

Chemical Forms and Distribution of Platinum Group Metals
and Technetium During Spent Fuel Reprocessing

Y. Pokhitonov

V.G. Khlopin Radium Institute, 28, 2nd Murinskiy Prospekt, St. Petersburg, Russia

ABSTRACT

Amongst the fission products present in spent nuclear fuel of Nuclear Power Plants there are considerable quantities of platinum group metals (PGMs): ruthenium, rhodium and palladium. At the same time there are considerable amounts of technetium in the spent fuel, the problem of its removal at radiochemical plants being in operation encountering serious difficulties. Increased interest in this radionuclide is due not only to its rather large yield, but to higher mobility in the environment as well. However, the peculiarities of technetium chemistry in nitric acid solutions create certain problems when trying to separate it as a single product in the course of NPP's spent fuel reprocessing.

The object of this work was to conduct a comprehensive analysis of platinum group metals and technetium behavior at various stages of spent fuel reprocessing and to seek the decisions which could make it possible to separate its as a single product.

The paper will report data on platinum metals (PGM) and technetium distribution in spent fuel reprocessing products.

The description of various techniques for palladium recovery from differing in composition radioactive solutions arising from reprocessing is given.

INTRODUCTION

The principal purpose of spent fuel reprocessing consists in the recovery of the uranium and plutonium and the separation of fission products so as to allow re-use of fissile isotopes and facilitate disposal of waste elements.

At the same time, a fair quantity of palladium and rhodium presents in spent fuel, but the problem of these elements recovery has not yet been decided at the operating radiochemical plants.

It should be noted the stable trend for increasing of the existing NPP power, it is possible to affirm that the quantities of palladium to be accumulated to the middle of the century will be comparable with those of the natural sources. The mentioned fact allows consider spent nuclear fuel generated at NPPs as a potential source for creation of a strategic stock of platinum group metals. Because of a number of reasons of technical and economical nature, the problem of palladium and rhodium recovery from the spent fuel is rather complicated one.

As for technetium, interest in this radionuclide is connected not only to its rather large yield, but to higher mobility in the environment as well. However, the peculiarities of technetium chemistry in nitric acid solutions create certain problems when trying to separate it as a single product in the course of NPP's spent fuel reprocessing.

In this section we tried to trace the peculiar properties of platinum group metals and technetium chemical behavior, which imports the choice of the most suitable composition of solution and accordingly the choice of separation technique during spent fuel reprocessing. To our mind the comprehension of these questions is of importance so products of reprocessing differing both by their specific activity and by the content of palladium and technetium.

The analysis of spent fuel various types, which were carried out at micron level, and the data for insoluble residues composition provide a sufficiently good knowledge of fission product chemical state [1 - 5].

When analyzing the chemical species of fission products occurring in spent fuel, all fission elements are generally classified in four categories including the following radioactive and stable nuclides:

- Gaseous (volatile) fission products: Kr, Xe, Br, I;
- Elements generating metal inclusions: Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sb, Te;
- Fission products forming oxide inclusions: Rb, Cs, Ba, Zr, Nb, Mo, Te;
- Fission products dissolved as oxides in fuel matrix: Sr, Zr, Nb and rare-earth elements.

In the course of fuel irradiation in reactor a constant transition of separate elements between the last three fission product groups occurs due to their limited solubility in fuel matrix [2], which changes, naturally, the fission product chemical state in irradiated fuel and affects their behavior at subsequent stages of fuel cycle.

The analysis of the spent fuel issued from reactors demonstrate that palladium presents in irradiated fuel in the form of intermetallic inclusions, forming an independent phase [1,6]. So, intermetallic compounds of rhodium and palladium with actinides ($U_{1-x}Pu_x$)($Rh_{1-y}Pd_y$) and (U_xPu_{1-x})(Rh_yPd_{1-y}) with the structure of $AuCu_3$ type were found in irradiated fuel.

Compounds of palladium in the form of Pd-Ag-Cd and Pd-Sn-Sb-Te were detected; in the latter one two phases were found with the following composition (mass. %): Pd – 81; Sb – 2; Te – 8 and Pd – 69; Sn – 3; Sb – 4; Te – 24. In central cavity and on the surface of fuel rods the compounds of $Pd(Pd,In,Sn,Te)_{3-x}$ type were detected.

