Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.23094

136 (2018) 268–272
December

Extraction of technetium ($HTcO_4$) with *N,N,N′,N′*-tetra(2-ethylhexyl) diglycolamide from simulated high level waste

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Received 5 January 2018; Accepted 2 September 2018

ABSTRACT

This paper investigates the extraction of technetium (VII) from simulated high level waste using TEHDGA-isodecyl alcohol/*n*-dodecane. The role of different process parameters affecting the extraction of technetium (VII) has been evaluated and used to arrive at optimum conditions for extraction of the metal ion. It is established that D_{Tc} of about 50 can be obtained from 0.5 M nitric acid using of 0.3 M TEHDGA in 5% isodecyl alcohol/*n*-dodecane system. Extraction from nitric acid medium and quantitative stripping of technetium using deionized water opens up possibility of successful deployment of the process for technetium separation from actual high level waste.

Keywords: TEHDGA; Technetium; Waste treatment

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1. Introduction

^{99}Tc, a long lived (2.11 × 10^5 y) and low energy beta emitting ($E_{\beta\text{-max}}$ = 295.5 keV) radionuclide, is produced in thermal neutron fission of ^{235}U with high yield (~6%). During dissolution of the spent fuel, it is oxidized to pertechnetate and thereafter it remains in this stable form throughout the course of reprocessing and is ultimately accumulated in high level waste (HLW) [1–3]. Most common practice for the management of HLW includes immobilization in borosilicate glass followed by disposal in deep geological repository. However, highly volatile nature of the radioelement limits its loading in glass. Further, high environmental mobility is a major radiation concern for long-term radiation risk assessment [4,5]. Separation of the radioelement from HLW followed by its immobilization in suitable matrix is necessary for management of the radioelement.

Based on recent literature review, it can be stated that TBP/dodecane system extracts a substantial amount of pertechnetate anion along with U and Pu in PUREX process [6]. In order to prevent such inadvertant partitioning of the radioelement and its presence in U product, several efforts have been made for its selective extraction prior to PUREX process [7]. Efforts have been made to separate the radioelement from nitric acid medium using selective extractants such as DHOA [8], picolinamides [9], cyclic amides [10], mixture of CMPO and TBP [11], tetraphenylarsonium chloride [12], 2,2′-(methylimino)bis(*N,N*-dioctylacetamide) [13] and Aliquat 336 [14]. Solvent extraction studies using crown ether [15] and crown ether embedded on organic matrix [16,17] has also been used for separation of Tc from alkaline solution.

In India, partitioning of radio nuclides from HLW followed by vitrification of the alpha rich liquid waste is being considered as an alternative approach to direct vitrification. This will not only substantially reduce the volume of vitrified waste product but also minimize the long-term hazard. In the partitioning process TEHDGA in isodecyl alcohol/*n*-dodecane system is used for quantitative separation

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of minor actinides and lanthanides [18,19]. The separation of minor actinides and lanthanides is accomplished through metal ligand complexation and co-extraction of nitrate for charge neutralization. As compared with nitrate, pertechnetate ion is more hydrophobic (softer anion) and has high solubility in organic phase. It can, therefore, be expected that pertechnetate ion will be extracted by TEHDGA during extraction of minor actinides from high level waste.

This paper reports the extraction behaviour of pertechnetate ion in TEHDGA-isodecyl alcohol/*n*-dodecane system. Various process parameters such as feed acidity, effect of interfering metal ions, nitrate ion concentration and kinetics of extraction were studied. To the best of our knowledge, the solvent extraction parameters for technetate extraction by TEHDGA is reported for the first time. This preliminary data can be used for development of a process for separation of technetium from HLW.

2. Experimental

2.1. Chemicals, isotopes and solutions

N,N,N′,N′-tetra(2-ethylhexyl) diglycolamide (TEHDGA) (Fig. 1) was synthesized in our laboratory. It was characterized using GC-MS, FTIR, and ^{1}H-NMR and found to be of good purity (~95%) [14]. Isodecyl alcohol and *n*-dodecane were obtained locally and used as received. Stock solution of ^{99}Tc was obtained from our waste management facility. For the extraction and stripping studies involving fission elements such as Zr(IV), Mo(VI), Sr(II) and Nd(III), a solution with each metal ion concentration shown in Table 2 was prepared by dissolving the required amount of their salts, that is, zirconium nitrate for Zr(IV), ammonium molybdate tetrahydrate for Mo(VI), strontium nitrate for Sr(II) and neodymium nitrate hexahydrate for Nd(III) in 0.5 M nitric acid. Ru(III) solution of 100 mg/L was prepared from ruthenium nitrosyl nitrate solution of composition, 1.5% Ru(III) in 0.5 M nitric acid.

