Uranium/technetium separation for the UREX process – synthesis and characterization of solid reprocessing forms

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Summary. In the context of the demonstration of the UREX (uranium extraction) process, a separation of uranium and technetium using an anion exchange resin was performed on a simulant solution containing 98.95 g/L of ^{238}U and 130.2 mg/L of ^{99}Tc. After sorption on the resin, TcO_4^- was eluted with NH_4OH, the eluting stream was treated, and the technetium converted to Tc metal (yield = 52.5%). The purity of the compound was analyzed: it contains less than 23.8 μg of ^{238}U per gram of ^{99}Tc. Tc metal was characterized by X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) spectroscopy; EXAFS analysis clearly confirms the hexagonal structure of the metal obtained after treatment. Uranium was converted to ammonium diuranate and to U_3O_8 in a yield of 88.2%, analysis indicates that the compound contains less than 0.16 μg of ^{99}Tc per gram of ammonium diuaranate.

1. Introduction

The U.S. Global Nuclear Energy Partnership Program (GNEP) is evaluating a suite of solvent extraction processes known collectively as UREX+ to treat light-water-reactor spent fuel to recycle the actinides and partition the fission products for efficient disposal. Uranium and technetium are extracted from a nitric acid solution of the dissolved fuel during the first step of this process using tributylphosphate in a hydrocarbon solvent (UREX segment) [1]. In previous work [1] done on separation of the Tc from the U in the UREX product stream, an anion exchange resin was used; TcO_4^- was sorbed on Reillex HPQ resin and successfully separated from the uranyl nitrate, however, recovery of the Tc from the resin and conversion to waste forms were not reported. The main goal of the effort reported here is to recover the ^{99}Tc and convert it into a final disposable waste form. Technetium is a long-term concern to the biosphere because of its long half-life (214 000 y) and high solubility and mobility in the environment as pertechnetate. This a particular concern for disposal in repository environments where atmospheric oxygen is accessible such as the proposed Yucca Mountain site in the U.S. Past work on disposal forms for wastes from electrochemical processing of spent fuel from the decommisioned EBR-II reactor examined alloys of Tc with stainless steel (SS) and zirconium as potential disposal forms for Tc and other metallic fission products [2]. Within the current GNEP Program, alloys of Tc with SS/Zr or Zr alone are under investigation as disposal forms. We report here on, studies to use the weak-base anion exchange resin Reillex HP to recover pertechnetate from solutions simulating the UREX U/Tc product stream, precipitate the uranium, elute the Tc, and convert the eluted Tc to metal.

2. Experimental method

Chemicals

The starting material NH_4TcO_4 was obtained from stocks at the Los Alamos National Laboratory originally purchased from the Oak Ridge Office of Isotope Sales. The compound contains a black impurity, presumably generated by radiolysis in the solid. Prior to use, the compound was purified by dissolution in a dilute NH_4OH/H_2O_2 solution followed by evaporation to dryness to yield a white crystalline solid. The pertechnetate solution ([Tc] = 0.253 M) used for preparation of the UREX simulant solution was synthesized by dissolution of NH_4TcO_4 in deionized (DI) water. Uranyl nitrate (depleted uranium) hexahydrate was purchased from International Bio-Analytical Industries, Inc.), 0.1 M HNO_3 and (n-Bu_4N)HSO_4 was purchased from Sigma-Aldrich, NH_4OH 28%–30% from JT baker and 68%–70% HNO_3 from VWR international.

The Reillex HP resin was purchased from Reilly Industries, Inc. This is a weak-base, highly-crosslinked macroporous polyvinylpyridine resin. In preliminary ion exchange studies of loading and elution of pertechnetate ion from dilute nitric acid solutions, ammonium hydroxide was identified as a good eluant, but significant "tailing" of the elution peak was observed. Pretreatment of the Reillex HP resin beads with concentrated nitric acid at elevated temperatures was observed to reduce the tailing of the elution peak substantially. The pretreatment with nitric acid was suggested by studies in the literature where reaction

