

**Spent Fuel Reprocessing Development and Usage of Fission Products as Starting Precursor for Ceramic Waste-Forms – 16498**

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**ABSTRACT**

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 waste preparing for disposal.

Reprocessing is a series of chemical operations that separates plutonium and uranium from other constituents in nuclear waste. Indeed, the plutonium separated can be used to fuel reactors, but also to make nuclear weapons.

Since reprocessing operations are far more expensive than using uranium fuel and disposing of the spent fuel directly, this process is not readily considered. Without doubts the reprocessing price of \$1000 per kilogram of heavy metal (kgHM), like uranium must be less by at least 2-3 times compared to directly depositing the spent fuel. And some more simple technology (in comparison with PUREX process) must be developed, for example, technology based on precipitation processes.

One of the options to change reprocessing technology is the idea to use certain fission products occurring in spent fuel in considerable amount and capable to form insoluble substances as suitable materials for long-term storage or final disposal of radioactive wastes.

The development of new materials for HLW immobilization are intended to reduce disposal cost.

The present work was aimed at the search for the simple engineering decisions that would provide opportunity of fission products usage as starting precursor for ceramic waste-forms. The results of experiments on synthesis of Pd-based metalloceramic compositions are presented in this paper.

**INTRODUCTION**

The principal purpose of spent fuel reprocessing is to recover unused uranium and plutonium in the spent fuel elements. This concept enables to use generated plutonium and unburned uranium-235 and to reduce the demand for natural uranium approximately 15 - 20%. Therefore, the adverse effects of uranium mining and subsequent stages of uranium ore processing on the environment decrease as well. A secondary reason is to reduce the volume of material to be disposed of as high-level waste. As of today, France, United Kingdom, Russia, Japan, India and China are trying to reprocess their spent fuel.

In open nuclear fuel cycle (NFC) spent fuel is considered as radioactive waste to be disposed into geological formations after preliminary management stages. In this case the elimination of hazardous consequences is made difficult by the fact that the SNF contains generated plutonium, other TRU elements and long-lived fission

products, Hence the SNF is not stable material from the standpoint of its long-term safety under disposal conditions.

The USA, Canada, Finland and Sweden have currently opted SNF for direct disposal repository. Although programs are developed, none of these countries are likely to have a repository in operation before 2020, maybe 2030. The safety of geological repository for disposal of SNF has not yet been demonstrated.

Most other countries have not yet decided which strategy to adopt. They are currently storing spent fuel and keeping abreast of developments associated with both alternatives [1].

One question that is being discussed in this paper: is it possible to reduce the cost of nuclear fuel cycle? Without doubts the reprocessing price of \$1000 per kgHM like uranium, is too much in comparison to direct storage and disposal [2]. According to our opinion there are two options that could change the situation and make spent fuel reprocessing more attractive.

The first option is the technology development based on precipitation and ion exchange processes.

The second option consists in usage of fission products and TRU occurring in spent fuel as usable materials for different application. Radioactive waste from nuclear reactors typically contains radionuclides with a wide variety of half-lives and chemical properties. Some radionuclides (for example Cs-137, Sr-90, Am-241) could be recovered and used in radiation and heat sources.

Amongst others fission products present in spent nuclear fuel, there are considerable quantities of platinum group metals (PGMs) and zirconium. The development of new materials intended for HLW immobilization providing costs reduction at the stage of subsequent storage. And the idea to use palladium and zirconium occurring in spent fuel for synthesis of compounds, suitable for long-term storage or final disposal seems to be rather attractive.

So the object of this work was to illustrate an opportunity of 'reactor' palladium and zirconium usage as starting precursor for ceramic waste-forms. The results of experiments on synthesis of Pd and Zr -based compositions are described below.

## **RESULTS OF EXPERIMENTS AND DISCUSSION**

The development of new materials intended for HLW immobilization will allow increasing of radionuclides concentration in solidified product so providing costs reduction at the stage of subsequent storage. (Amongst the fission products present in spent nuclear fuel, there are considerable quantities of platinum group metals (PGMs) (including palladium) and zirconium.)

The first ideas related to prospects of platinum group metals recovery from spent fuel and their utilization appeared as early as 50 years ago. However, several decades later it was quite obvious that the occurrence of palladium radionuclide Pd-107 (half-life  $6.5 \cdot 10^5$  years) in "reactor" palladium would exclude the possibility of its use in common industry.