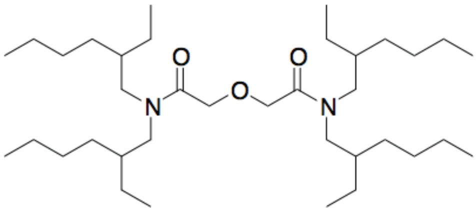

Fig. 1. Structures of *N,N,N´,N´*-tetra(2-ethylhexyl) diglycolamide (TEHDGA).

Table 1
Effect of sodium nitrate on uptake of nitric acid by TEHDGA

HNO_3 $(M)_{aq}$	$NaNO_3[M]_{aq}$	HNO_3 $(M)_{org}$
4	0	0.66
4	1	0.86
4	2	1.02
4	3	1.15
4	4	1.31

Note: Organic phase: 0.3 M TEHDGA + 5 isodecyl alcohol/*n*-dodecane; aqueous phase: 4 M nitric acid + $NaNO_3$

2.2. Distribution ratio measurements

For determination of distribution ratio (D_M) of the metal ions, the organic phase was equilibrated with equal volume of the corresponding aqueous solution containing metal ions for 30 min in a glass vial. After extraction, the phases were separated by centrifugation, and the aqueous phase was analyzed for metal ion concentration. Organic phase metal ion concentration was determined by mass balance. All the extraction experiments were carried out in a thermostat water bath maintained at temperature of 25°C ± 1°C. The distribution ratio of the metal ions was calculated as the ratio of concentration (or radioactivity) of metal ion in the organic phase (expressed as counts per unit time per unit volume) to the concentration in the aqueous phase.

2.3. Analysis of radionuclides, metal ions and acidity

The concentration of pertechnetate ion in the aqueous phase was measured using TPAC-nitrobenzene method as described by Sonar et al. [20]. The distribution ratio measurements using radiometry have a maximum error of ±5%. The estimation of the concentrations of inactive Sr(II) and other metal ions such as Ru(III), Zr(IV), Mo(VI), and Nd(III) were carried out by analysing the aqueous phase before and after equilibration with suitable dilution using ICP-AES. Metal concentration in organic phase was determined by difference in concentration in aqueous phase before and after equilibration. The quantification limit for ICP-AES analysis was 1.0 mg/L. The nitric acid concentrations of aqueous and organic phases were determined by titration with 0.1 M NaOH using a Metrohm 905 Titrando device.

3. Results and discussion

3.1. Kinetics of extraction

Prior to evaluating distribution behaviour of Tc(VII) with respect to various parameters, extraction of Tc(VII) was studied at different equilibration time, the kinetics of extraction was very fast and equilibrium was achieved within 10 min. Hence, for all the experiments contact time was kept as 30 min to ensure complete attainment of equilibrium.

Table 2
Extraction of Tc(VII) and other metal species

Metal ion	Feed (mg/L)	D_M
Tc(VII)	10^{-5}	30.16
Mo(VI)	102	12.3
Am(III)	10^{-7}	0.8
Nd(III)	84.5	0.45
Zr(IV)	42	0.3
Ru(III)	72.1	0.18
Sr(II)	120	0.08

Note: Extractant: 0.3 M TEHDGA + 5% isodecyl alcohol/*n*-dodecane. Aqueous feed: Am(III), Tc(VII), Ru(III), Mo(VI), Zr(IV), Nd(III) and Sr(II) in 0.5 M HNO_3 (298 K, 30 min equilibration, O/A: 1:1).

3.2. Extraction dependence of Tc(VII) on feed nitric acid and nitrate concentration

Extraction of Tc(VII) as a function of nitric acid concentration for solvent 0.3 M TEHDGA + 5% IDA/*n*-dodecane is shown in Fig. 2. D_{Tc} value increases with increase in nitric acid concentration up to 0.5 M nitric acid (D_{Tc} = 50.21), thereafter D_{Tc} decreases and only 2.01 is obtained at 4 M nitric acid. The same trend of Tc(VII) extraction from nitric acid medium was observed for other neutral solvents such as TBP or DHOA. As TcO_4^- has low hydration energy compared with nitrate, it therefore gets easily extracted at lower nitric acid concentration but with increase in nitric acid concentration D_{Tc} value falls off rapidly because of exchange of TcO_4^- with nitrate ion. Probable extraction mechanism could be solvation of $HTcO_4$ which at higher acidity is replaced by HNO_3 molecules. The extent of extraction of Tc(VII) found in our studies are quite similar to D_{Tc} value reported by Zhu et al. [21] using another well-studied glycolamide, TODGA. The D_{Tc} value reported for a solvent composition of 0.1 M TODGA in *n*-dodecane is ~1.2 for a feed acidity of 2.9 M nitric acid [21], which is 1.4 for TEHDGA under same solvent composition and feed acidity.

