Recovery of Americium from Actinide-Lanthanide Fraction of High-Level Waste during Its Transfer to the Oxidation State Am(V)

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Abstract—The conditions for the oxidation of Am(III) to Am(VI) and its reduction to Am(V) are shown, and the stability of these forms in a 0.1 M nitric acid model solution of the actinide-lanthanide fraction of high-level waste (HLW) containing isotopes of americium and curium and also praseodymium as a simulant of the behavior of fragmented lanthanides is defined. It was found that about 30% of americium in the Am(V) oxidation state of its initial content in a model solution containing a salting-out agent (ammonium nitrate) in an amount of 8 M, passes into the organic phase in one stage of extraction with a 30% solution of tributyl phosphate in Isopar-M. In this case, Cm and Pr are extracted by 80–85%. The distribution coefficient of Am was about 0.1, of Cm and Pr, about 1, and the separation factor of Am from Cm and Pr was about 10. Thus, the possibility of selective separation of americium from HLW for its subsequent transmutation in fast reactors was demonstrated.

Keywords: americium, curium, lanthanides, praseodymium, extraction, tributyl phosphate, recovery, separation, salting-out agent

INTRODUCTION

The spent nuclear fuel (SNF) reprocessing technology is based on the Purex extraction process, which uses tributyl phosphate (TBP) in a light diluent as an extractant. After the extraction of uranium and plutonium from the SNF solution, transplutonium elements (TPE)—long-lived isotopes ^{241,243}Am ($T_{1/2} =$ 433 and 7370 years, respectively) and relatively short-lived ^{244}Cm ($T_{1/2} =$ 18 years), as well as a group of fragmented lanthanides—remain in the raffinate. At the same time, in several hundred years, the main contribution to the HLW radioactivity will be made by long-lived isotopes of americium. The modern strategy for the development of the nuclear power industry in Russia provides for the closed nuclear fuel cycle (CNFC), including minimizing the radioactive waste volume for deep disposal. This can be reached with deep HLW fractionation enabling separation of the americium into an independent fraction with followed its transmutation in fast neutron reactors [1].

Previously, we proposed a method for separating the actinide–lanthanide fraction from a highly active raffinate during the extraction with TBP in an isoparaffin diluent in the presence of iron nitrate as a salting-out agent [2]. In this case, one of the most important radiochemical problems is the subsequent separation of americium from curium and lanthanides. This separation is necessary for a number of reasons. First, the lanthanides are neutron poisons; some isotopes have a high neutron capture cross section, and their presence in the fuel will inhibit the transmutation of americium [3, 4]. Secondly, the involvement of curium isotopes in a closed nuclear fuel cycle is problematic, since it has a high level of neutron and thermal radiation, which will complicate the manufacture and operation of regenerated homogeneous nuclear fuel or americium targets for its transmutation.

The well-known problem of separating Am, Cm, and lanthanides is caused by the similarity in their chemical properties [5, 6]. TPE and lanthanides are 5*f*- and 4*f*-elements, respectively, they are characterized by the filling of internal *f*-orbitals with increasing atomic number, which has little effect on the chemical properties that depend mainly on processes in the outer electron shells. In view of this fact, these elements predominantly exist in aqueous solutions in the oxidation state(III). The ionic radii of these cations are also comparable. Americium and curium ions have isostructural analogs in the lanthanide series: $r(Nd^{3+}) \approx r(Am^{3+})$, $r(Sm^{3+}) \approx r(Cm^{3+})$. Thus, it is difficult to separate trivalent Am and Cm from lanthanides by adjusting only the size of the coordination sphere of organic ligands.