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of strong nitric acid solutions with Reillex HPQ (a resin formed by methylating Reillex HP) was observed to oxidize ethylbenzene groups that are introduced by impurities in the crosslinking agent used in the manufacture of the resin [3]. The results of a detailed study of the effects of nitric acid pretreatment on the HP resin capacity and uptake kinetics for TcO_4^- will be reported elsewhere. Here we describe the pretreatment of a batch of resin used in the column tests; 15 g of Reillex HP as received from the manufacturer were gently stirred in 75 mL of 68%–70% HNO_3 and heated 6 h at 85–90 °C. The resin was recovered on coarse glass frit,washed with 3×150 mL of deionized water, and air-dried. The simulated UREX product solution, containing U = 98.95 g/L and Tc = 130.2 mg/L was synthesized by dissolving 209.54 g of $UO_2(NO_3)_2 \cdot 6H_2O$ in 995 mL of 0.01 M HNO_3 and adding 5.20 mL of the 0.253 M NH_4TcO_4 solution. The solution simulated a portion of the UREX product stream that would result form processing a light water reactor fuel with an average burn-up of 60 000 megawatt-days/metric ton of initial uranium in the fuel.

Experimental set up

The system used for U/Tc separation consisted of a polypropylene separation funnel (Nalgene, V = 250 mL) linked by tygon tubing (o.d. = 3.17 mm) to a variable flow peristaltic pump (VWR international, flow: 0.03 mL to 8.2 mL/min). The tubing from the pump was connected to two columns in series. The first column (Kontes, flex column, L = 15 cm, i.d. = 1.5 cm), containing the treated Reillex HP resin, was connected to a second one (L = 5 cm, i.d. = 1 cm, containing untreated Reillex HP resin) used as a guard to catch any breakthrough of pertechnetate from the first column. Before the experiment, the system was conditioned with 0.01 M nitric acid. The separation procedure was performed in three steps: absorption, washing and elution. During the absorption, the solution was passed though the first and second column at a constant flow rate. Then, the system was washed with DI water. For the elution step, the second column was disconnected, and the first column eluted with 1 M NH_4OH. During the experiment, samples were collected in polyethylene centrifuge tubes (V = 50 mL).

EXAFS

XAFS measurements were performed at the advanced photon source (APS) at the MR-CAT, ID-10 station. A metallic technetium ball (23 mg), obtained after separation and treatment of Tc stream, was polished with a 1200 grid paper and 1 μm alumina powder, the polished surface exhibits an area of ∼ 2 mm². The sample was triply contained in polyethylene vials and sent to APS for study. The sample was placed in an aluminum sample holder with kapton window. XAFS spectra were recorded at the Tc-*K* edge (21 044 eV) in fluorescence mode ($k = [0, 17]$ Å^{-1}) using a 13 element germanium detector at room temperature. A double crystal Si[111] was used to monochromate the beam. The energy was calibrated using Tc metal powder in a slurry of epoxy resin. Tc metal powder was prepared by decomposition of NH_4TcO_4 according to [4], the powder was mixed with an epoxy resin and the slurry disposed between kapton foil. For each sample, two spectra were recorded in the

k range ($k = [0, 17]$ Å^{-1}) and averaged. Self absorption was corrected by Athena 0.8.050 [5] software using the Booth algorithm [6]. The background contribution was removed using AutoBk [7] software and data analysis was performed using Winxas 3.1 [8]. For the fitting procedure, amplitude and phase shift function were calculated by Feff 8.2 [9]. Input files were generated by Atoms [10] using crystallographic structures of metallic hexagonal Tc [11].

Adjustments of the k^3-weighted EXAFS spectra were performed under the constraints $S_0^2 = 0.9$ (S_0^2 refers to the amplitude reduction factor). A single value of energy shift (ΔE_0) was used for all scattering. The uncertainty determined by EXAFS on the coordination number (CN) was $\pm 20\%$ and ± 0.02 Å on the atomic distance (*R*).

Other techniques

[99]Tc concentrations were determined by liquid scintillation (LS) counting using a Packard 2500 scintillation analyzer. The scintillation cocktail was ULTIMA GOLD AB™ (Packard). The concentration was determined using calibration curve performed in solution with composition similar to the experimental solution. Uncertainty on the concentration determined by LS is on the order of 2%. XRD patterns were obtained using a Philips Panalytical X'Pert Pro instrument with a Cu-K_α target and a Ni filter. XRD patterns were recorded between $2\theta = 12°$ and $2\theta = 100°$ with a step of 0.97° per minute. Data were analyzed using TOPAS software [12]. Time-resolved laser fluorescence spectroscopy (TRLFS) measurements were performed on VIBRANT II apparatus using Nd:μAG – Yttrium aluminum Granit Q-switched Laser. Sample, in 1 cm quartz cells, were excited with a 414 nm Optotek laser and monitored from 420 to 780 nm with a Princeton Instruments integrated spectrometer.

