

# Some Problems in Reprocessing of Fuel Spent by Modern Power Reactors

A. V. Ochkin

Mendeleev Russian University of Chemical Technology, Miusskaya pl. 9, Moscow, 125047 Russia

e-mail: ochkin@rctu.ru

Received July 3, 2013

**Abstract**—Some problems of reprocessing the spent fuel of power reactors have been considered. The process currently includes the extraction of uranium, plutonium, and neptunium with 30% tri-*n*-butylphosphate (TBP) in a hydrocarbon solvent. An aqueous phase that contains fission products, as well as americium and curium, is transferred into a glass matrix. An alternative process with the separation of americium and curium from the aqueous phase has been developed. Since the concentration of plutonium in the organic phase is very small, the organic phase can be thermodynamically described as the quinary  $\text{H}_2\text{O}-\text{HNO}_3-\text{UO}_2(\text{NO}_3)_2-\text{TBP}-\text{diluent}$  system. This system is divided into subsystems, which are described using component activities and rational activity coefficients. Some data on the calculation of three ternary subsystems and one quaternary subsystem are given.

**DOI:** 10.1134/S0040579514010084

## INTRODUCTION

The reprocessing of spent fuel is currently performed by the PUREX process. The initial name of the PUREX process implied the separation of plutonium (P) and uranium (UR) via the extraction (EX) with tri-*n*-butylphosphate (TBP) solutions. The dominant process wastes were fission products, and the formation of neptunium-237 and transplutonium elements (americium and curium) was negligible at that time. The radionuclide composition gradually changes upon passing to the reprocessing of power reactor fuels. An analysis of the fuel of a VVER-440 reactor at a burnup of 33.4 (MW day)/kg was performed in 1981 [1]. The fuel contained 957 kg of uranium, 0.445 kg of neptunium-273, 9.2 kg of plutonium, 124 g of americium and curium, and 33.3 kg of fission products per ton. During the storage of the fuel for 5 years for the purpose of reducing the concentration of short-lived fission product in it, the amount of americium grows nearly up to 300 g due to the decay of plutonium-241. The modern radiochemical reprocessing of spent fuel includes the use of 30-% TBP in a hydrocarbon diluent ( $\text{C}_{11}-\text{C}_{14}$  hydrocarbon mixture) [2]. In this process, uranium, plutonium, and neptunium are concentrated in the organic phase, and americium, curium, and fission products are concentrated in the aqueous phase. High-level radioactive wastes (HLRWs) are further formed based on the aqueous phase.

The further change of the radionuclide composition of fuel occurred in the 1990s due to the two following processes:

(1) The burnup was gradually increased from 33.4 to nearly 50–60 (MW day)/kg to reduce the radiation burden on nuclear station personnel. This increases the concentration of americium-243 and curium radionuclides in the conventional fuel [3].

(2) Europe began using MOX fuel (uranium dioxide and plutonium dioxide mixture). The concentration of plutonium will gradually grow during the radiochemical reprocessing of such a fuel, which leads to a further increase in the concentration of americium and curium in it.

For this reason, we have posed the problem of creating technology for reprocessing spent fuel, which would include the separation of americium and, possibly, curium from HLRWs formed in the extraction technology. The objective of this work is to consider the physicochemical problems arising in the reprocessing of spent fuel due to the properties of the organic phase.

## MODERN PUREX-PROCESS

The modern process of the radiochemical reprocessing of spent fuel may be represented by the following scheme (Fig. 1). The concentration of target elements in HLRWs does not exceed 0.01, 0.025, and 0.5% with reference to uranium, plutonium, and neptunium, respectively [2]. The radiation hazard of HLRWs is often estimated via the product  $\sum A_i \varepsilon_i$  [4], where  $A_i$  is the activity of the  $i$ th radionuclide, Bq/(t U) and  $\varepsilon_i$  is the dose coefficient of the  $i$ th radionuclide, Sv/Bq [5]. The estimate of the radiation hazard of HLRWs for the fuel [1] with allowance for the two most important fission products contained in it, such

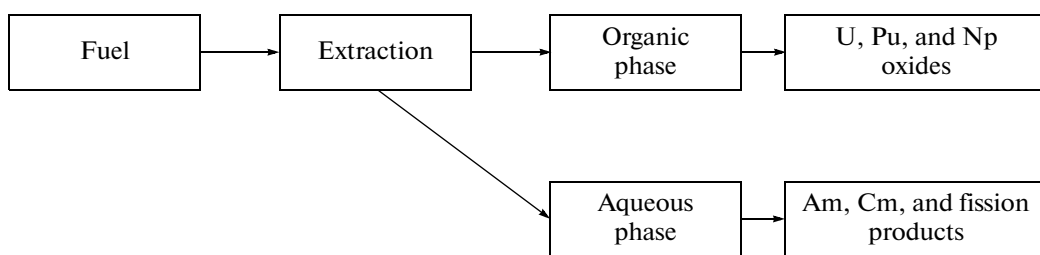


Fig. 1. Modern process of radiochemical reprocessing of spent fuel.

as  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , at two storage times, namely, immediately after reprocessing and 1000 years of storage, is given in Table 1.