There are several approaches to the separation of Am from Cm and lanthanides, and most of them are based on extraction methods [7, 8]. The key difference between these cations is that americium can be oxidized to higher oxidation states Am(V,VI), which changes its extraction behavior [9, 10]. Previously, in our works [11, 12], it was shown that, generating Am(VI) in weakly acidic solutions makes it possible to extract Cm(III) from their mixture using the extractants 1-phenyl-3-methyl-4-benzoylpyrosolone-5 and trioctylphosphine oxide, while Am(VI), being reduced by the organic phase to Am(V), remains in the aqueous solution. At the same time, the use of these extractants in industrial conditions is challenging. For this reason, it was proposed [13] to use TBP as a reliable and well-tested extractant in the technology to solve the problem of separating Am from Cm. For example, curium was extracted almost quantitatively from solutions containing ≤0.1 M HNO₃ and ~8 M NH₄NO₃ using 30% TBP in Isopar-M, while americium was only partially (≤30%) transferred to the organic phase in the Am(III) form. In this case, a high degree of separation of Cm from Am(V) remaining in the aqueous phase was attained (≥99.9%).

At the moment, only a few other works [14–16] are known on the use of TBP as an extractant for separating Am from other transuranium elements or lanthanides. For example, in [14, 16], it was proposed to extract Am(VI) directly from nitric acid solutions without adding a salting-out agent. Reaching high distribution coefficients can be performed by adjusting the solution acidity. At the initial stage, a decrease in acidity is provided for the efficient oxidation of Am(III) to Am(VI) , then its increase it to 1 M relative to HNO₃.

The separation factor for the Am–Nd pair was about 50; therewith separation of the Am–Np pair did not occur. In [15], it was proposed to use dihydrogen phosphate to bind Nd into a more stable complex compared to Am(VI), which allowed to reach a separation factor of about 120.
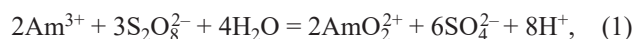
This work is aimed at studying the extraction of Am in higher oxidation states in weakly acidic solutions—simulants of the actinide–lanthanide fraction of a highly active raffinate, containing americium and curium isotopes and weight amounts of lanthanides (with praseodymium as an example)—using TBP and in the presence of ammonium nitrate as a salting-out agent, not forming insoluble salts with actinides and fission products, including lanthanides.

EXPERIMENTAL

The elemental composition of SNF from VVER-1000 reactors with a burnup of 60 GW day/(t U) and holding for 8 years was calculated in [17]. It is shown that the fraction of fragmented lanthanides is 17.2 mg per 1 g of initial uranium. Provided that during the dissolution of SNF it is planned to increase the uranium concentration to 600 g/L, the actinide-lanthanide fraction will account for up to 10.5 g/L of fragmented lanthanides. In this work, we used Pr as a lanthanide simulant, whose absorption bands do not coincide with those of Am(III), Am(V), and Am(VI), which makes it possible to determine the concentrations in solution of both Pr and Am in various oxidation states by the spectrophotometric method.

To prepare a model solution of the actinide–lanthanide fraction, the ²⁴¹Am, ²⁴³Am, and ²⁴⁴Cm isotopes were used, the concentrations of which in the initial solution were 2.48×10^{-3}, 1.28×10^{-1}, and 1.38×10^{-4} g/L, respectively. The Pr concentration was 10.5 g/L.

Americium was transferred to the highest oxidation states Am(VI) and then to Am(V) according to the following reactions (1) and (2), respectively:

$$2Am^{3+} + 3S_2O_8^{2-} + 4H_2O = 2AmO_2^{2+} + 6SO_4^{2-} + 8H^+, \quad (1)$$

$$2AmO_2^{2+} + 2H_2O_2 = 2AmO_2^+ + O_2 + 2H_2O. \quad (2)$$

Am(III) was oxidized to Am(VI) in a 0.1 M HNO₃ solution containing 0.2 M (NH₄)₂S₂O₈ as an oxidizing

agent by heating the solution at 90°C for 20 min according to the procedure described in [11]. The efficiency of this method is usually limited by nitric acid concentrations of no more than 0.5 M [18]. At higher acid concentrations, ammonium persulfate decomposes to form hydrogen peroxide, an effective reducing agent for AmO_2^{2+} [19]. However, this effect, apparently, can be leveled by increasing the concentration of the oxidizing agent to 1.6 M [14], which enabled oxidation of Am(III) to Am(VI) in 1 M HNO_3 by $90 \pm 5\%$.

