Influence of zirconium concentration on the extraction of technetium (VII) in the processing SNF

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Abstract. Technetium is part of the fission products of uranium formed during the operation of a nuclear reactor. The accumulation of technetium in the fuel is about 1090 g/t-U with a burn up of 40 GW.day/t-U. The half-life of Tc-99 is 212 thousand years and its removal into radioactive waste together with relatively short-lived (T_{1/2} = 30–50 years), the handling of which implies near-surface storage, seems unacceptable. In view of this, it is advisable to remove Tc from the 1st cycle raffinate before concentrating and solidifying. All known variants of Tc isolation are based on its ability to complexate with TBP with subsequent extraction, as well as to co-extract in anionic form with U (VI) and tetravalent elements. To this end, we studied the effect of zirconium (VI) concentration on the extraction of technetium (VII) in the processing of spent nuclear fuel (SNF).

1. Introduction
An important task of modern nuclear power engineering is the development of a completely closed nuclear fuel cycle. The final stage of this cycle is spent nuclear fuel (SNF) reprocessing. At this stage, the problem of providing nuclear power with fuel based on spent and recycled fissile materials is solved. At the moment, within the framework of the first extraction cycle of SNF reprocessing, the target components, U and Pu, are being isolated. However, due to the general trend towards an increase in the degree of burn up of nuclear fuel and, as a consequence, the formation of a large amount of fission products (FF), the extraction of target components, with the aim of their further use in the production of nuclear fuel, must be carried out with a high degree of purification from gamma emitting nuclides and minor actinides (Np, Am, Cm). For this purpose, the PUREX process is used, based on the extraction of uranium and plutonium using tributyl phosphate (TBP) in a non-polar diluents after dissolving the fuel in nitric acid [1, 2]. The main advantage of using TBP for the extraction of uranium and plutonium is that most of the fission products are not extracted into the organic phase. However, such an element as Tc, due to its chemical nature, still significantly complicates the isolation of target components (U, Pu) [1]. When SNF dissolves in nitric acid, technetium goes into solution in the form of pertechnetate ions. At the first stage, under the conditions of the current technological scheme, technetium (VII) partially passes into the organic phase. The degree of extraction depends on the conditions of the extraction process [3].

Tc(VII) is extracted into the organic phase in the form of an adduct of technetium acid with TBP, as well as in the form of compounds with SNF components - uranium in the form of UO_2(TcO_4)(NO_3)(TBP)_2 [1], plutonium in the form of Pu(TcO_4)(NO_3)(TBP)_2 [2, 4], replacing nitrate ions in the extracted complexes with pertechnetate ions. Technetium forms complexes not only with...
UO$_2^{2+}$ and Pu$_4^{6+}$, but also with zirconium in the form of Zr(TcO$_4$)(NO$_3$)$_3$(TBP)$_2$ [5]. The phenomenon of technetium co-extraction is most noticeable in the presence of zirconium [6]. It plays a special role in conditions when the extractant is not sufficiently saturated with uranium [7, 8, 9]. Comparison of the published data shows that the co-extraction of Tc (VII) with Zr (IV) [10, 11] is significantly stronger than the co-extraction with U (VI) [12, 13]. Co-extraction of pertechnetate ion with zirconium (IV) was studied in the TBP – nitric acid system [14]. At acidity above 1.5 mol/l HNO$_3$, where Zr has a significant tendency to be extracted into the organic phase (a strong increase in the TcO$_4^-$ distribution coefficients was observed). At an initial Zr concentration of 1 g/l, 5 mol/l HNO$_3$, and 30% TBP, the TcO$_4^-$ distribution coefficient increased about 100 times. The most likely explanation for this behavior is the formation of complexes Zr(TcO$_4$)(NO$_3$)$_3$(TBP)$_2$.

To find out the effect of the concentration of zirconium on the extraction of technetium (VII), we carried out several experiments.

2. Experiment
Zirconium nitrate Zr(NO$_3$)$_4$ was prepared by boiling ZrO(NO$_3$)$_2$·H$_2$O for 72 hours in concentrated nitric acid with a reflux condenser, followed by separation of the undissolved precipitate. Technetium (VII) was introduced into the model solution by dissolving ammonium pertechnetate NH$_4$TcO$_4$. The solutions were prepared by the volumetric method.

A 30% solution of tributyl phosphate (TBP) in a hydrocarbon diluent of Isopar-M brand was used as an extractant. The extractant was preliminarily purified from impurities by washing with a 5 wt% sodium carbonate solution in water, followed by washing with water. The operation was performed twice.

Experiments on the extraction of technetium for the construction of isotherms were carried out by changing the volume of phases under static conditions at a temperature of 20±1°C. In these experiments, the aqueous phase of a solution containing 125 mg/l Tc (VII), 4.02 mol/l HNO$_3$ in the presence of Zr (IV) with concentrations of 9.94 g/l and 3.64 g/l was used. The phases were stirred for 3 minutes in a rotary mixer (80 rpm). This time was enough to establish equilibrium in the system, which was confirmed by a control experiment with a 20-minute contact of the phases. The phases were separated by centrifugation. After separation of the phases, samples were taken for analysis. The distribution of technetium (VII) during extraction in both phases was monitored by liquid scintillation spectrometry (LSS) on an SKS-50M-B11 device.

