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# Effect of Some Reducing and Complexing Agents on the Extraction Behavior of Technetium in the TBP–$HNO_3$ System

**A. B. Melent'ev*[a], A. N. Mashkin[a], O. V. Tugarina[a], D. N. Kolupaev[a], B. Ya. Zilberman[b], and I. G. Tananaev**[c]**

[a] Mayak Production Association, Federal State Unitary Enterprise,
pr. Lenina 31, Ozersk, Chelyabinsk oblast, 456780 Russia; * e-mail: Melentev74@mail.ru
[b] Khlopin Radium Institute, Research and Production Association, Federal State Unitary Enterprise,
St. Petersburg, Russia
[c] Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

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**Abstract**—The effect of a series of complexing and reducing agents on the extraction-chemical behavior of technetium as applied to extraction splitting of uranium and plutonium in the Purex process was examined. Kinetic parameters of the catalytic decomposition of $N_2H_5NO_3$ under the action of Tc in the presence of these agents were evaluated. Variation of the ratio of the oxidized and reduced Tc species in the course of the process and in the hydrazine-free systems was determined. Reagents preventing oxidation of the reduced technetium and decomposition of $N_2H_5NO_3$ in nitric acid solutions (acetohydroxamic acid, hydroxylamine, ascorbic acid, etc.), inhibiting the reduction of Tc with hydrazine nitrate ($H_2O_2$, $HN_3$, etc.), and known as complexing agents toward quadrivalent actinides but indifferent to Tc were considered. The possibilities of using these reagents for modifying the Tc behavior in the course of SNF extraction reprocessing with the aim to direct this element to different process streams were discussed.

*Keywords: SNF reprocessing, uranium/plutonium splitting, technetium, hydrazine nitrate, redox processes, complexing agents*

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The presence of Tc strongly affects the course of reductive splitting of uranium and plutonium in the Purex process. Hydrazine nitrate used in this step as stabilizer efficiently converts Tc to the nonextractable Tc(IV) form, but Tc(IV) can undergo back oxidation to Tc(VII), which leads to its circulation within the extraction apparatus, excess consumption of the reductant, and worse process stability [1].

To modify the behavior of Tc, additional agents exerting complexing or mixed complexing/reducing effect can be introduced into the system. The course of the U/Pu splitting will largely depend on the performance of these agents and on their capability to fix Tc in the reduced state.

As shown previously [2], such complexing agents as DTPA can inhibit the Tc(IV) oxidation and decrease in a certain manner the degree of the $N_2H_5NO_3$ decomposition, which enhances the stability of the reduction operation and favors removal of Tc into the plutonium stream. Some complexones such as urea, on the contrary, do not interact with Tc but form stable complexes with Pu and Np, so that it becomes possible to perform the U/Pu splitting without altering the extraction behavior of Tc [3].

In this study we considered the effect exerted on the Tc behavior in the TBP–$HNO_3$–$N_2H_5NO_3$ system by a series of practically used or promising agents exhibiting both complexing and reducing properties. In addition, we studied how these reagents affect the $N_2H_5NO_3$ decomposition in the presence of Tc or interact with Tc in hydrazine-free systems.

## EXPERIMENTAL

To study experimentally the variation of the ratio of Tc valence forms in the course of the experiment and the catalytic decomposition of $N_2H_5NO_3$, to 1 M $HNO_3$

solutions we added definite amounts of $N_2H_5NO_3$, Tc(VII) (in the form of $HTcO_4$), and the tested complexing/reducing agent. At definite time intervals after the start of the experiments, aliquots were taken for the analysis. The aliquots were brought in contact with 100% TBP preequilibrated with a solution containing 1 M $HNO_3$. The phase ratio was kept equal to 1 : 1, and the aqueous phase temperature, within 40 ± 1°C. Analysis of the solution aliquots for Tc and $N_2H_5NO_3$ and mathematical processing of the analysis results were performed by the procedure used previously for determining the ratio of the Tc valence forms and the main parameters of the catalytic decomposition of $N_2H_5NO_3$ in nitric acid solutions in the presence of DTPA and $H_2C_2O_4$ [2].

