text{TcCl}_5(\text{H}_2\text{O})^-$, C: $\text{Tc}_2\text{OCl}_{10}^{4-}$ and D: TcO_4^- .

TABLE 3: G Values for TcO_4^- , TcCl_6^{2-} , $\text{Tc}_2\text{OCl}_{10}^{4-}$ and $\text{TcCl}_5(\text{H}_2\text{O})^-$ in 3 M Chloride ($\text{pH} = 1$) During Alpha Radiation Under a Constant Current ($i = -500 \mu\text{A}$)

Compound	G ($\text{mol}\cdot\text{J}^{-1}$)
TcCl_6^{2-}	$-2.8 \cdot 10^{-9}$
$\text{Tc}_2\text{OCl}_{10}^{4-}$	$-8.66 \cdot 10^{-9}$
$\text{TcCl}_5(\text{H}_2\text{O})^-$	$-1.58 \cdot 10^{-8}$
TcO_4^-	$2.98 \cdot 10^{-8}$

Dose rate: $34.40 \text{ Gy}\cdot\text{min}^{-1}$, argon atmosphere

4. Discussion

We showed in this paper that under alpha irradiations, the Tc(IV) complexes in 3 M chloride media undergo oxidation to Tc(VII). In the same medium, non irradiated solution of Tc(IV) complexes are stable against oxidation for times equivalent to those of irradiation experiments. Under alpha radiation, TcCl_6^{2-} is the most stable and the species having cores of the $[\text{Tc}-\text{O}-\text{Tc}]^{6+}$ and $[\text{Tc}(\mu-\text{O})_2\text{Tc}]^{4+}$ structures were oxidized easily.

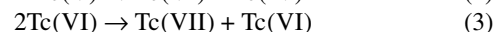
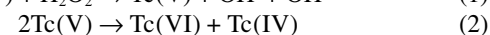
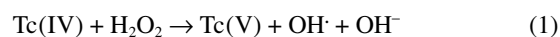
The determination of the initial radiolytic yields allows to classify the Tc(IV) complexes according to their stabilities: $\text{TcCl}_6^{2-} > \text{Tc}_2\text{OCl}_{10}^{4-} > \text{TcCl}_5(\text{H}_2\text{O})^- > \text{Tc}_n\text{O}_y^{(4n-2y)+}$.

This order suggested that the stability of Tc(IV) complexes depends on the number of oxygen and chlorine atoms in the structure. The presence of chlorine atoms in the structure can increase the stability of the Tc(IV) complexes, which is due to the electron donation capability of chlorine atoms. It is noteworthy that this phenomena has already been observed for rhenium¹⁵: the chlorinated Re(IV) complexes are obviously more

stable than oxygenated Re(IV) complexes. Furthermore, literature data reveal that the Tc(VII)/Tc(IV) potential value depends on the number of chlorine atoms in the Tc(IV) structure: this potential is equal to 0.595 V/ENH for $\text{Tc(IV)} = \text{TcO}(\text{OH})_2$ (Ref. 16) and 0.849 V/ENH for $\text{Tc(IV)} = \text{TcCl}_5(\text{H}_2\text{O})^-$.¹⁷ Thus, the increasing of Tc(VII)/Tc(IV) potential value with the number of chlorine atoms can also explain the relative stability of the Tc(IV) complexes.

Consequently, the experiment performed in $[\text{Cl}^-] = 3 \text{ M}$, $\text{pH} = 1$ showed that TcCl_6^{2-} , which exhibits six chlorine atoms in its structure, is the most stable of Tc(IV) complexes whereas $\text{TcCl}_5(\text{H}_2\text{O})^-$ and $\text{Tc}_2\text{OCl}_{10}^{4-}$ with each one five chlorine atoms/Tc are less stable. Between these two compounds, $\text{TcCl}_5(\text{H}_2\text{O})^-$ is less stable than $\text{Tc}_2\text{OCl}_{10}^{4-}$, which is probably due to the presence of π bonding in the $[\text{Tc}-\text{O}-\text{Tc}]^{6+}$ structure⁸ which stabilizes more strongly the valence IV than the H_2O ligand of $\text{TcCl}_5(\text{H}_2\text{O})^-$.

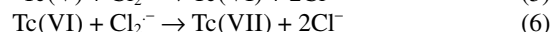
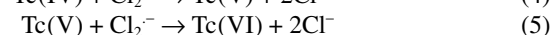
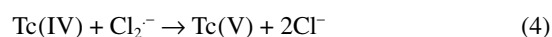
In a $[\text{Cl}^-] = 3 \text{ M}$ solution ($\text{pH} = 2.5$), the measurement of $[\text{H}_2\text{O}_2]$ in absence and presence of Tc(IV) have proved that this compound is involved in the radiolytic oxidation of Tc(IV), which corresponds to the previous studies realised under gamma radiation.^{5, 18} Among the reaction proposed,¹⁸ one is the oxidation of Tc(IV) to Tc(V) followed by disproportionation of Tc(V) to Tc(VI), Tc(IV) and Tc(VII):



Nevertheless, if oxidation of Tc(IV) to Tc(VII) occurs exclusively according to (1), (2) and (3), it implies that $G(\text{Tc(VII)}) = (1/2) G(\text{H}_2\text{O}_2)$. Considering the experimentally determined $G(\text{Tc(VII)})$ and $G(\text{H}_2\text{O}_2)$ values: $1.12 \cdot 10^{-7} \text{ mol}\cdot\text{J}^{-1}$ and $1.23 \cdot 10^{-7} \text{ mol}\cdot\text{J}^{-1}$, respectively, it appeared that $G(\text{Tc(VII)}) > (1/2)G(\text{H}_2\text{O}_2)$: this result indicated that other mechanisms than (1), (2) and (3) took place in the Tc(IV) oxidation.