At the same time, the use of palladium in radwaste reprocessing technology (where the presence of Pd-107 is of no importance) may also play a crucial role in forming the demand for this metal. Preliminary experimental results allow conclusion that the use of 'reactor' palladium as a material for I-129 immobilization seems to be quite justified [3].

The low-soluble palladium iodide use is known from the literature: it can be used as a compound for long-term storage and/or final disposal of iodine radionuclides. The use of "reactor" palladium for these purposes seems quite reasonable in this case. (It is evident that the use of natural palladium is impossible due to its high cost and availability concerns).

The technique of palladium iodide preparation is very simple [3, 4]. A precipitate of  $\text{PdI}_2$  could be obtained by mixing of solutions of KI and  $\text{Pd}(\text{NO}_3)_2$  in nitric acid. The value of  $\text{Pd}^{2+}/2\text{I}^-$  ratio varied during the experiments from 5 to 50% of palladium excess relative to stoichiometry of reaction. (Palladium iodide ( $\text{PdI}_2$ ) solubility was determined with the use of radiotracer I-125 (half-life period 60 days) and the value of  $\text{PdI}_2$  solubility was found to be as low as 2.5 mg/l.)

The yield of palladium iodide precipitates was almost the same in the majority of these experiments (98.1 – 98.6%). The specimens obtained were submitted for elemental, disperse and phase analyses. Electron-microscopic photos of the specimens are given in fig. 1.

Within the limits of experimental error I/Pd ratio value for all specimens agrees with stoichiometric ratio for  $\text{PdI}_2$ . The other elements have not been detected, whereas the occurrence of non-analyzable elements in amounts below 2-6% is possible.

The roentgenograms for two palladium iodide specimens indicated that specimen's structure was basically amorphous rather than crystalline. No differences between the structures of specimens have been revealed. No phase corresponding to metal palladium or palladium oxides has been detected.

The results of these pictures statistical analysis revealed that within the limits of experimental error the average sizes of initial particles were practically similar.

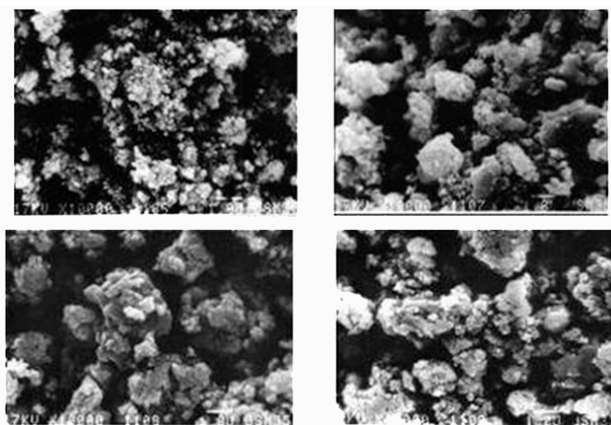


Fig. 1. Electron-microscopic photos of the  $\text{PdI}_2$  specimens.

At the next stage a pressing plant was used for preparation of Pd-based pellets containing  $\text{PdI}_2$  as filler. Weighted portion (3-4 g) of working mixture (metal palladium and palladium iodide) was poured into press-mold. The mold was inserted inside the inductor. The chamber was evacuated by means of fore pump and further filled with argon. Powder pressing was conducted for 1 hour at given temperature and pressure.

The studies of pressed pellet surface structure were conducted with the use of scanning electron microscope (SEM) JSM-35CF (manufactured by JEOL Company). The signals of secondary and reflected electrons (SE and RE) providing a morphologic and compositional contrasts of the picture were used to display the surface pattern.

Determination of pellet elemental composition was carried out by electron-probe microanalysis technique, which is based on comparison of characteristic X-ray spectra of the specimen to be analyzed with those of references of known compositions. (This technique sensitivity is about 0.5 mass. %.) Specimen's characteristics are presented in Fig 2.