Based on Table 1, it is possible to make the following conclusions.

(1) The existing system of the radiochemical reprocessing of spent fuel implies very high HLRW specific activities, which are predominantly determined by  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  fission products and americium and curium radionuclides. For this reason, the United States stopped the reprocessing of spent fuel in the mid-1980s. The European Union posed the problem of creating a technological process providing the separation of minor actinides, such as neptunium, americium, and curium (see, e.g., [6]).

(2) The concentration of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  is governed by their half-lives and burnups. At present, the decay of these radionuclides to a safe level requires nearly 600–650 years.

(3) It is necessary to reduce the amount of americium and curium in HLRWs to an admissible level.

The scheme of the reprocessing of spent fuel with the extraction of americium and curium is shown in Fig. 2. When analyzing Fig. 1, it is necessary to take into account the properties of the major americium and curium radionuclides formed in a nuclear reactor (Table 2).

It can be seen from Table 2 that americium and curium solutions develop a great amount of heat, and the heat emission of curium is more than ten times higher than the heat emission of americium (the content of  $^{242m}\text{Am}$  in the sum of radionuclides is small).

In the conventional regime of the radiochemical reprocessing of spent fuel (Fig. 1), the radiolysis of the aqueous phase predominates, whereas the radiolysis of

the organic phase is relatively negligible. However, when using the scheme shown in Fig. 2, it is necessary to take into account the radiolysis of the organic phase in some cases. The process includes the following stages:

(1) the separation of a mixture of rare-earth elements (fission products), americium, and curium from the aqueous phase of the extraction process;

(2) the extraction separation of americium and curium from rare-earth elements.

Here, there are the two possible variants: (1) the coextraction of americium and curium and (2) the extraction of americium only, whereas curium remains in the aqueous phase. The latter process was called EXAm [7] to denote the extraction of americium only and based on the difference between the heat emissions of americium and curium as can clearly be seen from Table 2. The specifics of americium and curium extraction processes due to radiolysis will not further be considered in this work.

## REPROCESSING OF THE ORGANIC PHASE

Extraction reprocessing is currently performed using centrifugal extractors to eliminate the radiolysis of TBP. 30-% TBP solutions in a hydrocarbon diluent are used. The initial concentration of TBP is nearly 1 mol/L. This means that the maximum concentration of uranyl nitrate will be less than 0.5 mol/L, and the concentration of plutonium nitrate depends on the composition of an initial fuel. Initially, the concentration was nearly 1% of that of uranium [1]; however, it grows with increasing burnup and may amount to several grams per liter during the reprocessing of sodium-cooled fast reactor fuels. Then the organic phase may

Table 1. Radiation hazard of the HLRW radionuclides in Sv/(t U) (reprocessing of fuel after 5-year storage)

Time	U	Np	Pu	Am	Cm	$^{90}\text{Sr}$	$^{137}\text{Cs}$
Immediately after reprocessing	0.409	6.40	10990	$2.87 \times 10^6$	$5.95 \times 10^6$	$9.2 \times 10^7$	$5.2 \times 10^7$
In 1000 years	0.391	6.47	2885	$1.36 \times 10^6$	$3.28 \times 10^4$	0	0

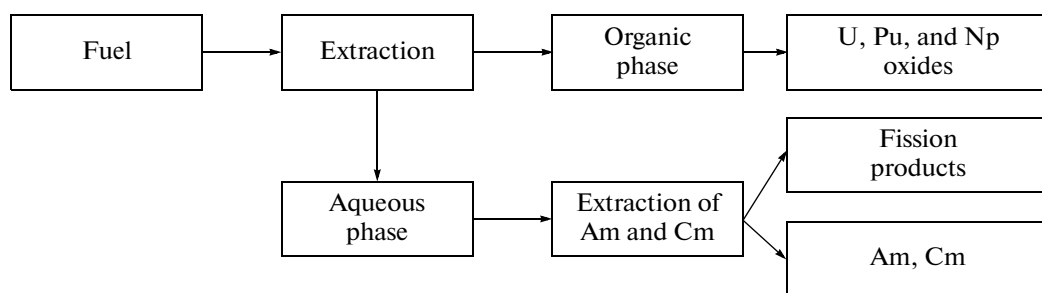


Fig. 2. Scheme for reprocessing of spent fuel with the extraction of americium and curium.