Similar parameters were considered for the systems studied in this work: $\tau_{1/2}$, time at which a half of the initial amount of $N_2H_5NO_3$ ($[N_2H_5NO_3]_0$) decomposed; $C_f$, fraction (% of $[N_2H_5NO_3]_0$) characterizing the residual (steady-state) amount of the reductant in the final step of the reaction; $\tau_{stab}$, time in which $C_f$ was attained; $k'$, apparent rate constant of the $N_2H_5NO_3$ decomposition in the fast step of the reaction; $D_{min}$ and $Tc(VII)_{min}$, minimal distribution ratio of technetium ($D_{Tc}$) in extraction with 100% TBP and minimal fraction (%) of the oxidized form of Tc in the solution, attained in the given experiment; $D_f$ and $Tc(VII)_f$, $D_{Tc}$ and content of the oxidized form of Tc in solution by the end of the experiment. The time that passed from the beginning of the experiment was designated as $\tau$.

Previously we found that, in the $Tc–HNO_3–N_2H_5NO_3$ system, the minimal distribution ratio $D_{min}$ of Tc was attained when the degree of the reductant decomposition was close to 1/2 [4] However, in the present study, with some reagents introduced into the system, this relationship was not observed. Therefore, we additionally took into account the parameter $\tau_{D\min}$ characterizing the time in which $D_{min}$ was attained in the course of the experiment.

The absorption spectra of the solutions were recorded in the visible and near-UV ranges with a Perkin–Elmer Lambda 35 spectrophotometer. Solution aliquots taken for the spectrophotometry were preliminarily cooled to 0°C, which allowed the $N_2H_5NO_3$ decomposition and concomitant gas evolution negatively affecting the spectrum quality to be practically fully stopped.

As complexing or complexing/reducing agents we used ascorbic acid behaving as reductant toward Tc [5]); $CH_3COOH$ and $H_2SO_4$; $H_2O_2$; hydroxylamine nitrate (HAN); acetohydroxamic acid (AHA); urea and thiourea; halides and pseudohalides; and also β-hydroxyethylhydrazine (β-HEH) suggested previously as reagent for plutonium reduction [6]. HAN and AHA were prepared directly before experiments by procedures of laboratory synthesis; the other chemicals were of chemically pure grade.

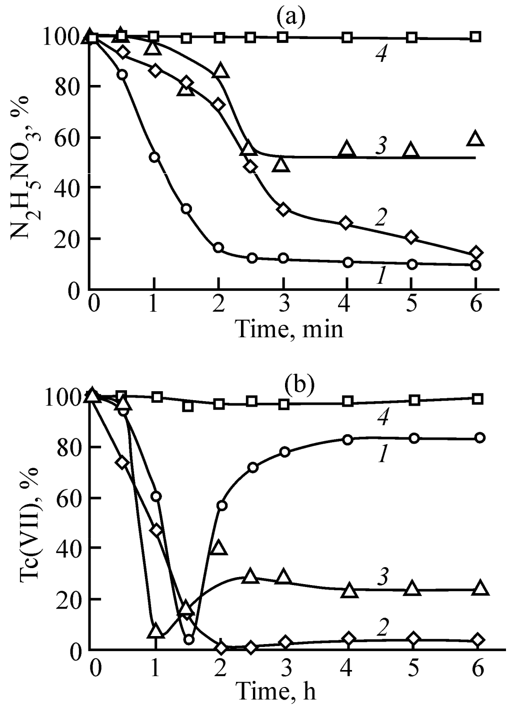

**Fig. 1.** (a) Decomposition of $N_2H_5NO_3$ and (b) variation of the Tc(VII) fraction in nitric acid solutions in the presence of additives. [Tc] = 2 × $10^{-3}$, $[HNO_3]$ = 1 M, 40°C; the same for Figs. 2–4. $[N_2H_5NO_3]$ = 0.2–0.3 M. Additives (0.05 M): (*1*) $H_2SO_4$, (*2*) AA, (*3*) $CS(NH_2)_2$, and (*4*) $H_2O_2$.