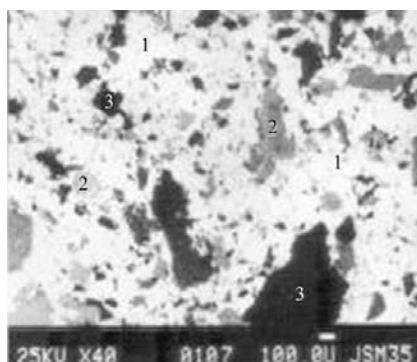


Fig. 2. The results of electron-microscopic analysis for Pd+PdI<sub>2</sub> pellets. (Phase structure, specimen No. 301. Reflected electrons: 1- PdI<sub>2</sub>, 2-Pd, 3- mixture: PdO, PdO·H<sub>2</sub>O, Na<sub>2</sub>Pd<sub>3</sub>O<sub>4</sub>.)

In the micrograph presented in Fig 2, one can clearly see three phases (1, 2, and 3) non-uniformly distributed throughout pellet surface. Phase 1 (white areas) consists mainly of palladium iodide (30% Pd and 70% I, as determined by means of electron-probe microanalysis technique). Phase 2 comprises metal palladium, whereas a phase 3 composition is more complicated and corresponds to the mixture of PdO, PdO·H<sub>2</sub>O, Na<sub>2</sub>Pd<sub>3</sub>O<sub>4</sub>. It should be noted that palladium iodide is X-ray amorphous constituent of pellet material.

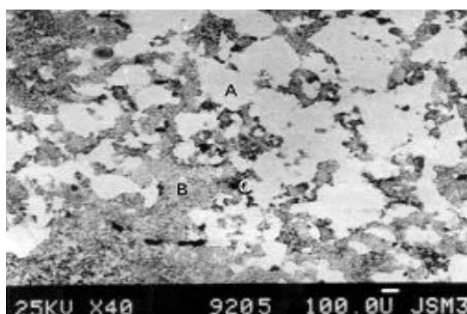
Lixiviation tests were conducted. The static technique of leaching rate determination in distilled water was chosen for chemical stability estimation. Experimental conditions prescribed by Russian Standard "ГОСТ 52126-2003" were set as the basic ones as, in our mind, this document takes into account the main requirements and operational conditions of other approved methods.

(The content of iodine and palladium in solutions were determined by using inductively coupled plasma - mass spectrometry (ICP-MS procedure).)

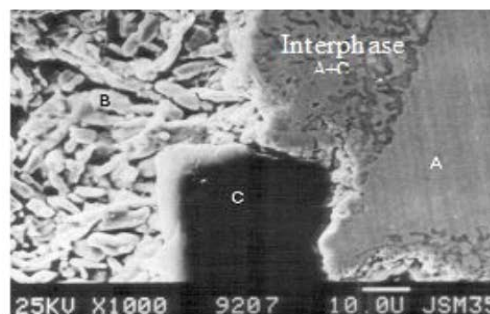
Data obtained point out to the large chemical stability of compositions on metallic palladium base. Initial leaching-out rates of iodine come to level  $2 \cdot 10^{-4}$  -  $8 \cdot 10^{-5}$  g/m<sup>2</sup> day. During further aging, leaching-out rates go down and come to  $8 \cdot 10^{-7}$  -  $9 \cdot 10^{-6}$  g/m<sup>2</sup> day depending on palladium iodide content.

Thus, the results of the experiments have demonstrated the possibility of producing the matrix metal-ceramic compositions based on metal palladium containing iodine compound inclusions.

Another possible application of compositions based on metal palladium containing iodine is targets for I-129 transmutation. Due there neutron physical characteristic (from the point of view the behavior under irradiation) compositions these metal-ceramic compositions could be used as target elements for iodine transmutation. Considering that rather low I-129 transmutation degree is expected to be achieved upon a single transmutation cycle (several percent), a complete I-129 transmutation would need several cycles, that is to say that iodine should be recovered from irradiated target and further directed again to transmutation. It's well known the most special palladium feature which differs this element from the other platinoides is its capacity to be dissolved into nitric acid. So if in the future the materials on Pd-base would be used for TRU immobilization and long-term storage, a simple dissolution of these materials in nitric acid followed by extraction recovery of target elements (americium , curium...) would be sufficient in case of TRU recovery need. (It is obvious also in the case if we include TRU into mineral-like matrices we lose opportunity to recover them forever.) Therefore, It was supposed that the incorporation of oxides of radioactive elements recovered from the wastes of various levels into the matrix of metal palladium would allow to decrease considerably their leaching-out rates and to organize a long-term safe storage of these radionuclides. In this connection resultes of Pd- and  $\text{Eu}_2\text{O}_3$ -based product synthesis are presented below [5, 6]. Weighted portion of 3-4 g, metal palladium and europium oxide mixture was poured into press-mold. The mixture of metal palladium and europium oxide was subjected to cold pressing for one hour under pressure of  $29 \cdot 10^3 \text{ kN/m}^2$ . After pressure release the mold was induction heated by gradually increasing the temperature from  $300^\circ\text{C}$  till  $1000^\circ\text{C}$ . The micrographs showed three phases (A, B, C) which are clearly non-uniformly distributed throughout the pellet surface (Fig. 3).