3. Results

3.1 Separation

The first and the second columns were charged with 7 g of treated Reillex HP and 1 g of untreated Reillex HP, respectively. Before the experiment, 250 mL of 0.01 M HNO_3 was pumped through the columns. The simulated UREX solution was added by 100 mL portions into the feed reservoir and pumped through the columns at a constant flow rate of 4 mL/min; the yellow solution was collected in fractions of 45 ± 0.5 mL in 50 mL centrifuge tubes; a total of 29 tubes was obtained. After passing all the feed solution, the system was washed with 1 L of DI water until complete disappearance of the yellow solution. After washing, the second column was disconnected from the set-up and the first column eluted with 350 mL of 1 M NH_4OH (flow rate = 4 mL/min). The colorless eluting solution was collected in fractions of 45 ± 0.5 mL in 50 mL centrifuge tubes; a total of 8 tubes was obtained. The Tc concentration in each tube was determined by LS counting. The number of Tc moles as a function of accumulated volume is presented in Fig. 1. From Fig. 1, a total sorption (R_{Abs}) of $97.8 \pm 4\%$ and elution (R_{Elu}) of $94 \pm 4\%$ of Tc on the first column were determined. The total absorption quantity was
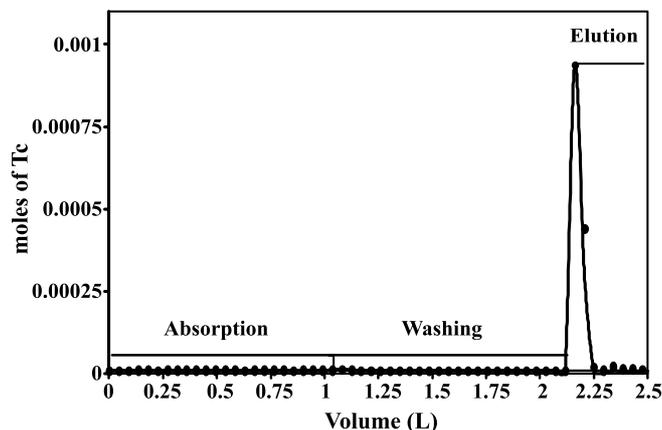
Fig. 1. Sorption/elution profile of ^{99}Tc during U/Tc separation. U = 98.95 g/L, Tc = 130.2 mg/L in 0.01 M HNO_3. ^{99}Tc was measured by liquid scintillation.

calculated using the formula: $R_{Abs} = [(n_I/n_I - n_F) \times 100]$; n_I (1.38(3) mmol) refers to the number of Tc moles initially introduced and was determined by LS counting of the initial UREX simulant solution; n_F (1.35(2) mmol) refers to the number of Tc moles sorbed on the resin. The amount eluted was calculated using the formula: $R_{Elu} = [(n_F/n_{El}) \times 100]$, n_{El} (1.27(3) mmol) refers to the number of Tc moles eluted from the first column.

3.2 Synthesis and characterization of solid forms

3.2.1 Uranium

The uranium obtained after separation was converted to ammonium diuranate (ADU) by precipitation with concentrated ammonium hydroxide. The resulting precipitate was washed, dried at 250 °C and thermally converted to U_3O_8 at 700 °C. Previous studies have shown that the precipitation of uranium nitrate solution with concentrated NH_4OH or NH_3 gas lead to ADU with the assumed formula $NH_4H[U_3O_8(OH)_4]$ [13], $UO_3 \cdot NH_3 \cdot 2H_2O$ [14] or $UO_3 \cdot xNH_3 \cdot yH_2O$ ($x = 0.77$–1.121, $y = 0.82$–1.14) [15]. Thermal studies [14, 16] have shown that ADU completely

dehydrates at 250 °C, and is converted to β-UO_3 by calcination between 300 °C and 500 °C, and to U_3O_8 by treatment between 550 °C and 700 °C.