In [4] the relationships between the composition of insoluble residues and their amounts are shown for LWR fuel with the burnup from 7 to 39 MWd/kg U.

Obtained results have shown that within the burnup range 7-30 MWd/kg U the amount of insoluble residues is nearly linearly dependent on the burnup. When fuel burnup exceeds 30 MWd/kg U the amount of insoluble residues grows more rapidly.

The results of the analysis of insoluble residues remaining after dissolution of VVER-1000 fuel with the burnup from 15 to 54 MWd/kg U are presented [5].

The main factors, determining the composition and amount of insoluble residues resulted from fuel reprocessing are the degree of fuel burnup and the conditions of the dissolution.

The burnup growth from 15 to 54 MW*day/kg U has led to residue mass increase by a factor 10 (0.027 and 0.37% respectively).

It is shown, that spent fuel dissolution conditions can affect the palladium distribution between solution and insoluble precipitates. Others important factors, which determine the composition and the yield of residues resulting from fuel dissolution, are the temperature and acid concentration [5].

It is necessary to note in the case of the adequate selection of fuel dissolution process parameters would make it possible to realize the conditions for maximal PGM separation in the form of insoluble residues with the purpose of their subsequent recovery. (The problem of subsequent PGM recovery from these residues seems rather complicated. Nevertheless, the feasibility of proper process is not to be denied and to our mind it is worthy of special studies.)

At the same time the technetium content in the insoluble residues is much lower in comparison with Ru and Rh. A noticeable amount of technetium (0.8 –4.7%) has been found in the spent fuel of high burnup (41 – 43 MWd /kg U). And after dissolution of the spent fuel in a

nitric acid the main part of technetium passes in a solution together with uranium to the first cycle of extraction.

Apparently, a careful selection of fuel dissolution process parameters would make it possible to direct the main part of palladium to the 1st cycle raffinate together with the other fission products. Extraction behaviour of palladium in the system "tributylphosphate-nitric acid" is studied quite extensively. It is known that palladium is extracted by 100 % TBP from nitric acid 0,1-1,0 mol/l, the distribution coefficients being 0,6-1,0, while from nitric acid 4 mol/l the extraction practically doesn't occur. Hence, at the stage of extraction recovery and separation of uranium and plutonium (Purex-process) only minor amount of palladium transfers in organic phase and the major part of this element remains in the raffinate.

A special feature of palladium behaviour during extraction doesn't let us complete here this part of our presentation. The matter concerns the processes of sludging which, generally, starts at the interface of aqueous and organic phases.

Even though palladium is not to be extracted by organic phase, one should take into account concurrent phenomena, which are due to the occurrence of various impurities in real industrial solutions. Particularly, this phenomenon may be responsible for palladium presence at the stage of reductive reextraction of plutonium and its reduction to metal, so resulting in the generation of interfacial precipitates and suspensions. The generation of precipitates and interfacial films not only worsens the quality of uranium and plutonium purification but also hampers the equipment operation. The generation of interfacial films is caused not only by finely dispersed slightly soluble compounds arising at fuel dissolution stage, but also by slightly soluble compounds with products of extractant destruction, for example, with monobutyl- and dibutylphosphoric acids [7]. Silica acid is another component participating actively in the formation of interfacial films. Each of these compounds, owing to important surface activity, contributes to generation of stabilized emulsions and interfacial precipitates. The amount of these species is associated with ionization load acting upon the extractant, which determines the level of extractant degradation and, consequently compounds. To reduce the adverse effect of precipitate formation on extraction formation, the amount of precipitated phosphorous-containing process, it is necessary to provide a careful clarification of fuel solution.

Thus, it may be concluded that when using conventional Purex-process, the major part of palladium remains in the raffinate of the I extraction cycle and a minor part is involved with the residues arising within the unit of fuel dissolution.