(Reflected electrons): A-Pd:  $S/S_0=0.5$ , B- $\text{Eu}_2\text{O}_3$ , C-X phase:  $S/S_0=0.07$ ,  $L_C=40 \times 80 \mu$ ,  $S/S_0$  - relative area of phase



(Secondary electrons): C-X phase -  $L_B=3 \times 7 \mu$  (Size of  $\text{Eu}_2\text{O}_3$  crystallites), Interphase: solid solution (Pd- $\text{Eu}_2\text{O}_3$ )

Fig. 3. The results of electron-microscopic analysis for pellet with  $\text{Eu}_2\text{O}_3$ . Specimen 50 mass.% Pd + 50% mass.%  $\text{Eu}_2\text{O}_3$ .

Phase A comprises mainly metal palladium whereas the phase B is constituted of europium oxide. The phase C is the most likely to be a solid solution of Pd-  $\text{Eu}_2\text{O}_3$  and an X-ray amorphous substance (the most likely – carbon of graphite press-mold). (Europium oxide and palladium contents were consistent with composition of

initial mixture being pressed. Determination of pellet elemental composition was carried out by electron-probe microanalysis technique.)

The leach rate of europium was determined and the results are given in Table I. These tests were conducted in distilled water, room temperature. In all cases the europium concentration was at the limit level of this technique sensitivity or is below it.) Consequently, these data must be considered as preliminary. However, calculated values of leaching rates are at the level of  $10^{-5} - 10^{-7}$  kg/m<sup>2</sup>·day.

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TABLE I. The leach rate of europium from Pd-base metalloceramic compositions.

Pellet composition, Pd/Eu <sub>2</sub> O <sub>3</sub>	t, days	The leach rate of europium (R), kg/m <sup>2</sup> ·day
70/30	1	$<4.3 \cdot 10^{-5}$
	5	$<1.2 \cdot 10^{-5}$
	67	$<1.6 \cdot 10^{-6}$
	128	$<7.7 \cdot 10^{-7}$
50/50	1	$<7.3 \cdot 10^{-5}$
	5	$<6.8 \cdot 10^{-6}$
	67	$2.2 \cdot 10^{-6}$
	128	$9.0 \cdot 10^{-7}$
30/70	1	$<1.6 \cdot 10^{-5}$
	5	$<4.0 \cdot 10^{-6}$
	67	$5.5 \cdot 10^{-7}$
	128	$3.8 \cdot 10^{-7}$

Literature data reviewed show that the leaching rates of uranium and plutonium from common matrices based on glass and ceramics of various types are at the level of  $10^{-3} - 10^{-4}$  kg/m<sup>2</sup>·day and those of REE and TPE (rare earth elements and trans plutonium elements) are at the level of  $10^{-5}$  kg/m<sup>2</sup>·day. Our experimental data show that chemical stability of the compositions under examination is as good as that of common matrices. Therefore, the use of these materials for radionuclide long-term storage and transmutation seems to be quite justified [6].

Palladium is not the only fission element suitable as starting precursor for ceramic waste-forms. Extensive information on zirconium (from claddings and fuel) is found in the literature documenting the mineral-like materials synthesis based on zirconium [7-9].

It is possible to assume using such zirconium for the purposes of synthesis of mineral-like matrices that would meet all requirements for safe HLW immobilization. Researches carried out at the V.G. Khlopin Radium Institute have demonstrated the possibility to immobilize actinide fraction of HLW in mono-phase or double-phase ceramics based on host-phase such as zircon, (Zr, An)SiO<sub>4</sub>, and

cubic zirconia,  $(Zr, Y, An)O_2$  [9]. Some examples of single-phase ceramic based on cubic zirconia and zircon been synthesized at V.G. Khlopin Radium Institute are given in Fig. 4 and Fig. 5.