3. Results and discussion
Due to the fact that in the simulating solution, in addition to the target technetium anion (TcO$_4^-$), the concentration of zirconium (IV) cations predominates, it was assumed that technetium (VII) is recovered in TBP in the form of the Zr(TcO$_4$)(NO$_3$)$_3$(TBP)$_2$ complex. The ability of zirconium tetranitrate to disolve with TBP to co-extract other anions has been known for a long time. In [14], the ability of zirconium tetranitrate to be co-extracted with perchlorate ion into the TBP phase was shown for the first time. The authors of [12, 15] investigated the extraction mechanism in the Zr(NO$_3$)$_4$–ATcO$_4$ (where A=NH$_4^+$, K$^+$) –HNO$_3$– TBP, system, and also developed a mathematical model of the process based on equation (1)

$$Zr^{4+} + 3NO_3^- + TcO_4^- + 2TBP = Zr(TcO_4)(NO_3)_3(TBP)_2$$

According to equation (1), the extraction of technetium into the organic phase containing TBP is determined by the ability of the organic ligand to coordinate zirconium. Accordingly, the more zirconium is extracted, the higher the degree of technetium extraction into the organic phase. To solve this problem, it is necessary to carry out a theoretical calculation of the required number of extraction stages of the countercurrent cascade. This requires data on the isotherm of technetium extraction in the Zr–TcO$_4$–HNO$_3$–TBP system.
Table 1. Scheme of obtaining isotherms by changing the volume of phases.

| Contact number | Volume organic phase, ml | O : A ratio | Volume aqueous phase, ml |
|----------------|--------------------------|-------------|-------------------------|
| 1              | 25                       | 5 : 1       | 5                       |
| 2              | 20                       | 4 : 1       | 5                       |
| 3              | 15                       | 3 : 1       | 5                       |
| 4              | 10                       | 2 : 1       | 5                       |
| 5              | 5                        | 1 : 1       | 5                       |
| 6              | 5                        | 1 : 2       | 10                      |
| 7              | 5                        | 1 : 3       | 15                      |
| 8              | 5                        | 1 : 4       | 20                      |
| 9              | 5                        | 1 : 5       | 25                      |

In the experiments, the influence of the concentration of zirconium on the distribution of technetium and nitric acid between the aqueous and organic phases was studied (figures 1 and 2).

Figure 1. Effect of zirconium concentration on technetium isotherms during the extraction of technetium (VII) in the presence of 9.94 g/l and 3.64 g/l Zr (IV).

Figure 2. Equilibrium content of nitric acid in the aqueous phase during the extraction of technetium (VII) in the presence of 9.94 g/l and 3.64 g/l Zr (IV).
As can be seen from figures 1 and 2, a decrease in the concentration of zirconium (IV) leads to a significant deterioration in the extraction of technetium (VII). At the same time, the extraction ability of TBP to extract nitric acid under the described experimental conditions increases sharply. This result is quite natural, since with a decrease in the content of zirconium in the extraction system, the concentration of the free extractant increases, which leads to an increase in the extraction of nitric acid into the organic phase.

To confirm the results obtained earlier, a calculation was carried out to assess the number of stages and the degree of technetium extraction. The calculation was carried out for a system where a solution containing 125 mg/l Tc (VII) and 4.02 mol/l HNO₃ in the presence of 9.94 g/l Zr, at which the maximum value of the degree of technetium extraction into the organic phase is achieved.

Graphical calculation of the number of theoretical extraction steps was carried out by the Thiele-McCab method, which is reduced to the construction of equilibrium and working line, and then the steps of concentration change between these two lines [16].

Figure 3 shows the isotherm of technetium (VII) extraction and the result of the calculation performed. The working line was constructed according to the data of the composition of the initial solution and the ratio of the flows of the organic and aqueous phases (O: A = 1: 1) in the extraction cascade.

\[ A(x_i - x_f) = O(y_f - y_i) \]  

(2)

Where:
- \( A \) is the flow of the aqueous phase;
- \( O \) is the flow of the organic phase;
- \( x_i, x_f \) are the initial concentration and the final concentration of technetium, respectively, in the aqueous phase, mg/l;
- \( y_i, y_f \) are the initial concentration and the final concentration of technetium, respectively, in the organic phase, mg/l.

Transforming the equation of the working line (2), we obtain the expression (3) for the concentration of technetium (VII) at the outlet of the countercurrent cascade:

\[ x_f = x_i - \frac{O}{A} (y_f - y_i) \]  

(3)

According to equation (3), the flow entering the countercurrent cascade with a technetium (VII) concentration of 125 mg/l in the aqueous phase and the outgoing flow of 99.8 mg/l in the organic phase, as well as a flow ratio of 1:1, we have 25.3 mg/l Tc (VII) in the effluent in the aqueous phase.

**Table 2. Concentrations in the cascade for technetium.**

| Organic phase | Aqueous phase |
|---------------|--------------|
| Input - 0 mg/l | Input - 125 mg/l |
| Output - 99.8 mg/l | Output - 25.3 mg/l |
Figure 3. Isotherm of Tc (VII) extraction from 125 mg/l Tc (VII) and 4.02 mol/l HNO₃ in the presence of 9.94 g/l Zr(IV) at 20 °C (1), working line (2) and extraction stages (3).

As a result of the above graphical calculation, seven theoretical degrees were obtained. The content of technetium (VII) at the outlet of a conventional countercurrent cascade with seven stages is 25 mg/l, which corresponds to 80% recovery from the initial solution. A further increase in the number of extraction stages will not lead to an increase in the degree of technetium extraction under the conditions considered (figure 3).

4. Conclusion
As a summary of the work, we can say that at a zirconium (IV) concentration of about 10 g/L and 4 mol/l HNO₃, with an insignificant content of oxo-cations ZrO²⁺ and Zr₂O₃²⁺ in the initial aqueous solution, the extraction of technetium (VII) in TBP (30% in isopar) is possible by 80% in seven stages of a counter-flow cascade at O: A = 1: 1.

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