The 29 tubes containing uranyl nitrate were combined ($\sim$ 1.3 L) and the uranium was precipitated with 25 mL of concentrated NH_4OH. The resulting yellow ADU was filtered on paper filter, washed with DI water and dried in an oven under air at 60 °C for 4 h, and 3 h at 250 °C; 119.44 g of dried ADU was obtained. Then, the compound was converted to U_3O_8 by treatment at 700 °C. A sample of 446.7 mg of ADU was placed in an alumina boat and heated under air for 10 h at 700 °C; 385.6 mg of U_3O_8 were obtained after transfering the compound from the alumina boat to a vial. Assuming the sample is representative of the bulk solid, a recovery yield of $88.2 \pm 0.8\%$ can be calculated.

Characterization

The U_3O_8 powder was placed on a silicon disk for XRD analysis, the pattern presented in Fig. 2 confirmed the formation of U_3O_8 ; no other phases were detected. The fitted lattice parameters (*i.e.*, $a = 6.71762$ Å, $b = 11.95912$ Å, $c = 4.14676$ Å) are in good agreement with those referenced in the litterature (*i.e.*, $a = 6.716$ Å, $b = 11.96$ Å, $c = 4.147$ Å) [17].

Purity analysis

To detect the presence of ^{99}Tc in the ADU obtained after drying at 250 °C, a liquid scintillation analysis was performed; 60.1 mg of ADU were dissolved in 1 mL of 0.01 M HNO_3 and a 10.0 µL sample pipetted for counting. The result indicates that the Tc level is below the detection limit (10^{-7} M) that is less than 0.16 µg of Tc per gram of ADU.

3.2.2 Technetium

Synthesis

The synthesis of Tc metal from the eluting solution was performed in three steps, i) evaporation of the solution to dryness, ii) dissolution of the powder in water followed by
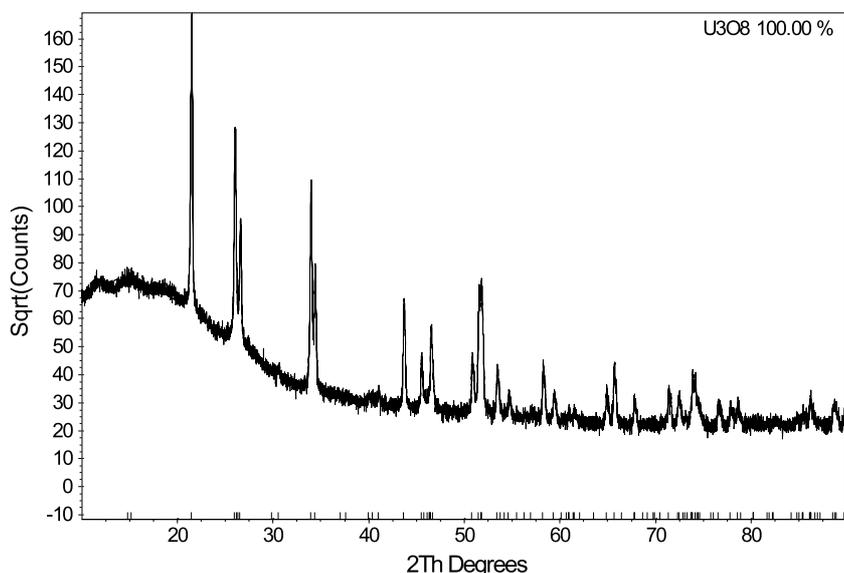
Fig. 2. Experimental XRD pattern of U_3O_8 obtained after thermal conversion of ammonium diuranate at 700 °C.

the precipitation of TcO_4^- as $(n\text{-}Bu_4N)TcO_4$ and iii) conversion of $(n\text{-}Bu_4N)TcO_4$ to Tc metal by pyrolysis and steam reforming under argon. In the first step, the presence of NH_4NO_3 was detected by XRD, since NH_4NO_3 represented a serious hazard (potentially rapid gas release) for the further conversion of the Tc to metal, the separation of pertechnetate from NH_4NO_3 was performed by selective precipitation using $(n\text{-}Bu_4N)HSO_4$. In the second step, the very insoluble [18] $(n\text{-}Bu_4N)TcO_4$ was precipitated by addition of $(n\text{-}Bu_4N)HSO_4$ while $(n\text{-}Bu_4N)NO_3$ largely remained in solution. In the last step, the conversion of $(n\text{-}Bu_4N)TcO_4$ into Tc metal was performed by thermal treatment using a pyrolysis and steam reforming method [4]. In this method, $(n\text{-}Bu_4N)TcO_4$ was placed in a boat, disposed in a quartz tube and heated at $800\,°C$ under a wet argon atmosphere with activated carbon nearby. In the presence of carbon, steam reforming under wet Ar near $800\,°C$ forms CO and H_2 gases and the reduction to Tc metal can occur after reaction between of $(n\text{-}Bu_4N)TcO_4$ with these reducing gases.