## RESULTS AND DISCUSSION

We found that, under the examined conditions, introduction of such agents as $H_2SO_4$, $CH_3COOH$, and thiourea did not noticeably affect the course of the $N_2H_5NO_3$ decomposition. The process was, on the whole, similar to that occurring in the base system without additives, whose behavior was considered in more detail in the previous study [2]. At the same time, it was noted that, with sulfuric acid additive, the induction period usually observed in catalytic decomposition of $N_2H_5NO_3$ was practically absent (Fig. 1a, curve *1*); therefore, $\tau_{1/2}$ was as short as 1 h. At the same time, $C_f$ and $k'$ were comparable to those observed in the base

**Table 1.** Summary of data on the effect of various substances on the redox behavior of Tc and oxidation of hydrazine nitrate. Solution components: [Tc] = $2 \times 10^{-3}$, [$HNO_3$] = 1.0, [reagent] = 0.05 M; 40°C; the same for Table 2

| Initial parameters of systems | | $N_2H_5NO_3$ decomposition | | | | Tc behavior | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reagent | $N_2H_5NO_3$, M | $\tau_{1/2}$, h | $\tau_{stab}$, h | $C_f$, % | $k'$, $h^{-1}$ | $\tau_{D\min}$, h | $D_{min}$ | Tc(VII)$_{min}$, % | $D_f$ | Tc(VII)$_f$, % |
| None | 0.24 | 1.6 | 3.0 | 10 | 0.83 | 1.5 | <0.10 | <1 | 4.2 | 82 |
| AHA | 0.26 | –[b] | – | – | – | 1.5 | 0.15 | 4 | 0.43 | 24 |
| HAN | 0.26 | –[b] | – | – | – | 3.0 | 0.20 | 9 | 0.38 | 21 |
| AA | 0.30 | 2.4 | >6.0[c] | 13 | 0.82 | 2.0 | <0.10 | <1 | 0.13 | 3 |
| Thiourea | 0.20 | 2.9 | 3.0 | 51 | 0.36 | 1.0 | 0.16 | 7 | 0.41 | 23 |
| Urea | 0.21 | 1.3 | 3.0 | 6 | 1.67 | 1.5 | 0.14 | 4 | 5.7 | 86 |
| $H_2SO_4$ | 0.20 | 1.1 | 2.5 | 10 | 1.11 | 1.5 | 0.13 | 3 | 4.7 | 83 |
| $CH_3COOH$ | 0.30 | 1.4 | 3.0 | 5 | 1.12 | 1.5 | 0.12 | 2 | 6.22 | 87 |
| $F^-$ | 0.25 | 1.1 | 2.5 | 7 | 1.60 | 1.5 | 0.28 | 15 | 5.06 | 84 |
| $Cl^-$ | 0.25 | 1.4 | 2.5 | 6 | 1.73 | 1.5 | 0.77 | 39 | 2.35 | 69 |
| $N_3^-$ | 0.23 | 1.5 | 2.5 | 8 | 1.50 | 1.5 | 0.59 | 32 | 5.79 | 86 |
| $N_3^-$ | 0.05 | –[d] | >6.0[c] | 56 | 0.09 | 2.0 | 7.94 | 90 | 23.4 | 98 |
| $N_3^-$ [a] | 0.05 | 1.0 | 3.0 | 25 | 0.64 | 1.0 | 1.52 | 58 | 19.1 | 97 |
| $CNS^-$ | 0.20 | –[d] | 3.0 | 62 | 0.28 | 2.0 | 13.8 | 95 | 19.0 | 97 |
| $H_2O_2$ | 0.28 | –[d] | 0.0 | 99 | – | 3.0 | 19.2 | 97 | 23.4 | 98 |
| β-HEH | 0.30 | 4.0 | >6.0[c] | 37 | 0.19 | 1.5 | 0.42 | 23 | 0.67 | 35 |

[a] Reagent concentration 0.025 M.