Fig. 3 shows the effect of nitrate ion concentration on extraction of Tc(VII). Uptake of Tc is found to decrease with increase in nitrate concentration mainly due to exchange of pertechnetate ion by nitrate and also by increase in uptake of nitric acid by TEHDGA at higher nitrate concentrations. Nitric acid uptake of 0.3 M TEHDGA + 5% IDA/*n*-dodecane for feed acidity of 4 M nitric acid at different sodium nitrate concentration is shown in Table 1. It is found that with increase in sodium nitrate concentration, extraction of nitric acid increases. At 4 M sodium nitrate concentration, nitric acid in the organic phase is about 1.3 M while it is only 0.66 M in absence of any sodium nitrate salt. This can be explained by salting out effect of sodium nitrate. More acid extraction leads to decrease in Tc(VII) extraction with increase in sodium nitrate concentration. Fig. 4 shows the log-log plot of D_{Tc} vs. nitrate concentration of sodium nitrate at 2 M nitric acid exhibiting a linear decrease with a slope of –1, suggesting the exchange of TcO_4^- by one mole of NO_3^- ion in the extraction process. Experimental results indicated exchange of TcO_4^- with nitrate ion or HNO_3.

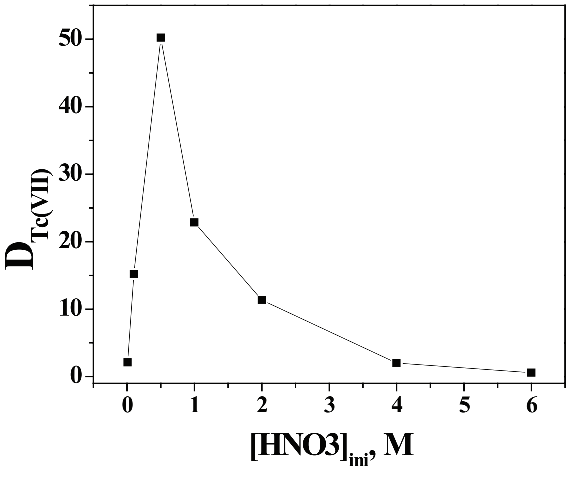

Fig. 2. Extraction of Tc(VII) using TEHDGA as a function of initial aqueous phase nitric acid concentration (organic phase: 0.3 M TEHDGA + 5% isodecyl alcohol/*n*-dodecane; aqueous phase: Tc(VII) in HNO_3; 298 K; 30 min equilibration; O/A: 1:1).

3.3. Extraction dependence of Tc(VII) on TEHDGA concentration

To gain an insight into the stoichiometry of complex formed between TEHDGA and $HTcO_4$, dependence of D_{Tc} on TEHDGA concentration was determined. Typical log-log plot of D_{Tc} vs. TEHDGA concentration is shown in Fig. 5. The slope of this plot is found to be 1 indicating a 1:1 complex between TEHDGA and $HTcO_4$. In acidic solution, Tc(VII) exists as $HTcO_4$, it is extracted by interaction with basic amidic moiety of TEHDGA molecule resulting in formation of solvated adduct as $HTcO_4$-TEHDGA. For monodentate solvating ligands such as TBP or DOHA, formation of a 3:1 complex with $HTcO_4$ was observed whereas in the present case

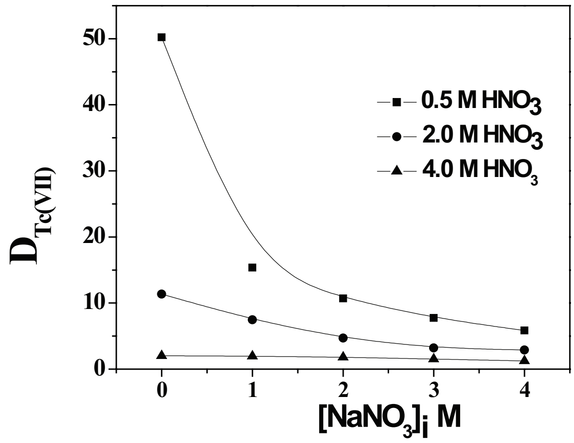

Fig. 3. Extraction of Tc(VII) as a function of nitrate ion concentration (organic phase: 0.3 M TEHDGA + 5% isodecyl alcohol/*n*-dodecane; aqueous phase: (0.5, 2,4) M nitric acid + Tc(VII); 298 K; 30 min equilibration; O/A: 1:1).