i)   The tubes containing eluting solution were combined in a 500 mL flask and connected to a rotary evaporator. The flask was heated in an oil bath at 90–$100\,°C$ under vacuum for 1 h. The resulting white powder (1.138 g) was analyzed by XRD which indicates the presence of NH_4TcO_4 (17%) and NH_4NO_3 (83%).

ii) The white powder containing NH_4TcO_4 and NH_4NO_3 was dissolved in 14 mL of DI water. The solution was divided in two fractions of 7 mL, each fraction was placed in a 15 mL centrifuge tube. Then, 2.5 mL of solution containing 350 mg $(n\text{-}Bu_4N)HSO_4$ were added to each tube and the white $(n\text{-}Bu_4N)TcO_4$ precipitated. The compound was centrifuged and washed with 5 mL of cold water. After drying overnight in a dessicator, 520 mg of $(n\text{-}Bu_4N)TcO_4$ were obtained.

iii) The $(n\text{-}Bu_4N)TcO_4$ product was placed in a fused quartz boat in presence of activated carbon and heated slowly up to $800\,°C$ under wet argon and maintained at $800\,°C$ for 5 h. A bubbler containing 1 M NaOH solution was connected to the quartz tube and used to trap eventual volatile Tc species, after the reaction, LS measurements of the NaOH solution indicate absence of Tc. A grey-black powder containing Tc metal was obtained. The powder was pressed into three cylindrical pellets using a 3 mm die, each pellets was arc melted and Tc balls with a shiny metallic aspect were obtained (mass $= 68.2 \pm 0.1$ mg, yield $= 52.5 \pm 0.1\%$). The low yield obtained is due to the use of some product for the different characterization (XRD, TRLFS) before weighing the arc melted metal and some product impregnated in the quartz boat. The yield of Tc can certainly be improved with larger samples and better technique. Recently, a larger scale experiment performed with a simulant solution with a 5-L volume gave a yield of Tc metal of greater than 90%.

XRD analysis

One of the technetium balls was flattened, placed on a silicon disk, disposed in the sample holder and measured by XRD. The XRD pattern presented in Fig. 3 confirms the
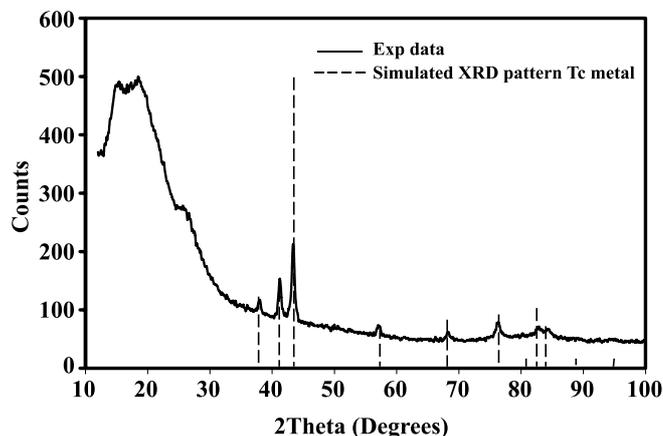

Fig. 3. Experimental XRD pattern of Tc metal obtained after treatment of the Tc stream. The dotted line represents the theoretical pattern of Tc metal calculated from [11].

presence of Tc metal; no other crystalline products were detected. The fitted lattice parameter (*i.e.*, $a = 2.755$ Å, $c = 4.406$ Å) are in good agreement with those reported for the hexagonal phase (*i.e.*, $a = 2.743$ Å, $c = 4.400$ Å) [11].