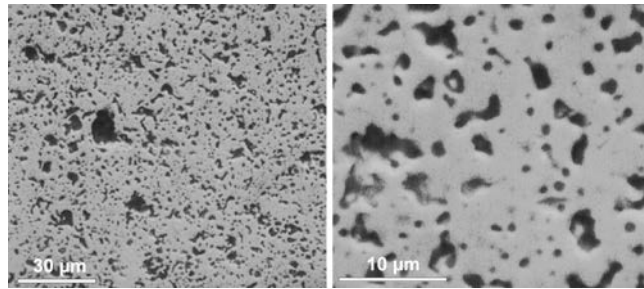


Fig. 4. SEM-BSE images of single-phase ceramic based on cubic zirconia  $(Zr_{0,72}Gd_{0,22}Pu_{0,06})O_{1,89}$  matrix. (Sample was synthesized using co-precipitated precursor, which was cold-pressed and sintered in air at 1500°C for 3 hours. Content of  $^{239}Pu$  – 10.3 wt.%. Black dots are pores.)

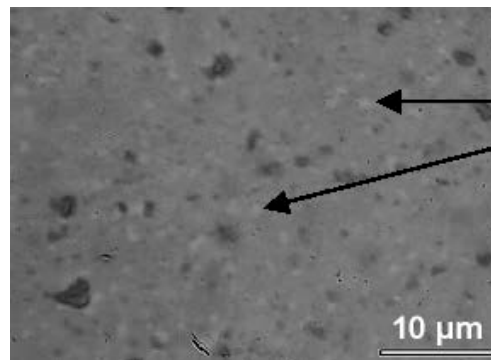


Fig. 5. Reflected light optical microscope image of double-phase ceramic based on zircon  $(Zr_{0,955}Pu_{0,045})SiO_4$  and tetragonal zirconia  $(Zr_{0,964}Pu_{0,036})O_2$  matrices. Light inclusions marked by arrows. Bulk content of  $^{238}Pu$  – 4.7 wt.%, other isotopes of Pu – 1.1 wt.%. (Sample was synthesized using sol-gel precursor, which was cold-pressed and sintered in air at 1500°C for 3 hours. Black dots are pores.)

## CONCLUSIONS

Is it possible to find the correct balance between the application of the spent fuel reprocessing and the disposal of it? And is it necessary to set the long term disposal of the spent fuel against the reprocessing of it?

Those two processes are, indeed, inseparably linked, and the problem of issue is to determine the required combination of the two in time taking into account the following:

- the demand in the plutonium and uranium recycling for the mixed fuel production is going to grow with the ever increasing fast neutron reactor NPP capacities and with the price advance of the natural uranium. Further simplification of the PUREX process should result in the reduced spent fuel reprocessing costs;

- a long spent fuel cooling time prior to reprocessing will simplify the task of the reliable waste immobilization, and the reduced volume of the final waste forms could be stored in the same repositories formerly used for the reprocessed spent fuel storage;

- the separation and utilization of a number of valuable radionuclides, including the platinum group metals, is going to be in favor of the reprocessing costs and hence, on the costs of the storage-reprocessing cycle as a whole.

Considering the future of spent fuel reprocessing it is necessary to underline that all possible changes in process structure and in the usage of new techniques must fulfill the task of the fuel reprocessing cost decreasing and solidification of radionuclides in the forms, which satisfy the requirements of their final removal from biosphere. Solving this problem would be the goal of all researchers in the near future. .

Preliminary experimental results presented in this paper allow conclusion that the use fission products as a material for long lived radio nuclides immobilization seems to be quite justified. The application of "reactor" palladium and zirconium for the purpose indicated would be the first step on the way of new advanced technology spent fuel reprocessing development.

In the near future one can expect the occurrence of publications proposing the techniques allowing the use of not only "reactor" palladium and zirconium, but technetium as well. It seems advisable to examine in future the opportunity of technetium usage for solving problems of HLW immobilization. (In author's opinion it's of interest to use technetium as material to obtain protective covering on granulated wastes or to encapsulate solidified HLW.)

The authors do not believe the application of fission products as a starting precursor for ceramic waste-forms is likely to trigger a revision of the spent fuel reprocessing technology used to date. On the other hand, the application of Pd and Zr (or Tc) - based compositions may appear to be effective enough to prevent the migration of radionuclides into the environment.

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