[b] Analysis for $N_2H_5NO_3$ content was not performed

[c] The $N_2H_5NO_3$ content decreased throughout the monitoring period, but after $\tau = 3$ h the hydrazine nitrate oxidation considerably decelerated.

[d] Decomposition of 1/2 of $[N_2H_5NO_3]_0$ was not attained in the monitoring period.

system (Table 1). In the presence of acetic acid and urea, the induction period was well pronounced, as in the system without additives.

The maximal yield of the reduced Tc in the systems in which the effect of additives was insignificant was observed at $\tau_{1/2}$; at that moment, the residual content of Tc(VII) was 2, 3, and 4% in the presence of $H_2SO_4$, $CH_3COOH$, and urea, respectively. Also, appreciable oxidation of the reduced Tc under the action of the nitric acid medium was observed in these systems. As in the base system, the process practically stopped after reaching $\tau_{stab}$, when the reductant content in the solutions stabilized on a definite level. For the system with urea, the parameter $C_f$ characterizing this state was 6%, and with $H_2SO_4$ it was 10%. Variation of the fraction of Tc(VII) in the reaction with $N_2H_5NO_3$ in the presence of the above additives (with $H_2SO_4$ as example) is shown in Fig. 1b (curve *1*). It should be noted that, after keeping the solutions for 6 h, the Tc(VII) content exceeded 80% in all the systems where the effect of additives was not manifested (Table 1).

Some reagents, on the contrary, significantly affected both the reductant decomposition and the extraction behavior of Tc (Figs. 1a and 1b, curves *2–4*). For example, addition of 0.05 M $H_2O_2$ fully prevented formation of nonextractable Tc species, and $N_2H_5NO_3$ decomposition was not observed.

On adding thiourea [$CS(NH_2)_2$], technetium rapidly ($\tau_{D\min} = 1$ h) passed into the reduced state. The subsequent oxidation of Tc was minimal, and, after reaching $\tau_{stab}$ equal to 3 h, the Tc(VII) content kept on the level of 23%. The reagent also exerted a strong protective effect on the reductant: Its decomposition was considerably inhibited, and $C_f$ was 51% (Table 1). These effects were apparently caused by the fact that thiourea not only exhibits reducing properties, but also forms stable compounds with reduced technetium [7].

Ascorbic acid (AA) exerted a similar but more pronounced effect on Tc. In the presence of this reagent, noticeable oxidation of the reduced Tc was not observed throughout the observation period. The Tc(VII) fraction at $\tau = 6$ h was as low as 3%, i.e., the stabilizing power of AA in mixtures with $N_2H_5NO_3$ is very high. At the same time, $N_2H_5NO_3$ was consumed more intensely than in the above-considered system with thiourea. At $\tau = 3$ h, the $N_2H_5NO_3$ decomposition rate decreased considerably, but full stabilization (cessation of $N_2H_5NO_3$ decomposition), as in the other systems, was not observed. Gradual decomposition of the reductant continued even 6 h after the start of the experiment (Fig. 1a, curve *2*).

It should also be noted that AA exhibits strong intrinsic reducing properties with respect to Tc. The reduction of pertechnetate ion under the action of AA in a hydrochloric acid medium was studied in detail previously [8]. In this study we showed that, in nitric acid solutions without $N_2H_5NO_3$, in the presence of 0.05 M AA, on keeping the system for more than 2 h, Tc(VII) was practically completely converted into the reduced form nonextractable with TBP. The fraction of the reduced Tc remained on the attained level for a long time (Table 2).