be considered as the senary  $\text{H}_2\text{O}-\text{HNO}_3-\text{UO}_2(\text{NO}_3)_2-\text{Pu}(\text{NO}_3)_4-\text{TBP}-\text{diluent}$  system. However, the quinary  $\text{H}_2\text{O}-\text{HNO}_3-\text{UO}_2(\text{NO}_3)_2-\text{TBP}-\text{diluent}$  should be taken as a basis because of the small content of plutonium in this system, and the effect of plutonium on the equilibrium may be taken into account with empirical equations as in work [8].

#### THERMODYNAMIC DESCRIPTION OF THE $\text{H}_2\text{O}-\text{HNO}_3-\text{UO}_2(\text{NO}_3)_2-\text{TBP}-$ DILUENT SYSTEM

The principles of the description of a quinary system are given in [9] and include the three principal points:

- (1) The major system is divided into subsystems that are described separately.
- (2) Each subsystem is described using molar fractions and rational activity coefficients.
- (3) The equilibrium between solution components is described using the mass law and the equations relating the activity coefficients.

The thermodynamic functions are calculated using the molar fractions  $x_i$  and the rational activity coefficients  $f_i = a_i/x_i$ , where  $a_i$  is the thermodynamic activity. The differences between the rational activity coefficients  $f_i$ , the molar activity coefficients  $y_i$  ( $y_i = a_{im}/c_i$ , where  $c_i$  is the molar concentration of the  $i$ th compo-

nent, and  $a_{im}$  is the thermodynamic activity in terms of molar concentrations), and the molal activity coefficients  $\gamma_i$  ( $\gamma_i = a_{im}/m_i$ , where  $m_i$  is the molality of the  $i$ th component, and  $a_{im}$  is the thermodynamic activity in terms of molal concentrations) are illustrated by Table 3 using the  $\text{H}_2\text{O}-\text{TBP}$  system [10] as an example.

It can be seen from Table 3 that the rational activity coefficients of TBP ( $f_t$ ) and water ( $f_w$ ) are close to 1, whereas the molar and molal activity coefficients considerably differ from 1 at high water concentrations. The reason for this divergence is the difference between the molar volumes of TBP ( $V_t = 273.9 \text{ cm}^3/\text{mol}$ ) and water ( $V_w = 17.1 \text{ cm}^3/\text{mol}$ ). As a result, it becomes impossible to use the molar and molal activity coefficients. On the other hand, when calculating the equilibrium, it is also reasonable to use the volumetric fractions  $\varphi_i$  that were originally proposed by A. M. Rosen [11] and determined as

$$\varphi_i = V_i x_i / \sum V_j x_j. \quad (1)$$

alongside the molar fractions  $x_i$ .

The basic expression for the calculation of activities is the Gibbs–Duhem equation

$$x_i d \ln a_i + \sum x_j d \ln a_j = 0. \quad (2)$$

The following equation holds true in all cases:

$$x_i d \ln x_i + \sum x_j d \ln x_j = 0. \quad (3)$$

Table 2. Some properties of major americium and curium radionuclides

Radionuclide	$T_{1/2}$ , years	Concentration, g/(t U) [1]	Decay type	Decay product	Heat emission, W/g
$^{241}\text{Am}$	432.2	269	$\alpha$	$^{237}\text{Np}$	0.111
$^{242m}\text{Am}$	152	0.64	IT (>99.5%) $\alpha$ (<0.5%), $\beta$	$^{242}\text{Am}$ $^{238}\text{Pu}$	0.301
$^{243}\text{Am}$	7380	49	$\alpha$ , $\beta$	$^{239}\text{Pu}$	0.0062
$^{243}\text{Cm}$	28.5	0.34	$\alpha$	$^{239}\text{Pu}$	1.73
$^{244}\text{Cm}$	18.1	16.3	$\alpha$	$^{240}\text{Pu}$	2.78