A solution containing Am(V) was obtained by adding 1 μL of a 37% H_2O_2 solution to 1 mL of an Am(VI) solution in 0.1 M HNO_3 previously prepared as described above. The authors of [20] report the possibility of direct preparation of Am(V) in 0.1 M HNO_3 by heating to 80–100°C and an ammonium persulfate concentration of 1 M.

The completeness of Am(III) oxidation to Am(VI) and its subsequent reduction to Am(V), their behavior during extraction, as well as the concentration of Pr(III) in the solution were monitored by a spectrophotometric method (Unicam UV-300, Unicam Instruments, UK) according to absorption bands at 503 and 814 nm for Am(III), 513 and 717 nm for Am(V), 666 and 996 nm for Am(VI), and 445 and 592 nm for Pr.

In extraction experiments, a 30% TBP solution in Isopar-M was used, which was preliminarily contacted for 5 min with an equal volume of a 0.1 M HNO_3 solution containing 0.2 M $(NH_4)_2S_2O_8$.

Before extraction, a weighed portion of NH_4NO_3 was introduced into the resulting solutions containing Am(VI) or Am(V), as well as trivalent Cm and Pr, to achieve its concentration in the solution of 8 M, as in [13]. Extraction of actinides and Pr was carried out for 1 min at a ratio of aqueous (A) and organic (O) phases of 1 : 5.

As we determined earlier [13], 1 min is enough to set thermodynamic equilibrium at the distribution of Am(III) and Cm between a nitric acid solution containing NH_4NO_3 as a salting-out agent and 30% TBP in isopar-M. The phases were brought into contact with each other by shaking the tubes by hand for 1 min. The phases were then centrifuged to separate them for about 1 min at 2000 rpm. After the phases were separated and analyzed.

The total concentration of Am and Cm in the used solutions was found by alpha spectrometry (Alpha Analyst, Canberra, USA).
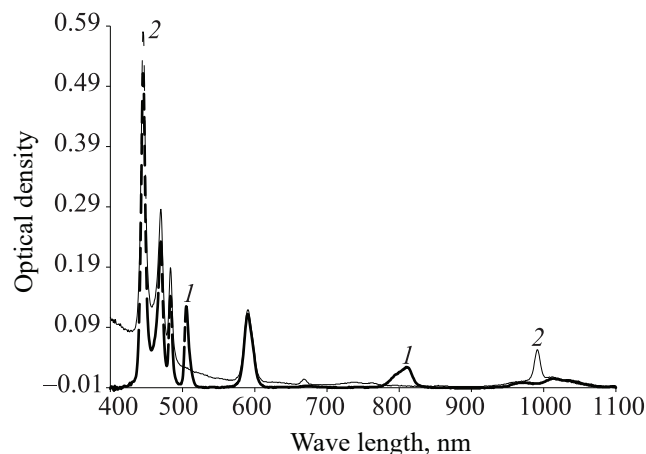
Fig. 1. Absorption spectra of Pr(III) and Am(III) in 0.1 M HNO_3 (1) and of the same solution after quantitative oxidation of Am(III) to Am(VI) (2).

The ammonium nitrate, praseodymium nitrate hexahydrate, ammonium persulfate, nitric acid, and hydrogen peroxide used in the work were of analytical grade.

RESULTS AND DISCUSSION

Figure 1 shows the spectrum (1) of an initial 0.1 M HNO_3 solution containing trivalent Am, Cm, and Pr with the concentrations given in Table 1 as well as spectrum (2) of the same solution after the quantitative oxidation of Am(III) to Am(VI) according to the procedure described in the experimental part. As can be seen from Fig. 1, the presence in the solution of an almost 100-fold excess of Pr compared to Am (10.5 and 0.13 g/L, respectively) does not affect the Am(III) oxidation.