**Table 2.** Reduction of technetium with various agents in the absence of hydrazine nitrate

| Reagent | Reagent concentration, M | Tc(VII) fraction, %, after keeping for indicated time, h | | |
|---|---|---|---|---|
| | | 2 | 4 | 6 |
| $HN_3$ | 0.10 | 99 | 99 | 98 |
| AA | 0.05 | <1 | <1 | <1 |
| AHA | 0.10 | 98 | 96 | 93 |
| HAN | 0.10 | 97 | 95 | 91 |
| DTPA | 0.05 | 97 | 95 | 94 |
| Urea | 0.10 | 98 | 98 | 98 |
| $CH_3COOH$ | 0.05 | 99 | 99 | 99 |
| β-HEH nitrate | 0.11 | 42 | <1 | <1 |

The course of the $N_2H_5NO_3$ decomposition in the presence of halides was, on the whole, similar to the systems without additives. At the same time, in solutions containing fluoride ion, the induction period decreased relative to the system with chloride ions (Fig. 2a, curves *1*, *2*). For these systems, $\tau_{1/2}$ was equal to 1.1 and 1.4 h, respectively (Table 1).

It was noted that halides decrease the yield of the reduced Tc: In the presence of fluoride and chloride ions, the $Tc(VII)_{min}$ fraction was 15 and 27%, respectively. The additives also affected the fraction of the reduced Tc remaining in the final step of the reaction. The parameter $Tc(VII)_f$ appeared to be the smallest with chloride ions: 69%. These facts suggest that halides present in the system can shift the equilibrium in the redox cycles observed with Tc in these media.

Similar effect was observed with pseudohalides. In the presence of 0.05 M azide ions, the $N_2H_5NO_3$ decomposition occurred similarly to the systems with halides, also with decreased degree of Tc reduction (Fig. 2b, curve *4*). Introduction of azide ions into the systems in amounts corresponding to the ratios $N_2H_5NO_3 : N_3^- = 2 : 1$ and $1 : 1$ led to further decrease in the degree of Tc(VII) reduction. The parameter $Tc(VII)_{min}$ was 58% in the first case and 90% in the second case, after which both systems returned to the initial state (Fig. 2b, curve *5*; Table 1). The reductant after $\tau = 3$ h decomposed at a considerably lower rate than in the fast step of the reaction, and $C_f$ was 56% (Fig. 2a, curve *5*). Introduction of thiocyanate ions exerted a similar effect. It should be noted that, in the process, technetium remained practically fully in the extractable form, and half decomposition of the reductant was not attained throughout the observation period (Table 1). At the same time, the presence of colored compounds, untypical of Tc(VII), in both the aqueous and organic phases suggests the occurrence of more complex processes in the system.

The data obtained in the experiments with azide ions confirm the previously revealed protective effect

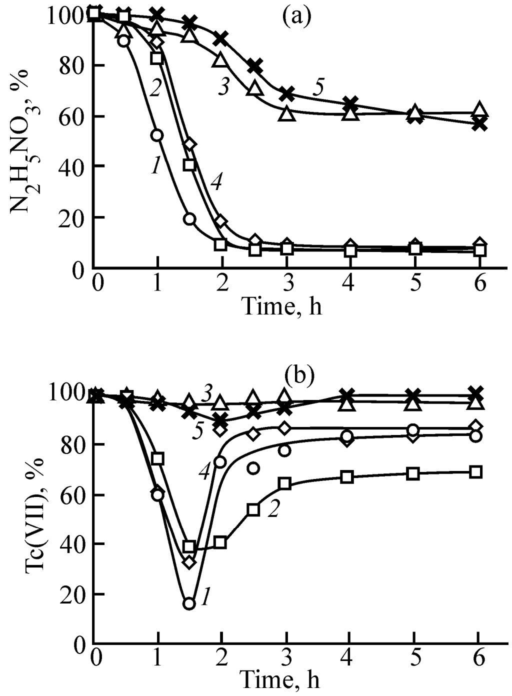

**Fig. 2.** (a) Decomposition of $N_2H_5NO_3$ and (b) variation of the Tc(VII) fraction in nitric acid solutions in the presence of halides and pseudohalides. $[N_2H_5NO_3]$, M: (*1–4*) 0.23–0.25 and (*5*) 0.05. Additives (0.05 M): (*1*) $F^-$, (*2*) $Cl^-$, (*3*) $CNS^-$, and (*4*, *5*) $N_3^-$.