Purity analysis

A TRLFS analysis was done on metallic Tc; 1.0 mg of Tc metal was dissolved in 1 mL of concentrated HNO_3, then $500\,\mu L$ of the solution was mixed with $500\,\mu L$ of concentrated phosphoric acid and the resulting solution measured by TRLFS. No signal was obtained which indicated that the U amount was below the detection limit ($< 10^{-7}$ M), *i.e.*, less than $23.8\,\mu g$ of U per gram of metallic Tc.

EXAFS spectroscopy

In order to confirm the formation of Tc hexagonal phase after arc melting, XAFS measurements were performed on one arc-melted ball. EXAFS spectra of a polished technetium ball were recorded in the *k*-range $[0, 17]$ Å^{-1} in fluorescence mode. The spectra were k3-weighted and Fourier transformed in the *k* range $[3.5; 16]$ Å^{-1}. The adjusting procedure was conducted using the scattering determined by FEFF8.2 in the hexagonal phase of Tc metal. The amplitude and path of the scattering wave functions are presented in Table 1. The adjusting procedure was performed in two steps: (a) adjustment between $R + \Delta R = [1, 2.80]$ Å, (b) adjustment of the total spectra using the parameters previously determined in (a).

A window filter was done on the FT between $R + \Delta R = [1, 2.80]$ Å. The Fourier transform was back transformed and the corresponding EXAFS spectra fitted in the *k*-range $[3.5, 16]$ Å^{-1} using the scattering $Tc_0 \leftrightarrows Tc_1$ and $Tc_0 \leftrightarrows Tc_2$. For the adjusting procedure, the number of Tc_1 and Tc_2 atoms around the absorbing atom was correlated to a same value. All the other parameters were allowed to vary.