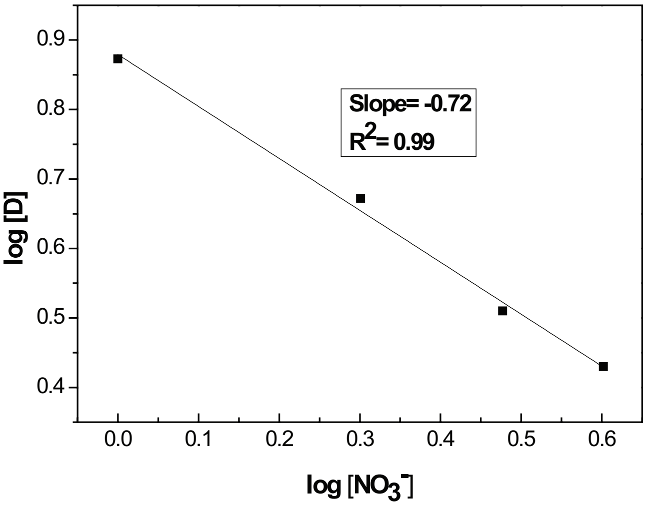

Fig. 4. log [D] vs. log [NO_3^-] plot for Tc(VII) extraction (organic phase: 0.3 M TEHDGA + 5% isodecyl alcohol/*n*-dodecane; aqueous phase: 2 M nitric acid + (1 to 4) M $NaNO_3$ + Tc(VII); 298 K; 30 min equilibration; O/A: 1:1).

because of higher denticity of TEHDGA the stoichiometric ratio is found to be less. The stoichiometry of complexation is found to be independent of nitric acid concentration whereas in case of TBP or DOHA stoichiometry changed with nitric acid concentration [6].

Based on the above results of log-log plots, extraction mechanism at lower acidity up to 0.5 M proceeds as adduct formation:

$$TcO_4^-{}_{aq} + H^+_{aq} + TEHDGA_{org} \leftrightarrows HTcO_4.TEHDGA_{org} \quad (1)$$

Whereas, at higher acidity (>0.5 M), decrease in extraction of Tc(VII) takes place due to extraction of nitric acid over $HTcO_4$. With increase in nitrate ion, extraction of technetium decreases due to exchange of TcO_4^- with nitrate ion. The reaction would then proceed as:

$$HTcO_4.TEHDGA_{org} + HNO_3 \rightleftharpoons HNO_3.TEHDGA + HTcO_4$$

$$HTcO_4.TEHDGA_{org} + NO_3^- \rightleftharpoons HNO_3.TEHDGA + TcO_4^-$$

where the subscript 'org' refers to species in organic phase and 'aq' subscript refers to those present in aqueous phase.

3.4. Effect of isodecyl alcohol concentration

Glycolamide based solvents are prone to third phase formation during extraction at higher nitric acid concentration and in the presence of high amount of extractable species [22]. To mitigate the third phase formation, phase modifier, isodecyl alcohol (IDA), has been used while constituting TEHDGA solvent. The role of IDA concentration on $HTcO_4$ extraction has been studied and shown in Fig. 6. It is observed that with increase in IDA concentration up to 50% v/v, D_{Tc} remained constant. In our earlier studies [23] on extraction of Am(III) and Sr(II) with TEHDGA/IDA/*n*-dodecane solvent we have reported a decrease in extraction of these metal ions with increase in IDA concentration in the solvent phase due to intermolecular hydrogen bonding between TEHDGA and IDA which results in decrease of donor sites of TEHDGA molecule. However, in the present case due to strong acid-base interaction between $HTcO_4$ and TEHDGA, the role of IDA in decreasing the extraction of $HTcO_4$ is negligible; rather it helps in solvation of $HTcO_4$ due to its high polarity.

3.5. Effect of interfering ions

TEHDGA is characterized for high extraction of trivalent actinides, lanthanides and relatively low extraction for strontium, zirconium and molybdenum from nitric acid medium. Therefore, selectivity of TcO_4^- extraction was studied in the presence of other extractable metals such as Zr(VI), Mo(IV), Ru(III), Sr(II), Am(III) and Nd(III) at 0.5 M nitric acid. The composition of the solution and distribution ratio of each metal ion (D_M) is shown in Table 2. It was found that only Mo(VI) is co-extracted significantly while other metal species are extracted to a lesser extent with distribution ratio varying from 0.08 (for Sr(II)) to 0.8 (for Am(III)).