At the same time when reprocessing NPP's spent fuels an essential role is played by both extraction interaction of technetium with Zr, U, Pu and redox reactions with actinides being in the lowest state of oxidation as well as with hydrazine in the course of plutonium reductive reextraction.

In the authors' opinion, the development of an efficient technology for palladium and technetium recovery requires the conception of a suitable flow-sheet and the choice of optimal regimes of "reactor" palladium recovery concurrently with the resolution of the problem of HLW partitioning when using the same facilities.

The technology of HLW partitioning, which is being developed in recent years, provides a precondition for the use of an alternative source for platinum group metals and technetium recovery: the solutions resulted from this operation which are lesser active and lesser complicated as compared with the raffinates of the I extraction cycle, comprising the total sum of fission products.

RESULTS OF EXPERIMENTS AND DISCUSSION

In this section we tried to present some examples of process flowsheet, suitable for palladium recovery from spent fuel.

According our opinion as the first stage of such flowsheet in any case should be partitioning technology of HLW. (It should be noted also this approach ought to adhere when we say about technetium recovery.)

The results of the experiments on sorption palladium recovery.

Reasoning from the results of our preliminary studies, it was suggested to use anion-exchanger VP1-AP for palladium recovery from real high-level solutions, operation conditions being as follow:

Nitric acid concentration in initial solution: 2.5 – 3.5 mole/l.

The sorption is to be performed at ambient temperature, contact time being no less than 30 minutes. The exchanger flushing is carried out by two column volumes of 3 mole/l nitric acid. The desorption is performed with 0.1 mole/l solution of DTPA in 3.0 mole/l nitric acid at 60°C, contact time being 30 minutes again.

A high-level solution resulted from the processing of the spent fuel was used in this work. (Palladium concentration 115 mg/l, total beta-activity 3.15×10^{10} Bq/l).

Working volume of the sorption column was 25 cm³.

Experimental conditions and the results of solution analysis are shown in Table I.

Table I. Experimental conditions for palladium extraction on anion-exchanger VP1-AP.

Volume of the solution passed through the column, l	Pd, concentration, mg/l	Total beta-activity, Bq/l	Notes
0,8	41	$28,3 \cdot 10^9$	Initial solution. Solution flow rate – 150 ml/h.
1,5	116	$33,6 \cdot 10^9$	Initial solution
2.0	114	$33,7 \cdot 10^9$	Initial solution
0,15			Washing by nitric acid, 3 mole/l
0,3	690	$59,2 \cdot 10^7$	Desorbate: 0,1 mole/l solution of DETA in 3,0 mole/l nitric acid

These operations sorption-desorption made it possible to achieve the purification from beta-active radionuclides as high as 3×10^2 , palladium extraction ratio being 88.6%.

Resulted solution of palladium nitrate was subjected to additional purification by means of precipitating technique. Carbon monoxide was used as the reactant. The operation of platinum black deposition allowed us to get an extra purification from the most of radionuclides. In Table II the purification factors (total and for separate operations) are presented.

Table II. The palladium purification factors after sorption-desorption and platinum black precipitating.

Total activity, Bq/l	Spectrum analysis					
	Am-241	Ru-106	Sb-125	Eu-154	Cs-137	Ce-144
Activity of initial solution, Bq/mg Pd						
$2,74 \cdot 10^8$	$8,6 \cdot 10^7$	$1,4 \cdot 10^7$	$1,4 \cdot 10^7$	$1,2 \cdot 10^8$	$1,4 \cdot 10^6$	$8,3 \cdot 10^6$
Activity of desorbate of palladium after sorption, Bq/mg Pd						
$8,6 \cdot 10^5$	$1,9 \cdot 10^5$	$4,2 \cdot 10^5$	$1,3 \cdot 10^4$	$1,3 \cdot 10^5$	$1,8 \cdot 10^4$	$4,5 \cdot 10^4$
<i>Decontamination ratio after sorption</i>						
$3,19 \cdot 10^2$	$4,5 \cdot 10^2$	$3,3 \cdot 10^1$	$1,05 \cdot 10^3$	$9,2 \cdot 10^2$	$0,8 \cdot 10^2$	$1,85 \cdot 10^2$
Activity, Bq/mg Pd, after precipitating Pd						
$1,43 \cdot 10^4$	$0,3 \cdot 10^2$	$1,4 \cdot 10^4$	$0,7 \cdot 10^2$	$0,2 \cdot 10^2$	$0,3 \cdot 10^2$	$0,2 \cdot 10^2$
<i>Decontamination ratio after precipitating Pd</i>						
$6,0 \cdot 10^1$	$6,0 \cdot 10^4$	$3,0 \cdot 10^1$	$1,8 \cdot 10^2$	$6,0 \cdot 10^3$	$6,0 \cdot 10^2$	$2,0 \cdot 10^3$
<i>Decontamination ratio after sorption and precipitating Pd</i>						
$1,9 \cdot 10^4$	$2,9 \cdot 10^6$	$9,8 \cdot 10^2$	$1,9 \cdot 10^5$	$5,8 \cdot 10^6$	$4,8 \cdot 10^4$	$4,2 \cdot 10^5$