Furthermore, irradiation of NaCl solution leads to formation of chlorinated species¹⁹: Cl_2^- , Cl_2 and Cl_3^- , these species may also be involved in Tc(IV) oxidation.

It has been discussed⁵ that under gamma radiation, Cl_2^- is involved in Tc(IV) oxidation. The mechanisms proposed are listed below:



Considering the presence of H_2O_2 and Cl_2^- , it was proposed that G (Tc(VII)) can be formulated as :

$$G(\text{Tc(VII)}) = 1/3 G(\text{Cl}_2^-) + 2/3 G(\text{H}_2\text{O}_2) \quad (7)$$

However, in the present work, we think that the mechanism described in (4), (5) and (6) may occur in the Tc(IV) oxidation. Nevertheless, the presence of Cl_3^- during alpha irradiation, indicates that this species may also be involved in Tc(IV) oxidation. Radiolytic oxidation of Tc(IV) in concentrated chloride media can be considered as a complex process. And for clarifying the mechanisms of this oxidation, further experiments by pulsed alpha radiolysis have to be performed in order to specify the different chlorinated radicals in absence and presence of Tc.

5. Conclusion

This work showed that among the Tc(IV) complexes under alpha irradiation TcCl_6^{2-} is stable whereas the other complex undergo oxidation to TcO_4^- . This work has permitted to classify the Tc(IV) complexes as function of their stabilities under alpha radiation.

- It showed that H₂O₂ is involved in the radiolytic oxidation of Tc(IV)
- The experiments realised under electrochemical potential proved that in spite of a reducing potential the radiolytic oxidation of Tc(IV) can still occur. This result indicated that in a deep storage media, without organic species, the mobility of Tc can be dependant on TcO₄⁻ produced by the radiolytic oxidation of Tc(IV) compounds.

For understanding better the oxidation mechanisms, it will be interesting to perform experiments by alpha pulsed radiolysis in presence and absence of Tc(IV) and determine the role of chlorinated radicals. In this aim, the cell developed in this work will be used for further experiments on ⁹⁹Tc at the future cyclotron of Nantes.

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References

- (1) K. Ben-Said, Y. Seimbille, M. Fattahi, C. Houée-Levin, and J. C. Abbé, *J. Appl. Radiat. Isot.* **54**, 45 (2001).
- (2) W. W. Lukens, J. J. Bucher, N. M. Edelstein, and D. K. Shuh, *Environ. Sci. Technol.* **36**, 1124 (2002).
- (3) T. Sekine, H. Narushima, Y. Kino, H. Kudo, M. Lin, and Y. Katsumura, *Radiochim. Acta* **90**, 611 (2002).
- (4) T. Sekine, H. Narushima, T. Suzuki, T. Takayama, H. Kudo, M. Lin, and Y. Katsumura, *Colloids and Surfaces A: Physicochem. Eng. Aspects.* **249**, 105 (2004).
- (5) M. Fattahi, L. Vichot, C. Houee-Levin, F. Poineau, and B. Grambow, *Radiochim. Acta* (in press).
- (6) M. Lefort, *Bull. Soc. Chim. Fr.* 882 (1963).
- (7) L. Vichot, M. Fattahi, C. Musikas, and B. Grambow, *Radiochim. Acta* **91**, 263 (2003).
- (8) F. Poineau, M. Fattahi, G. Montavon, and B. Grambow, *Radiochim. Acta* (Submitted).
- (9) T. Mennecart, Thèse université de Nantes (2004).
- (10) K. Ferrand, Thèse université de Nantes (2004).
- (11) C. Corbel, G. Sattonay, J. F. Lucchini, C. Ardois, M. F. Barthe, F. Huet, P. Dehaut, B. Hickel, and C. Jégou, *Nucl. Inst. Meth. Phys. Res. B.* **179**, 225 (2001)
- (12) H. Fricke and E. J. Hart, *Radiation dosimetry.* (Academy Press, New York 1966).
- (13) A. O. Allen, C. J. Hochanadel, J. A. Ghormley, and T. W. Davis, *J. Phys. Chem.* **56**, 575 (1952).
- (14) R. K. Broszkiewicz, *Radiat. Phys. Chem.* **15**, 133 (1980).
- (15) J. A. Casey and K. R. Murman, *Inorganic Chemistry.* **6**, 1055 (1967).
- (16) J. A. Rard, URCL-53440, Lawrence Livermore National Laboratory, Livermore, California (1983).
- (17) K. Ben-said, M. Fattahi, C. Musikas, and J. C. Abbé, *Radiochim. Acta* **83**, 195 (1998).
- (18) L. Vichot, Thèse université de Paris XI (2001).
- (19) T. Lundstrom, H. Christensen, and K. Sehested, *Radia. Phys. Chem.* **61**, 109 (2001).