**Table 3.** H<sub>2</sub>O–TBP system

No.	$a_w$ [10]	$c_t$ [10], mol/L	$c_w$ [10], mol/L	$f_t$	$f_w$	$y_t$	$y_w$	$g_w$
1	0.11	3.638	0.2	0.999	1.012	0.951	0.932	0.929
2	0.224	3.623	0.439	1.000	0.992	0.899	0.865	0.857
3	0.33	3.607	0.682	0.999	0.993	0.850	0.820	0.808
4	0.427	3.592	0.967	1.008	0.959	0.806	0.748	0.731
5	0.5	3.579	1.15	1.005	0.976	0.774	0.737	0.714
6	0.529	3.573	1.199	0.996	1.008	0.762	0.748	0.731
7	0.618	3.555	1.484	0.997	1.002	0.722	0.706	0.684
8	0.8	3.508	2.173	0.998	1.002	0.642	0.624	0.599
9	0.842	3.494	2.436	0.997	1.002	0.623	0.586	0.580
10	0.902	3.473	2.778	1.020	0.970	0.595	0.550	0.521

Another form of the Gibbs–Duhem equation

$$x_i d \ln f_i + \sum x_j d \ln f_j = 0, \quad (4)$$

is obtained by substituting Eq. (3) into Eq. (2).

The objective of the mathematical modeling of the system is to calculate the activity or activity coefficients of components from the activities or activity coefficients of other components. To accomplish this, it is possible to use cross relationships. For example, the change in the activity or activity coefficients of some components upon the addition of water can be determined using the equation

$$(\partial \ln a_i / \partial m_j)_{m_i, m_k} = (\partial \ln a_j / \partial m_i)_{m_j, m_k} \quad (5)$$

or

$$(\partial \ln f_i / \partial m_j)_{m_i, m_k} = (\partial \ln f_j / \partial m_i)_{m_j, m_k}, \quad (6)$$

where the first derivative is calculated at  $m_i = \text{const}$  and  $m_k = \text{const}$ .

Using these principles, we have studied the systems H<sub>2</sub>O–TBP and H<sub>2</sub>O–TBP–diluent [12], H<sub>2</sub>O–HNO<sub>3</sub>–TBP [13], H<sub>2</sub>O–HNO<sub>3</sub>–TBP–dodecane [14, 15], and H<sub>2</sub>O–UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>–TBP [9, 16]. It should be noted that two variants were used to calculate the H<sub>2</sub>O–HNO<sub>3</sub>–TBP–dodecane and H<sub>2</sub>O–

UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>–TBP systems due to some problems estimating the error in the constants. The major problem is to create a substantiated calculation model suitable for estimating molar concentrations in the organic phase under different conditions.

Some calculation results are given in Table 4. Here,  $s_i$  is the relative root-mean-square deviation of experimental data, and  $\delta_i$  is the relative root-mean-square deviation of calculated data from experiment. Since the TBP concentration is determined from the density and the difference of concentrations,  $s_t$  is omitted in Table 4.

## CONCLUSIONS

The performed studies have resulted in substantiating the possibility of modeling the extraction (TBP based) reprocessing of spent nuclear reactor fuels with the use of thermodynamic calculations. A mathematical technique for the calculation of the molar concentrations of components has been developed. The calculations of two ternary mixtures and one quaternary mixture have been performed. The major problem in calculations is the creation of a substantiated model for optimizing the used constants.

## NOTATION

$a$ —thermodynamic activity;  
 $c$ —molar concentration;  
 $f$ —rational activity coefficient;  
 $m$ —molality;  
 $n$ —number of experimental points;  
 $s$ —relative root-mean-square deviation of experimental data;  
 $V$ —molar volume;  
 $x$ —molar fraction;  
 $y$ —molar activity coefficient;

**Table 4.** Principal results of estimating the deviations of calculated data from experiment

System	$n$	Component	$s_i$	$\delta_i$
H <sub>2</sub> O–HNO <sub>3</sub> –TBP	31	H <sub>2</sub> O	0.030	0.022
		HNO <sub>3</sub>	0.012	0.023
		TBP	—	0.0036
H <sub>2</sub> O–UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> –TBP	27	H <sub>2</sub> O	0.066	0.074
		UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	0.070	0.061
H <sub>2</sub> O–HNO <sub>3</sub> –TBP– $n$ -dodecane	94	HNO <sub>3</sub>	0.025	0.041
		TBP	—	0.072

$\gamma$ —molal activity coefficient;  
 $\delta$ —relative root-mean-square deviation of calculated data from experiment;  
 $\Sigma$ —summation symbol in calculations;  
 $\varphi$ —volumetric fraction.

### SUBSCRIPTS AND SUPERSSCRIPTS

$c$ —thermodynamic parameters in terms of molar concentrations;  
 $i, j, k$ —components listed in formulas;  
 $m$ —thermodynamic parameters in terms of molal concentrations;  
 $t$ —TBP;  
 $w$ —water.