After additional purification through precipitating technique the palladium black was produced. The activity of this product didn't exceed 0.8 mCi/1 g Pd, total purification factor being 1.9×10^4 .

The results of the experiments on palladium recovery with using extraction technology

Besides of sorption technique of palladium recovery there is opportunity to use extraction technology to this effect.

In radiochemical literature the HLW partitioning options with the use of different carbamoylphosphine oxides as extractants are now under consideration. TRUEX-process is essentially intended for recovery of transplutonium and rare-earth elements, as well as for additional recovery of U, Pu and Np. The following carbamoyl phosphine oxides have been most extensively studied:

- octyl [phenyl]-N, N-diisobutylcarbamoylmethylphosphine oxide (CMPO-1)
- diphenyl-N, N-dibutylcarbamoylphosphine oxide (CMPO-2)

The following conditions for palladium recovery in TRUEX-process could be proposed [8]: CMPO-2 (0.2 M/l) is used as extractant for combined recovery of Pd, TPE, REE, U and Pu from solutions in the acidity range of 0.1-5.0 M/l. (In TRUEX-process the selective stripping of palladium should precede the stripping of TPE and REE, which in accordance with partitioning flowsheets are directed to solidification without separation.)

A flowsheet including the following operation can be proposed for palladium recovery from high-level waste in spent nuclear fuel reprocessing [8]:

- combined extraction of palladium, actinides and rare-earth elements;
- selective stripping of palladium.

To check the feasibility of this process, the simulated I extraction cycle raffinate of spent fuel reprocessing was prepared and a stand of centrifugal contactors consisting of 24 stages was mounted. (Acidity of this solution was 2.1-2.2 M/l HNO_3).

Palladium black was precipitated from the resultant palladium strip product with its subsequent dissolution.

A bench-test has revealed the principal possibility of using CMPO for palladium recovery and subsequent purification of palladium from most impurities.

The palladium purification factors according the tests results are shown in Table III.

Table III. Purification of palladium from individual elements and its total purification.

Product	Operation	La	Ce	Eu	Fe	Cr	U	Cs	Sr	Ba	Ni	Pb	Total, K _{purific}
Pd concentrate	Extraction	2.2	2.3	1.7	11	470	0.34	770	600	810	510	160	2.9
Solution after black precipitation	Precipitation	230	250	240	2.8	2.2	7.2	20	6.5	8.7	3.0	1.3	100
	Extraction + precipitation	510	580	400	30	1050	2.5	15200	3870	7040	1540	200	290

CONCLUSIONS

As the most favorable feed solutions for platinum metals recovery during spent fuel reprocessing, it's possible to use the solutions formed at the partitioning stage after first extraction cycle. In the framework of the developed TRUEX-process variants, along with TPE, REE, U and Pu recovery, it is also possible to attain the selective Pd recovery.

Basing on partitioning principle once more alternative version of the flowsheet may be proposed composing conjoint removal of Tc and Np during the first cycle followed by their separation by means of ion exchange or extraction technique.

Just on this account the further studies on effective technology of technetium, palladium and other platinum metals recovery should be carried out concurrently with the resolution of HLW partitioning problem.

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