OUTLOOKS OF HLW PARTITIONING TECHNOLOGIES USAGE FOR RECOVERING OF PLATINUM METALS FROM SPENT FUEL

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ABSTRACT

The existing practice of management of high level waste (HLW) generated by NPPs, call for a task of selective separation of the most dangerous long-lived radionuclides with the purpose of their subsequent immobilization and disposal. HLW partitioning allows to reduce substantially the cost of vitrified product storage owing to isolation of the most dangerous radionuclides, such as transplutonium elements (TPE) into separate fractions of small volumes, intended for ultimate storage. By now numerous investigations on partitioning of HLW of various composition have been carried out in many countries and a lot of processes permitting to recover cesium, strontium, TPE and rare earth elements (REE) have been already tested. Apart from enumerated radionuclides, 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. A negative effect of platinum group metals (PGM) occurrence is determined by the formation of separate metal phase, which not only worsens the conditions of glass-melting but also shortens considerably the service life of the equipment. At the same time, the exhaustion of PGMs natural resources may finally lead to such a growth of their costs that the spent nuclear fuel would became a substituting source of these elements industrial production. Allowing above mentioned, it is of interest to develop the technique for "reactor" palladium and rhodium recovery process which would be compatible with HLW partitioning and could be realized using the same facilities. In the report the data on platinum metals distribution in spent fuel reprocessing products and the several flowsheets for palladium separation from HLW are presented.

INTRODUCTION

One of the advantages of closed nuclear fuel cycle is in that it provides the possibility of ultimate resolution for the problem of long-term safe management of long-lived radionuclides. It has been just the reprocessing that enables to separate individual radionuclides (or their fractions) into individual streams with subsequent special approach to each of them. It’s seems reasonable to separate the long-lived radionuclides from the whole HLW bulk and concentrate them within a small volume for subsequent vitrification or immobilization in mineral like matrixes. After that, the remaining part of wastes can be considered as LLW, and, consequently, low-cost technology, as, for example, cementation for surface storage, can be utilized for their management.

Besides the hazardous radionuclides, which deserve more attention (TPE, Sr, Cs etc), spent nuclear fuel contains considerable amounts of platinum metals, which are now not recovered. (It should be noted that in WWER fuel palladium content attains 1.0-1.8 kg/t depending on burnup degree. As to fast reactors with higher fuel burnup values, the palladium content is still higher and comes to even several kilograms per ton). The presence of platinum metals in wastes has an adverse effect on glass melting process and can shorten service life of equipment to a large extent.

At the same time, the depletion mineral platinum metals reserves will sooner or later lead to rise in the cost to the point when their recovery from spent fuel may be economically justified. At present it is difficult to predict all possible fields of application for "reactor" palladium in the future, but one can assume that the use of palladium in radwaste reprocessing technology (for example, J-129, TPE or 3H immobilization) may play a decisive role in forming of demand for this metal. It should be noted that any technical solution for palladium (rhodium) recovery must be fully compatible with the HLW reprocessing methods and must not increase total waste quantity.

Extraction processes fill a special place among various techniques of HLW processing (precipitation, sorption, etc.). The most interesting of numerous proposals related to extraction system composition are those concerning the systems based on neutral oraganophosphorus compounds: alkyl-
phosphine oxides (1-3) or carbamoylphosphine oxides (4-7). These systems are the most studied in respect of their extraction and physico-chemical properties.

The present work is aimed at research of palladium extraction process with the use of extractants based on carbamoylphosphine oxide. For palladium recovery from high-level waste in spent nuclear fuel reprocessing it is proposed a flowsheet which permits to separate palladium from HLW into an individual product or in combination with TPE and REE.

RESULTS AND DISCUSSION

Depending on selected parameters of dissolution process, the palladium and rhodium are distributed between solution coming at extraction processing, and insoluble residue. The most important factor which determines the constitution and the yield of residues resulted from fuel dissolution are the temperature and acid concentration. Residue composition change may, in its turn, result in modification of their specific activity and content of PGMs, uranium and plutonium. (Specific activity of the residues is from 20 to ~ 840 Ci/kg. (8).

Depending on dissolution conditions palladium and rhodium contents in residues are as much as 3 - 20%, and 3 - 50% respectively. Among other fission products, molybdenum and zirconium make the most contribution (8, 9).

Apparently, an adequate selection of fuel dissolution process parameters would make it possible to realize the conditions for maximal PGM (palladium, rhodium) 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.)

Extraction behavior of palladium in the system “tributylphosphate-nitric acid” is studied quite extensively. It is known that palladium is poorly extracted by TBP at the operation of extraction separation and recovery of uranium and plutonium (PUREX process) and the major part of this element remaine in the raffinate. The raffinates of the first extraction cycle containing more then 99 % of fission products belong to the main type of HLW arising from nuclear fuel reprocessing.

The raffinate resulted from the reprocessing of fuels with burnup of 40 MWd/kg U contains about 40 kg of fission products per ton of uranium, including about 6 kg of PGMs, 1.9 kg of this mass being represented by palladium. It should be noted that this amount of palladium is calculated one, and it doesn’t take into account palladium repartition between insoluble residues and eventual losses in the first extraction cycle.