We preliminarily studied the extraction of Am(VI) and trivalent Cm and Pr from 0.1 M HNO_3 in the presence of 8 M NH_4NO_3 with 30% TBP in Isopar-M (Table 1). It can be seen from the data in Table 1 that both trivalent Cm and Pr and Am(VI) are extracted to a high degree (up to 95 wt %) under the conditions of the study. The distribution coefficients (D) of Am(VI), Cm(III), and Pr(III) per an extraction were about 2.5, 3.6, and 1.8, respectively. $D_{Am(VI)} = 2.5$ correlates with the data of [21], where the maximum distribution coefficient was achieved at 4 M HNO_3 and the minimum phase contact time, and, however, it was slightly lower than in [16], where 100% TBP was used for extraction. Spectrophotometric method was applied to prove that

Table 1. Extraction of Am(VI), Cm(III), and Pr(III) from 0.1 M HNO_3 in the presence of a salting-out agent (8.0 M NH_4NO_3) with 30% TBP in Isopar-M. The content of Am, Cm, and Pr in the initial solution is 0.13, 1.38×10^{-4}, and 10.5 g/L, respectively; ratio of volumes A : O = 1 : 5

Solution	Element	Element concentration, g/mL	D	Element content in solution, wt % from initial
Extract	Am	2.42×10^{-2}	2.5	92.7
	Cm	2.62×10^{-5}	3.6	94.7
	Pr	1.89	1.8	90.0
Raffinate	Am	9.49×10^{-3}	–	7.3
	Cm	7.31×10^{-6}	–	5.3
	Pr	1.05	–	10

Table 2. Extraction of Am(V), Cm(III), and Pr(III) from 0.1 M HNO_3 in the presence of a salting-out agent (8.0 M NH_4NO_3) with 30% TBP in Isopar-M. The concentrations of Am, Cm, and Pr in the initial solution are 0.13, 1.38×10^{-4}, and 10.5 mg/mL, respectively; ratio of volumes A : O = 1 : 5

Run no.	Solution	Element	Element concentration, mg/mL	D	Element content in solution, wt %	SF
1	Raffinate	Am	8.64×10^{-2}		67	
		Cm	2.35×10^{-5}		17	
		Pr	1.58		15	
	Extract	Am	8.72×10^{-3}	0.10	33	
		Cm	2.29×10^{-5}	0.99	83	9.9[a]
		Pr	1.78	1.15	85	11.5[b]
2	Raffinate	Am	8.77×10^{-2}		68	
		Cm	2.21×10^{-5}		16	
		Pr	0.21		20	
	Extract	Am	8.46×10^{-3}	0.10	32	
		Cm	2.32×10^{-5}	1.05	84	10.5[a]
		Pr	0.17	0.81	80	8.1[b]

[a] Separation factor $SF_{Cm/Am}$. [b] $SF_{Pr/Am}$.

Table 3. Extraction of Pr(III) from 0.1 M HNO_3 in the presence of a salting-out agent (8.0 M NH_4NO_3) with 30% TBP in Isopar-M using a three-stage extraction at a volume ratio of A : O = 1 : 1

Stage no.	[Pr(III)], 0.046 M	REE content in solution from its initial content, wt %	D
1st	Raffinate-1	51.2	1.0
	Extract-1	48.8	
2nd	Raffinate-2	10.5	8.5
	Extract-2	89.5	
3rd	Raffinate-3	1.2	82.3
	Extract-3	98.8	

Am(VI) in organic phase is reduced mainly to Am(V) and partially to Am(III), and after 1 day storage, Am(V) completely transforms into Am(III). However, in some works, contradictions were noted regarding the stability of Am(VI) in the presence of TBP. Thus, the authors of [14, 16] point to the relative stability of Am in the organic phase, while it was stated in [21] that contact with organic phase led to a rapid americium reduction resulting in a lower D(Am) than expected. Thus, from the data in Table 1, it can be concluded that Am(VI), as well as trivalent Cm and Pr, is successfully extracted with 30% TBP in Isopar-M from 0.1 M HNO_3 in the presence of NH_4NO_3 salting-out agent. Therefore, this approach to the separation of Am(VI) from Cm and lanthanides under these conditions is technologically unrealizable.