The fitted k^3-EXAFS spectra and the Fourier transform obtained are presented in Fig. 4. The structural parameters are presented in Table 2. The results of the adjustments indicate that the first coordination shell around Tc_0, is constituted by 6.8 Tc_1 atoms at 2.70(2) Å and 6.8 Tc_2 atoms at 2.72(2) Å. The distance Tc_0-Tc_2 represents the lattice parameter "*a*" of the Tc metal hexagonal phase, the value
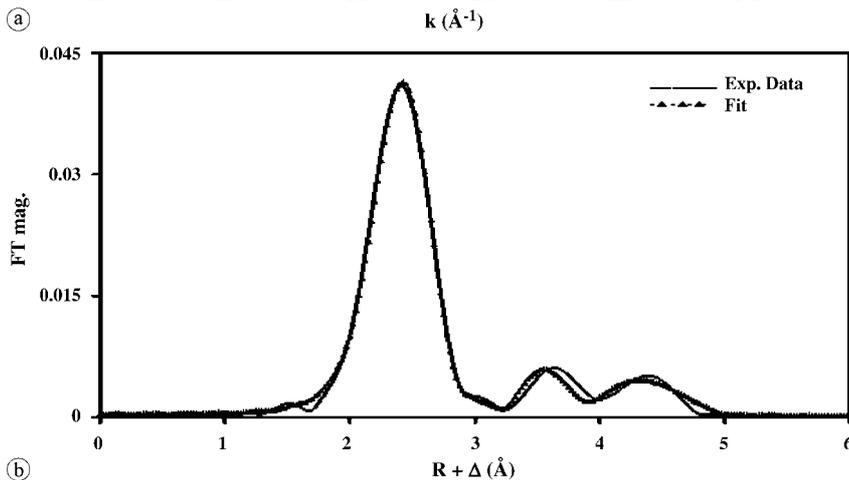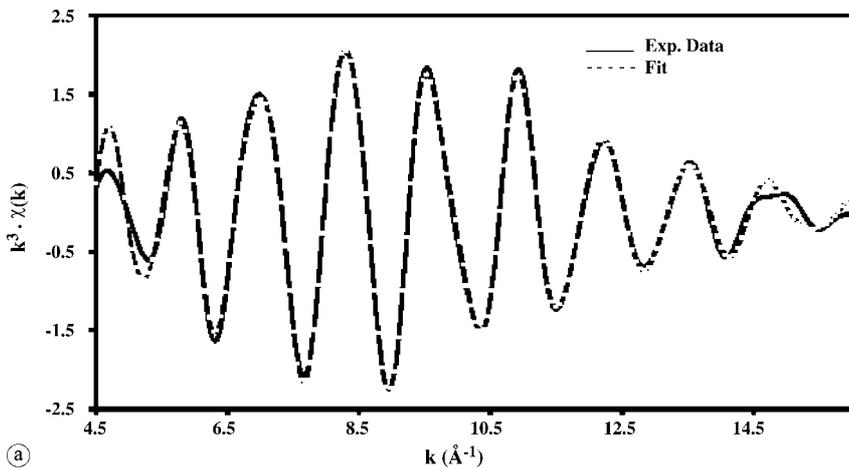
Fig. 4. Fitted k^3-EXAFS spectra (**a**) and Fourier transform of k^3-EXAFS spectra (**b**) of Tc metal obtained after treatment of the Tc stream. Fourier transform between $R + \Delta R = [1, 2.8]$ Å. Adjustment between $k = [3.5, 16]$ Å^{-1}. Residual $= 0.58\%$.
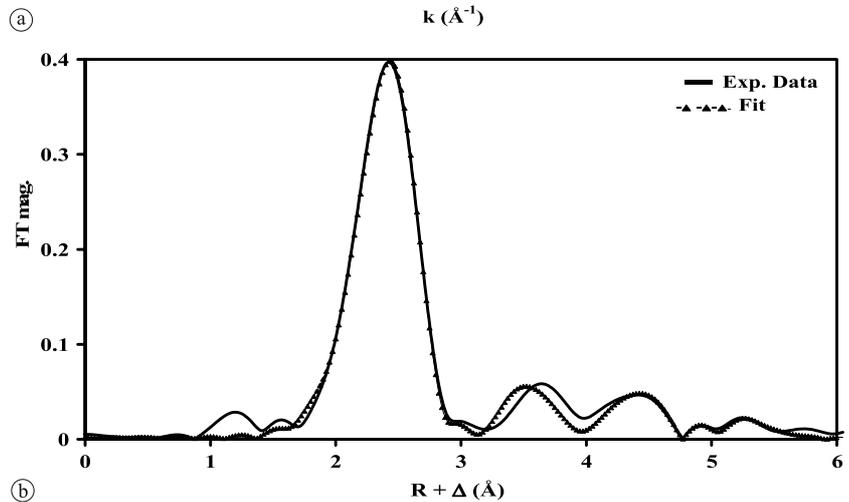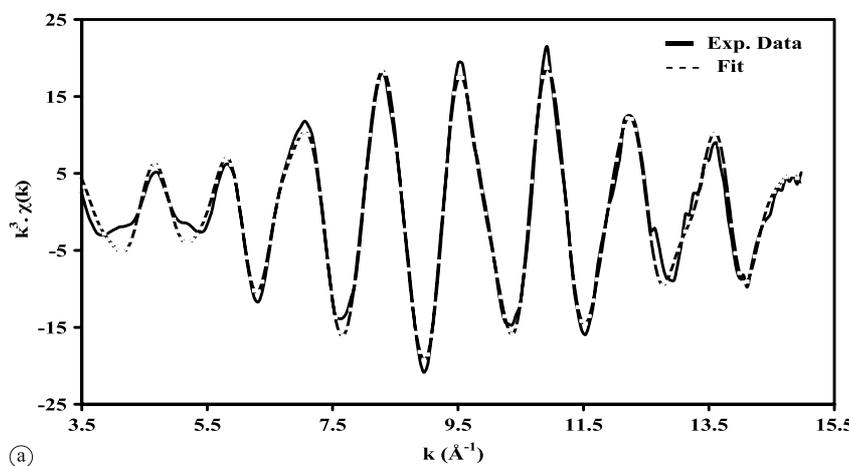
Fig. 5. Fitted k^3-EXAFS spectra (**a**) and Fourier transform of k^3-EXAFS spectra (**b**) of Tc metal obtained after treatment of the Tc stream. Adjustment between $k = [3.5, 15]$ Å^{-1}. Residual $= 6.22\%$.

Table 1. Scattering used for adjustement of the EXAFS spectra of Tc metal. Tc_6 refers to Tc atoms at 5.486 Å and Tc_0 to the absorbing atom.