In radiochemical literature the HLW partitioning variants with the use of different carbamoylphosphine oxides as extractants (TRUEX-process) are now under consideration. TRUEX-process is primarily intended for recovery of transplutonium and rare-earth elements, as well as for additional recovery of uranium, plutonium and neptunium. As it has been already noted in the Introduction, the following carbamoyl phosphine oxides are most extensively studied:

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

As diluents one can use light diluent with addition of solution solubilizers (like TBP) and heavy polar diluents (metanitrobenzotrifluorode (F-3), for instance), which do not need special additions for better solubility of extractant.

In our work F-3 was used as diluent for carbamoylphosphine oxides. Extractant concentration (0.2 and 0.1 M/l) was selected in the basis of practical use of different TRUEX-process versions.

Palladium content in aqueous solutions was determined by photometry of palladium-thiourea complex.

Palladium distribution coefficients (Kd) between organic and aqueous phases were calculated in accordance with the following expression:

\[
Kd = \frac{(C_{aq.}^{aq.} - C_{equil.}^{aq.}) \cdot V^o}{C_{equil.}^{aq.} \cdot V_{org.} \cdot V^o} \quad \text{(Eq. 1)}
\]
Analysis of some products for impurity content was carried out by Plasma-induced mass-spectrometry with ICP MS VG Plasma Quad instrument.

First of all, we studied the dependence of palladium extraction on solution acidity for extractant based on COMP-1 and CMPO-2 (Table I).

<table>
<thead>
<tr>
<th>CMPO-1</th>
<th>C HNO$_3$ , M/l</th>
<th>0.1</th>
<th>0.5</th>
<th>2.0</th>
<th>4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M/l CMPO-1</td>
<td>Kd Pd</td>
<td>0.84</td>
<td>0.76</td>
<td>0.14</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>0.2 M/l CMPO-1</td>
<td>Kd Pd</td>
<td>2.1</td>
<td>2.5</td>
<td>0.46</td>
<td>0.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CMPO-2</th>
<th>C HNO$_3$ , M/l</th>
<th>0.1</th>
<th>0.5</th>
<th>2.0</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M/l CMPO-2</td>
<td>Kd Pd</td>
<td>1.5</td>
<td>0.76</td>
<td>0.62</td>
<td>0.44</td>
</tr>
<tr>
<td>0.2 M/l CMPO-2</td>
<td>Kd Pd</td>
<td>3.6</td>
<td>2.2</td>
<td>1.9</td>
<td>0.8</td>
</tr>
</tbody>
</table>

It follows from comparison of the obtained data that CMPO-1 extractant at acidities 2 M/l and higher cannot be used for palladium recovery, while CMPO-2 allows to use it up to concentration of 5 M HNO$_3$.

In experiments on extraction of trivalent TPE and REE by neutral organophosphorus extractants a salting-out effect was observed in presence of non-extractable nitrates and it was further used for practical purposes. This effect is most pronounced at low acidities of the solution; then it decreases with growth of acid concentration and, as a rule, transfers into an antisalting-out effect. It follows from the data given in Table II that in the case of palladium extraction the salting-out process proceeds very weakly or does not practically occur.

<table>
<thead>
<tr>
<th>C NaNO$_3$ , M/l</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M/l HNO$_3$</td>
<td>1.50</td>
<td>1.68</td>
<td>1.74</td>
<td>1.80</td>
</tr>
<tr>
<td>0.5 M/l HNO$_3$</td>
<td>0.65</td>
<td>0.57</td>
<td>0.40</td>
<td>0.34</td>
</tr>
<tr>
<td>2.0 M/l HNO$_3$</td>
<td>0.20</td>
<td>0.26</td>
<td>0.35</td>
<td>0.36</td>
</tr>
</tbody>
</table>

To elucidate the palladium extraction mechanism, a set of tests was conducted with diphenyl-N,N-dibutilcarbamoilphosphine oxide extractant in F-3 diluent.

The dependence of palladium distribution coefficients (K$_D$) on extractant concentration at different concentration of HNO$_3$ was investigated. Results are presented on Fig. 1 as a logarithmic dependence lg(K$_D$) – lg(C$_{extractant}$). (Slope angle tangent of straight line (linerlized) of logarithmic dependence lg(K$_D$) – lg(C$_{extractant}$) is a value of solvate number.)

From the results obtained one can draw a conclusion that the solvate number depends on the acidity of aqueous solution and changes almost twofold in the studied ranges of CMPO and HNO$_3$ concentrations (from 0.76 for 2 M/l HNO$_3$ to 1.6 for 0.5 M/l HNO$_3$). The change of apparent solvate number may be caused by changing both H$^+$-ion and NO$_3^-$ ion concentrations.

In order to reveal the effect degree of each factor, several test series were performed for determining the dependence of palladium distribution coefficients on extractant concentration at various concentrations of sodium nitrate (0.2 M/l) for two fixed HNO$_3$ concentrations (0.25 and 0.5 M/l). The obtained data and the processing results are presented on Figures 2 and 3.
Fig. 1. Plots of logarithmic dependence between $K_D$ Pd and CMPO concentration at various HNO$_3$ concentrations.