The extraction of Am(V) and trivalent Cm and Pr from 0.1 M HNO_3 in the presence of 8 M NH_4NO_3 with 30% TBP in Isopar-M was studied. It was preliminarily confirmed that the addition of the salting-out agent NH_4NO_3 to the solution does not lead to a change in the oxidation state of Am(V) (Fig. 2). Experiments were conducted in which the Pr content was 1.05 or 10.5 g/L at a constant content of Am(V) and Cm; extraction was performed at a ratio of A : O = 1 : 5.

Data of Table 2 show that different Pr content does not lead to a change in the degree of extraction of Am(V) in a one-stage extraction. The distribution coefficient of Am(V) is found to be about 0.1; americium is extracted in organic phase by no more than 30% of its content in the initial solution, which is consistent with the data of [13]. At the same time, the distribution coefficients of Pr and Cm are found to be very close, about 1 (Table 2), and the degree of their extraction is 80–85% per extraction cycle.

It was noted that the separation factor $SF_{Cm/Am}$ is found to be significantly lower than in [13], when it was possible to extract Cm almost completely in organic phase ($SF_{Cm/Am}$ was 65). Obviously, this can be explained by the effect of more than a hundredfold amount of Pr present in the solution relative to the initial Am content. It should also be taken into account that the concentrations of Am and Cm in the initial solution were several orders of magnitude higher (0.13 and 1.38×10^{-4}, respectively) than in [13].

At the same time, it was shown that the separation factor can be increased by using a three-stage extraction at a volume ratio of A : O = 1 : 1, as it was demonstrated for Pr in the absence of TPE (Table 3). In this case, the degree of its extraction reached 98%, even though the total volume of the extractant was 1.6 times less than in the case of one-stage extraction with the ratio A : O = 1 : 5.

CONCLUSIONS

It was found that about 30% of Am(V) is extracted with a 30% TBP solution in Isopar-M from 0.1 M HNO_3 in the presence of 8 M NH_4NO_3 during a one-stage extraction at a volume ratio of A : O = 1 : 5, while Cm and Pr are recovered by more than 80%. Using Pr as an example, it was shown that the replacement of one-stage extraction with a ratio of A : O = 1 : 5 by a three-stage one with a volume ratio of A : O = 1 : 1 makes it possible to quantitatively extract Cm and Pr.
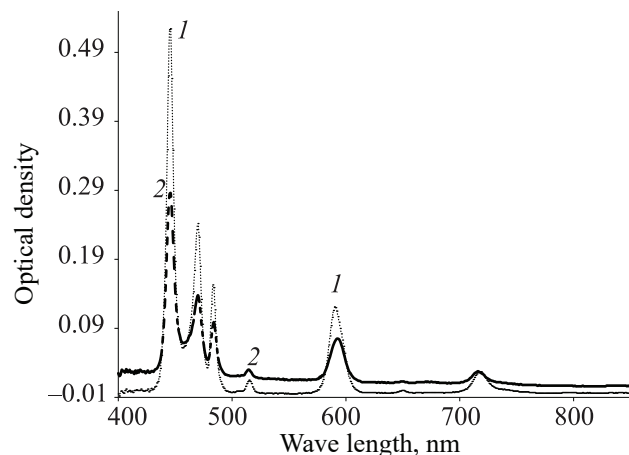
Fig. 2. Absorption spectra of Am(V) and Pr(III) in 0.1 M HNO_3 before (*1*) and after (*2*) adding salting-out agent (8 M NH_4NO_3).

The main problem of using Am(V) for its separation from Cm and REE is its reduction to Am(III), which is well extractable under these conditions. The Am(V) reduction occurs under the action of radiolysis products [22], disproportionation of Am(V) [23], and due to contact with organic phase. Selection of the conditions under which the extraction of Am(V) in TBP will be minimal without replacing TBP with the TODGA extractant, which is not yet available for industrial technology, as was done in [24, 25], will make it possible to achieve the quantitative separation of americium from curium, as well from lanthanides.

Thus, an important task for future research is the stabilization of americium in its weakly extractable form Am(V).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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