Scattering	Amplitude (%)	deg.	Path	R path (Å)
A	100	6	$Tc_0 \leftrightarrows Tc_1$	2.710
B	97.15	6	$Tc_0 \leftrightarrows Tc_2$	2.743
C	39.71	6	$Tc_0 \leftrightarrows Tc_3$	3.856
D	43	12	$Tc_0 \leftrightarrows Tc_4$	4.732
E	32.15	12	$Tc_0 \leftrightarrows Tc_5$	5.185
F	38.22	24	$Tc_0 \rightarrow Tc_5 \rightarrow Tc_1 \rightarrow Tc_0$	5.303
G	58.58	12	$Tc_0 \rightarrow Tc_6 \rightarrow Tc_2 \rightarrow Tc_0$	5.486
H	66.24	6	$Tc_0 \leftrightarrows Tc_2 \leftrightarrows Tc_6$	5.486

a: Adjustment between $R + \Delta R = [1, 2.80]$ Å.

Table 2. Structural parameters for Tc metal obtained after Fourier filtering between $R + \Delta R = [1, 2.80]$ Å.

Tc Scattering		Structural parameter		
	CN	R (Å)	σ^2 (Å²)	ΔE_0 (eV)
Tc_0-Tc_1	6.8	2.701	0.0080	7.28
Tc_0-Tc_2	6.8	2.723	0.0068	7.28

b: Adjustment of the total EXAFS spectra.

Table 3. Structural parameters obtained by adjustment of the k^3-EXAFS spectra of Tc metal.

Tc Scattering		Structural parameter		
	CN	R (Å)	σ^2 (Å²)	ΔE_0 (eV)
Tc_0-Tc_1	6.8 ± 1.3	2.70(2)	0.0080	9.90
Tc_0-Tc_2	6.8 ± 1.3	2.72(2)	0.0068	9.90
Tc_0-Tc_3	4.8 ± 0.9	3.85(2)	0.0068	9.90
Tc_0-Tc_4	14.7 ± 3	4.77(3)	0.0073	9.90
Tc_0-Tc_5	12	5.19(4)	0.0076	9.90
F	24	5.32(4)	0.0080	9.90
G	12	5.52(4)	0.012	9.90
H	6	5.52(4)	0.012	9.90

ported for the hexagonal phase. As previously mentioned, the value of the lattice parameter obtained by EXAFS is well in agreement with the one reported in the literature.

Previous studies [19–21] have reported a face-centered cubic (fcc) phase that undergoes transformation to a hexagonal phase above 800 °C. In the fcc phase, the number of Tc atoms around the absorbing atoms at $R = 4.76$ Å is expected to be 24 [19]; this value is not in agreement with our EXAFS results (see Table 3) and indicates the absence of the fcc phase in the sample. These results are further corroborated by XRD analysis.

4. Conclusion

The present study has shown the ability to separate uranium from technetium as well as the ability to synthesize solid materials of these products. The synthesized uranium is free of any traces of Tc and was recovered in a yield of 88.2%. The final technetium metal product is also pure and was obtained in a yield of 52.5%. The low yield obtained is caused by removal of some small samples for analysis and characterisation before weighing and some product that was impregnated in the quartz boat. The process described here can be optimized further to increase the technetium yield. For example, a similar more recent test using five liters of a simulant solution has recovered Tc in a yield greater than 90%. In the context of the UREX+ process, waste forms containing Tc metal are under consideration. Currently, advanced technetium waste forms containing Tc metal are under development and studies on the synthesis and characterization of Tc-Zr alloys will be reported in due course.

determined by EXAFS (*i.e.*, $a = 2.72(2)$ Å is in good accordance with the one referenced in the literature (*i.e.*, $a = 2.743$ Å).

The total EXAFS spectrum was adjusted between $[3.5, 15]$ Å^{-1} using all the scattering presented in Table 1. The adjustment was conducted according the following procedure:

- The number of Tc_1, Tc_2 atoms and the corresponding distances were fixed to the value previously determined.
- The degeneracy of the multi scattering (F, G and H) was fixed to the value presented in Table 1.
- The distances and σ^2 values of multi scattering G and H were correlated to the same value.
- All the other σ^2 and distances were allowed to vary.

The fitted Fourier transform and k^3-EXAFS spectra are shown in Fig. 5. The structural parameters are presented in Table 3.

For the metal obtained after arc melting, the parameters presented in Table 3 are in good agreement with those re-

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