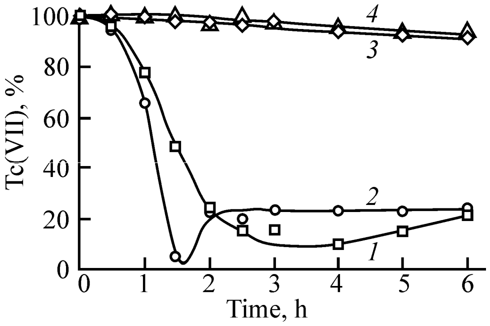

**Fig. 3.** Variation of the Tc(VII) fraction in the reaction with $N_2H_5NO_3$ in nitric acid solutions in the presence of AHA and HAN. [$N_2H_5NO_3$], M: (*1*, *2*) 0.26 and (*3*, *4*) 0. Additives: (*1*) HAN, 0.05 M; (*2*) AHA, 0.05 M; (*3*) HAN, 0.1 M; and (*4*) AHA, 0.1 M.

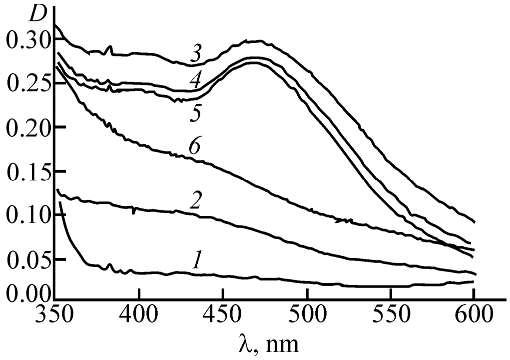

**Fig. 4.** Variation of the absorption spectra of Tc in the presence of $N_2H_5NO_3$ and AHA. [$N_2H_5NO_3$] = 0.26 M. Time from the start of the experiment, h: (*1*) 0, (*2*) 0.5, (*3*, *6*) 1.5, (*4*) 2, and (*5*) 4. AHA added, M: (*1*–*5*) 0.05 and (*6*) 0.

of hydrogen azide (product of catalytic decomposition of $N_2H_5NO_3$ in the systems under consideration) toward $N_2H_5NO_3$, which may be due to competition between these compounds for the reaction with $HNO_2$, also playing an important role in catalytic cycles involving Tc [3, 9]. Introduction of $N_3^-$ into the Tc-containing nitric acid solutions under the examined conditions without $N_2H_5NO_3$ did not affect the fraction of Tc(VII) (Table 2).

Systems with additions of AHA and HAN should be considered in more detail, because these agents can both affect Tc in mixtures with hydrazine nitrate and exert a reducing effect independently [10, 11]. Here we present the refined data on the behavior of Tc in the presence of AHA and HAN (Fig. 3).

In the presence of AHA and HAN in the hydrazine-containing systems, we observed an induction period preceding the fast step of the Tc reduction. In both systems, we noted relatively high yield of reduced technetium species. The parameter $Tc(VII)_{min}$ was 4 and 9% in the systems with AHA and HAN, respectively. It should be noted that the curve reflecting variation of the Tc(VII) content in the system with HAN was less steep than in the system with AHA (Fig. 3, curves *1* and *2*). The minimum in the Tc(VII) content was attained at $\tau_{D\min}$ = 3 h; at the same time, the values of $D_{Tc}$ were relatively low already in 2 h after the start of the experiment (Table 1).

Reliable retention of Tc in the reduced nonextractable form under the action of AHA and HAN may be due to the occurrence of a complex reaction of reductive nitrosylation of Tc in the presence of these reagents with the formation of a series of stable compounds. For example, Gong et al. [12] showed that, in a nitric acid solution in the presence of AHA, the complex $[Tc(NO)(AHA)_2H_2O]^+$, nonextractable with TBP, is formed via several intermediates. The Tc(IV) ions are considerably more reactive in the process and more susceptible to reductive nitrosylation than Tc(VII).