### REFERENCES

- Zelenkov, A.G., Pirozhkov, S.V., Pchelina, V.A., Rodionov, Yu.F., Tarasevich, V.P., Sinyutina, Z.M., Chistyakov, L.V., Shatinskii, V.M., Shvetsov, I.K., Shubko, V.M., and Baranov, S.A., Complete analysis of spent fuel from power stations with VVER-440 reactors, *Sov. At. Energy*, 1981, vol. 51, no. 1, p. 471.
- Glagolenko, Yu.V., Dzekun, E.G., Rovnyi, S.I., Sazhnov, V.K., Ufimtsev, V.P., Broshevitskii, V.S., Laptev, G.A., Osnovin, V.I., Zakharkin, B.S., Smelov, V.S., and Nikipelov, B.V., Utilization of spent nuclear fuel on the RT-1 complex, *Vopr. Radiat. Bezop.*, 1997, no. 2, p. 3.
- Zilberman, B.Ya., Application of Purex process to highly burned-up NPP fuel in closed nuclear fuel cycle from the viewpoint of long-lived radionuclide localization, *Radiochemistry*, 2000, vol. 42, no. 1, p. 1.
- Babaev, N.S., Merkushev, A.O., Ochkin, A.V., and Rovnyi, S.I., Calculation of the time for establishing radiation equivalence of high-level wastes, *At. Energy*, 2005, vol. 98, no. 2, p. 115.
- International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources*, Safety Series, no. 115, Vienna: International Atomic Energy Agency, 1997.
- Poinsot, C., Rostaing, C., Grandjean, S., and Boullis, B., Recycling the actinides, the cornerstone of any sustainable nuclear fuel cycles, *Proc. Chem.*, 2012, vol. 7, p. 349.
- Rostaing, C., Poinsot, C., Warin, D., Baron, P., and Lorrain, B., Development and validation of EXAm separation process for single am recycling, *Proc. Chem.*, 2012, vol. 7, p. 367.
- Zil'berman, B.Ya., Fedorov, Yu.S., Puzikov, E.A., and Blazheva, I.V., Creation of a database and adaptation of a Purex process mathematical model for utilization of highly burned-up spent nuclear fuel from nuclear power stations, *Preprint of Radium Inst.*, St. Petersburg, 2009, no. 264.
- Ochkin, A., Gladilov, D., and Nechaevskiy, S., Optimization of solvent extraction reprocessing using mathematical modeling, *Proc. Chem.*, 2012, vol. 7, p. 315.
- Roddy, J.W. and Mrochek, J., Activities and interaction in the tri-*n*-butyl phosphate–water system, *J. Inorg. Nucl. Chem.*, 1966, vol. 28, no. 11, p. 3019.
- Rozen, A.M., Khorkhorina, L.P., Agashkina, G.D., Teterin, E.G., Mal'tseva, A.N., and Voronetskaya, E.V., Extraction of water with tributyl phosphate and tributyl phosphate solutions in diluents, *Radiokhimiya*, 1970, vol. 12, no. 2, p. 345.
- Gladilov, D.Yu., Nekhaevskii, S.Yu., and Ochkin, A.V., A thermodynamic description of the distribution of water in H<sub>2</sub>O–tributyl phosphate and H<sub>2</sub>O–tributyl phosphate–solvent systems, *Russ. J. Phys. Chem.*, 2006, vol. 80, no. 12, p. 1934.
- Ochkin, A.V., Gladilov, D.Yu., and Nechaevskiy, S.Yu., Calculation of the composition of the organic phase of the H<sub>2</sub>O–HNO<sub>3</sub>–tri-*n*-butylphosphate system, *Russ. J. Phys. Chem.*, 2009, vol. 83, no. 10, p. 1803.
- Ochkin, A.V., Afonina, M.A., Merkushev, A.O., and Nechaevskiy, S.Yu., Extraction of nitric acid by tributyl phosphate solution in *n*-dodecane, *Russ. J. Phys. Chem.*, 2010, vol. 84, no. 9, p. 1526.
- Ochkin, A., Afonina, M., Merkushev, A., and Nechaevskiy, S., Nitric acid extraction with TBP solutions in *n*-dodecane, *Proc. 19th Int. Solvent Extraction Conf. (ISEC 2011)*, Santiago, 2011, p. 168.
- Ochkin, A., Gladilov, D., and Nechaevskiy, S., Calculation of organic phase composition of H<sub>2</sub>O–UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>–TBP system, *Proc. 19th Int. Solvent Extraction Conf. (ISEC 2011)*, Santiago, 2011, p. 131.

Translated by E. Glushachenkova