3.6. Stripping of pertechnetate from loaded organic phase

Stripping of TcO_4^- from loaded solvent was studied with deionized water and dilute sodium hydroxide solution. Five contacts of deionized water at 1:1 phase ratio was needed to strip about 99% of loaded technetium, while three contacts with 0.1 M NaOH resulted in complete stripping of technetium from loaded solvent.

3.7. Stability test of solvent

The present studies have shown that 0.3 M TEHDGA + 5% IDA/*n*-dodecane is a promising solvent for technetium separation from acidic nuclear waste. Stability of the ligands was studied by measuring the extraction and stripping efficiency of the solvent for consecutive six runs of extraction and stripping. After each cycle of extraction and stripping, organic sample was separated and washed with deionized water and tested for next cycle. There was no change

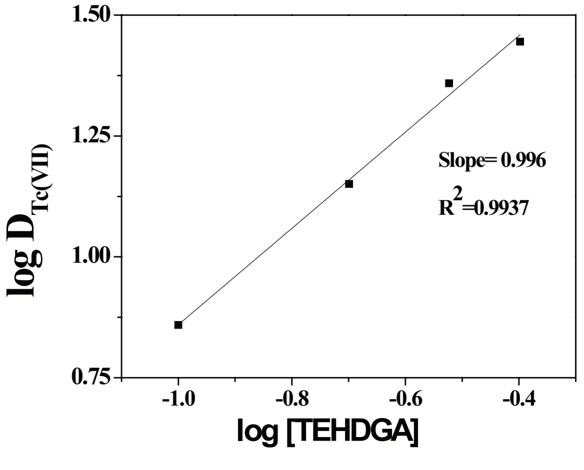

Fig. 5. Extraction of $^{99}Tc(VII)$ as a function of TEHDGA concentration (organic phase: (0.1–0.4 M) TEHDGA – 5% isodecyl alcohol/*n*-dodecane; aqueous phase:1 M nitric acid + Tc(VII); 298 K; 30 min equilibration; O/A: 1:1).

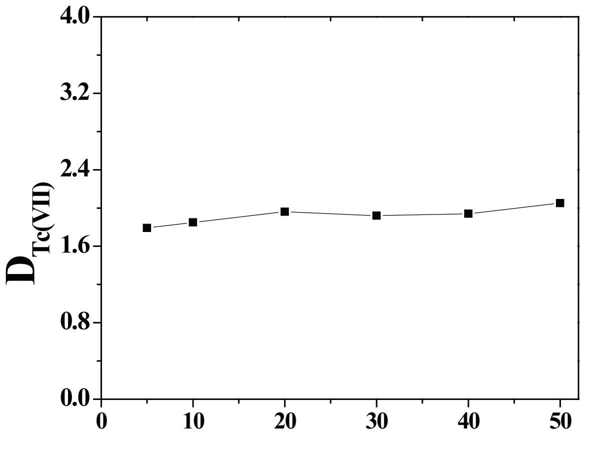

Fig. 6. Extraction of Tc(VII) as a function of IDA concentration. Organic Phase: 0.3 M TEHDGA + (5% to 50%) isodecyl alcohol/*n*-dodecane; aqueous phase: 4 M nitric acid + 99Tc(VII) in tracer quantity.

observed in extraction behaviour with time and solvent was found to retain its extraction and stripping properties, thus indicating that the solvent is hydrolytically and radiolytically stable for at least six cycles of operation.

4. Conclusions

In conclusion, the results obtained on detailed studies for extraction of Tc(VII) from simulated acidic waste solution using 0.3 M TEHDGA + 5% isodecyl alcohol/*n*-dodecane, indicated better extraction of Tc(VII) at lower acidities, with a maxima at 0.5 M nitric acid (D_{Tc} = 30.16). Extraction of Tc(VII) was found to decrease both with increase in nitric acid as well as nitrate ion concentration. It is inferred that $HTcO_4$.TEHDGA adduct formation is the possible mechanism for extraction of technetium at lower acidity. On considering very high D_{Tc} in a single contact at 0.5 M nitric acid, it is possible to quantitatively separate Tc(VII) from high level waste by adjusting the nitric acid concentration of the waste. Significant co-extraction of Mo(VI) was observed along with marginal co-extraction of other extractable metal ions. Tc(VII) can be stripped from the loaded TEHDGA phase using deionized water or 0.1 M NaOH. Technetium separation from high level waste solution at lower acidity seems to be a viable option at plant scale.

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