The near-UV and visible absorption spectra of the solution containing AHA in the initial reaction step (Fig. 4, curves *1* and *2*), on the whole, reproduced the absorption spectra of the system without additives under similar conditions. In 1.5 h after the start of the experiment in the system with AHA, the optical density of the solution increased, with a maximum observed at λ = 470 nm (Fig. 4, curve *3*). This peak apparently characterizes a Tc complex compound formed in the process. Further keeping of the solution was accompanied by a slow decrease in the optical density throughout the examined wavelength range (Fig. 4, curves *4* and *5*). In the system without additives at $\tau$ = 1.5 h, the absorption maximum at λ = 470 nm was absent (Fig. 4, curve *6*). The spectra similar to those observed in the Tc–$HNO_3$–$N_2H_5NO_3$–AHA system at $\tau > 1.5$ h are known for the product of the reaction of $NH_4TcO_4$ with a mixture of AHA and HAN [12].

The reaction of Tc with HAN cal also yield several complex products [13, 14]. It should be noted that AHA in a nitric acid solution undergoes hydrolysis to HAN and acetic acid [15], which further complicates the reaction pattern in the system.

These facts suggest that accumulation of Tc(IV) in the initial step of the reaction under the action of hydrazine nitrate in a nitric acid solution can lead subsequently to fast formation of stable compounds of Tc (in lower oxidation states) both with AHA and with HAN, so that the major fraction of Tc is fixed in the nonextractable state.

The pattern we observed can also be accounted for by blocking of the autocatalytic decomposition of hydrazine owing to fast scavenging of the generated nitrogen oxides (NO, $NO_2$), which are reduced to $N_2$ or $N_2O$.

In the systems without hydrazine nitrate in the presence of AHA and HAN, the technetium reduction under the examined conditions, on the contrary, was rather slow, with the Tc(VII) fraction decreasing uniformly throughout the experiment (Fig. 3, curves *3* and *4*). After 6 h of the reaction, the Tc(VII) fraction was 93 and 91% for the solutions with AHA and HAN, respectively (Table 2).

Gradual and insignificant decrease in the Tc(VII) fraction on keeping for 6 h was also noted in the hydrazine-free system with the addition of DTPA. Apparently, this reagent is not only a complexing agent for Tc reduced, e.g., under the action of $N_2H_5NO_3$, but also a weak reductant.

Urea and acetic acid in hydrazine-free systems exerted no reducing effect on technetium under the conditions of the experiment (Table 2). β-HEH suggested as alternative to hydrazine nitrate and forming no undesirable decomposition products [16] ensured complete reduction of Tc(VII), but the process was, on the whole, slower than with $N_2H_5NO_3$ (Table 1). At $\tau$ = 2 h, the Tc(VII) fraction in the system was 42%. The maximal yield of the reduced Tc was observed after keeping for 4 h (Table 2). At the same time, a mixture of hydrazine and β-HEH reduces Tc rapidly and completely, and the $N_2H_5NO_3$ decomposition rate in the presence of β-HEH is considerably lower than in the base system, with only weak back oxidation of Tc (Table 1). The observed pattern is similar to that in mixtures of hydrazine with AHA, HAN, or ascorbic acid and is apparently caused by the same factors. Because complexation of β-HEH with Tc(IV) can hardly be assumed, the alternative mechanism gains additional support, but studies in this field should be continued.

The results given in this paper can be important for the development of new or modification of existing technologies for extractive reprocessing of SNF, so as to control by using combinations of reducing and complexing agents the extraction behavior of SNF components being separated [3].

Today the traditional way of uranium/plutonium splitting is reduction of plutonium to a nonextractable state, which is attained, as a rule, under the action of U(IV). The process is performed in the presence of hydrazine nitrate, with technetium removed together with the nonextractable Pu form and then separated from Pu in the corresponding refining cycle. However, the use of $N_2H_5NO_3$ gives rise to certain problems. The most serious problem is contamination of the solutions with undesirable products of decomposition of this reductant, namely, with the already mentioned azide and also ammonium compounds, which makes utilization of the raffinates obtained fire- and explosion-hazardous [17]. Also, under the conditions of hydrazine deficiency, characteristic of some zones of extraction apparatuses, technetium can be partially oxidized again, leading to disturbances of the reduction process [18].