Fig. 2. Plots of logarithmic dependence between $K_D$ Pd and CMPO concentration at various concentrations of sodium nitrate (0.25 M HNO$_3$).
Analysis of the obtained data allows to make the following conclusions:

at lower concentration of HNO$_3$ (0.25 M/l) the effect of nitrate on apparent solvate number is less marked than in the case of higher concentration (0.5 M/l);

sodium nitrate suppresses palladium extraction even at minor concentrations of HNO$_3$.

The limiting capacity of extractant corresponds to the formula of Me(NO$_3$)$_3$·3S, where S is a molecule of extractant. Such high capacity permits to reprocess practically all solutions up to evaporated raffinates of I extraction cycle.

Reasoning from the results obtained, the following conditions for palladium recovery in TRUEX-process could be proposed:

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 variant of selective stripping with complexone is used for palladium recovery.

**Stand testing of palladium extraction process.**

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

combined extraction of palladium, actinides and rare-earth elements;
extract washing;
selective stripping of palladium;
washing of palladium strip product with extractant;
combined stripping of TPE and REE;
washing (regeneration) of recycle extractant.

Block-diagram of the process is shown on Fig. 4.

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. Tables III and IV present the data on analysis of extraction flowsheet products and analysis of solution resulting from dissolution of precipitated palladium black, as well as the obtained palladium purification coefficients.
The performed test has revealed the principal possibility of using CMPO for palladium recovery from raffinates arising from spent nuclear fuel reprocessing and subsequent purification of palladium from most impurities. (Inadequate recovery degree of palladium in this test, as well as moderate purification of tit from REE at the stage of selective stripping can be easily corrected by changing the stage number and the stream ratio at the appropriate process stages).

Table III. Distribution of elements over process products.

<table>
<thead>
<tr>
<th>Product</th>
<th>Concentration, mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd</td>
</tr>
<tr>
<td>Initial solution</td>
<td>136</td>
</tr>
<tr>
<td>Raffinate</td>
<td>11</td>
</tr>
<tr>
<td>Pd concentrate</td>
<td>396</td>
</tr>
<tr>
<td>REE concentrate</td>
<td>1.5</td>
</tr>
<tr>
<td>Solution after black precipitation</td>
<td>1090</td>
</tr>
</tbody>
</table>
Table IV. Purification of palladium from individual elements and its total purification.

<table>
<thead>
<tr>
<th>Product</th>
<th>Operation</th>
<th>La</th>
<th>Ce</th>
<th>Eu</th>
<th>Fe</th>
<th>Cr</th>
<th>U</th>
<th>Cs</th>
<th>Sr</th>
<th>Ba</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Total, K_{purific}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd concentrate</td>
<td>Extraction</td>
<td>2.2</td>
<td>2.3</td>
<td>1.7</td>
<td>11</td>
<td>470</td>
<td>0.34</td>
<td>770</td>
<td>600</td>
<td>810</td>
<td>540</td>
<td>510</td>
<td>160</td>
<td>2.9</td>
</tr>
<tr>
<td>Solution after black precipitation</td>
<td>Precipitation</td>
<td>230</td>
<td>250</td>
<td>240</td>
<td>2.8</td>
<td>2.2</td>
<td>7.2</td>
<td>20</td>
<td>6.5</td>
<td>8.7</td>
<td>2.5</td>
<td>3.0</td>
<td>1.3</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Extraction + precipitation</td>
<td>510</td>
<td>580</td>
<td>400</td>
<td>30</td>
<td>1050</td>
<td>2.5</td>
<td>15200</td>
<td>3870</td>
<td>7040</td>
<td>1340</td>
<td>1540</td>
<td>200</td>
<td>290</td>
</tr>
</tbody>
</table>

CONCLUSION

Origination of the demand for "reactor platinum group metals (palladium and rhodium) should be expected not earlier than after 30-40 years, when the possibility for reprocessing (or wastes arising from reprocessing) of fuel with rather prolonged cooling. On the other hand, in order to maintain the feasibility of using the spent fuel as platinum metals source in the future, provision should be made even now for recovering and storing the concentrate of these metals before originating the real and stable demand for them. Therefore, in existing (or being under development) flowsheets it is necessary to envisage the operations of Rh-Pd concentrate recovery for its storage and further separation of individual metals.

In our opinion, the single direction in developing an efficient Pd recovery process is concerned with elaboration of a flowsheet and optimal conditions for the "reactor" Pd (Rh) recovery with simultaneous resolution of HLW partitioning problems.

On the basis of the performed work the following conclusions can be drawn:

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 into an individual product.

Pd recovery in TRUEX-process requires to adjust the composition of initial solution, i.e. decrease of acidity to 2 M/l or less.

Feasibility of Pd selective recovery is confirmed by stand testing with simulated solution (raffinate of extraction cycle reprocessing).

REFERENCES

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6. FACCINI A. et al./ GLOBAL'95. V. 1, P. 1032.