Introduction into the stripping solution of complexing agents used today, e.g., of DTPA [19], somewhat decreases the rate of hydrazine nitrate oxidation, which allows only partial solution of the problem of the process instability [2]. Therefore, search for flowsheets in which hydrazine will be used to a smaller extent or abandoned at all remains topical.

The use of AHA and HAN as stabilizing agents can ensure in the presence of $N_2H_5NO_3$ reliable fixation of Tc in the nonextractable state, which should appreciably reduce the hydrazine nitrate consumption. Another important factor is that the decomposition products of AHA and HAN contain no substances complicating the subsequent solution reprocessing.

Among reagents alternative to hydrazine nitrate but ensuring complete reduction of Tc under the conditions of the experiment are β-HEH and ascorbic acid. AA behaves as reductant when taken both separately and in combination with $N_2H_5NO_3$, which allows it to be considered, in particular, as complexing agent for Tc. Whereas the rate of technetium reduction with ascorbic acid is sufficiently high, the rate of technetium reduction with β-HEH is relatively low and can be insufficient for complete reduction of Tc in fast extraction processes. To attain the acceptable characteristics, more severe conditions (e.g., elevated temperature) are required than when performing the corresponding operations within the framework of the Purex process. At the same time, possible effect of AA decomposition products in nitric acid solutions on the course of reductive U/Pu splitting can also restrict the applicability of this reagent in the industrial process.

In contrast to the above reagents, hydrogen peroxide practically fully blocked the technetium reduction in nitric acid solutions. This may be due to the effect of this reagent on the initial steps of the technetium catalytic cycle, preventing generation of Tc(IV) in an amount sufficient for the normal progress of the reaction of Tc with hydrazine nitrate. The reaction is also inhibited by azide ions formed by decomposition of hydrazine.

A number of other substances known as complexing agents appeared to be practically indifferent to the technetium reduced with hydrazine. For example, urea and sulfate ions, which are strong complexing agents for Pu(IV) and Np(IV) [19–21], showed no complexing properties with respect to Tc(IV). Acetic acid, which can appreciably decrease $D_{\mathrm{Pu(IV)}}$ in nitric acid solutions [22], also exerted no effect on the reduced technetium.

This group of reagents also includes AHA and HAN, and also ascorbic acid and β-HEH, which slowly reduce Tc in hydrazine-free systems but interact with Np and Pu with the reduction of these elements and/or formation of their nonextractable complexes, ensuring efficient stripping of Pu and Np [10, 11, 23, 24].

With such inhibiting or indifferent agents used as additives to stripping solutions, the directions of streams with the target components in the extraction scheme can be cardinally changed, and the reductive splitting of U and Pu (Np) can be organized in a more favorable mode by eliminating cyclic redox reactions with Tc. In the operation designed in this manner, technetium remains in the organic phase and is removed with the extract to the uranium stream. In so doing, disturbances of the process become considerably less probable. Furthermore, the problem associated with undesirable decomposition products of hydrazine nitrate is eliminated.

At the same time, an extraction flowsheet that does not involve the Tc valence state in the course of reduction operations in the first extraction cycle should involve separation of technetium from uranium in the uranium refining cycle or in a separate unit for Tc stripping in the first cycle [25]. It should be noted that this sequence of operations was used as the basis for actinide separation in the project of the RT-2 plant [25]. In this reduction operation, only those reduction systems can be used which efficiently convert Tc to a nonextractable form. As such reagents we can suggest $N_2H_5NO_3$–AHA, $N_2H_5NO_3$–HAN, or $N_2H_5NO_3$–β-HEH mixtures, as well as other high-performance reducing and complexing agents.

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