PROSPECTS ON IMMOBILIZATION TECHNOLOGIES OF LONG-LIVED RADIONUCLIDES WITH USE OF "REACTOR" PALLADIUM

Y. A. Pokhitonov, V.N. Romanovski, S.A. Strelkov
Khlopin Radium Institute
St. Petersburg, Russia

ABSTRACT

At present the spent fuel reprocessing is the only most effective way of localization and immobilization of all fission products and transuranium elements (TUE), including relatively both short-lived (caesium, strontium, ruthenium and others) nuclides and those with the half-live of thousands years and more. The use of the partitioning techniques in combination with synthesis of mineral-like materials provides highest possible safety during subsequent storage and final disposal all of kinds of radioactive wastes. The idea to use for synthesis of compounds, suitable as materials for long-term storage or final disposal of radwastes some fission products occurring in spent fuel in considerable amount and capable to form insoluble substances seems to be rather attractive. One of such elements is palladium; it's accumulation in spent PWR fuel, coming to 1.0 - 1.8 kg per ton. One could suppose that the inclusion of the radioactive elements oxides or slightly soluble iodine compounds in the matrix of metal palladium would allow to produce materials with low leaching rate and suitable for a safe long-term storage or final disposal. In author's opinion such materials could be used as targets for long-lived radionuclides transmutation as well. The object of this work was to carry out a study on searches of engineering decisions, which would allow using of 'reactor' palladium for immobilization of such long-lived radionuclides as I-129 and transplutonium elements (TPE). Are presented in this paper the results of experiments on Pd-based metalloceramic compositions synthesis, these compositions including metal oxides or palladium iodide, and the results of electron microprobe analysis and lixiviation rates for Eu, U and I are given.

INTRODUCTION

One of essential problems facing radiochemical industry is the utilization of HLW, which have been and are being accumulated after uranium, plutonium and neptunium recovery in the course of spent nuclear fuel reprocessing. Long-lived radionuclides presenting in HLW make it potentially hazardous for hundreds and thousands years. One of the lines of risk degree reduction during HLW storage is HLW reprocessing with the intent of separating, concentrating and isolating long-lived radionuclides fractions (partitioning operations). HLW partitioning allows reducing the solidified products storage costs due to isolation of the most hazardous radionuclides such as TPE requiring perpetual storage, in a separate fraction of small volume [1, 2]. It must be emphasized here, that only during reprocessing it is possible to distribute various radionuclides (or their fractions) between separate flows, each of them requiring a specific approach for subsequent treatment. At present the works on partitioning of HLW of various compositions are carrying out in many countries and a number of processes for Cs, Sr, TPE and rare-earth elements (REE) separation have been already tested [2].

At the same time the partitioning is only the first step on the road of subsequent synthesis of materials assuring a safe storage of long-lived radionuclides for many thousands years. The last decades the woks on HLW immobilization having been carried out in many countries and considerable advances have been made in this area.

Fission products, which are abundant in irradiated fuel and capable to produce slightly soluble compounds with the most harmful nuclides, are very tenting to be used for synthesizing of the materials suitable for radionuclides long-term storage or final disposal.
The developments 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.

There is the literature information on zirconium - based mineral-like materials synthesis [3, 4]. (Zirconium buildup at fuel burnup of 40 -50 MW•day/kg U is about 4 -5 kg/t.)

In authors opinion in the nearest future one can expect the occurrence of publications proposing the techniques allowing the use of 'reactor's zirconium or molybdenum (perhaps, technetium, as well) with the aim of preparing materials suitable for long-lived radionuclides immobilization.

The other element, which is generated in the reactor and worth mentioning, is undoubtedly, palladium. The prospects for using palladium are defined not only by its higher generation in the reactor (at burnup level of 40 MW•day/kg U the content of platinum group metals in fuel is about 6 kg per ton, palladium part being about 1.9 kg), but by a number of its chemical properties as well.

The low-soluble palladium iodide is known in literature; it can be used as a compound for long-term storage and/or final disposal of iodine radionuclides. The use of technogeneous "reactor" palladium for these purposes seems quite reasonable in this case [5,6]. (It is evident that the use of natural palladium is impossible due to its high cost and deficiency).

It is worth noting that a feature of metal palladium in comparison with the other platinum group metals is its capability to dissolve in nitric acid. Therefore in the case of eventual recovery of TPE from Pd-based matrix used for TPE immobilization it would suffice to dissolve it in nitric acid and further carry out extraction recovery (separation) of target elements (e.g. americium, curium). In so doing, unlikely the case of vitreous and ceramic compositions, rather simple in composition solutions would be obtained and the recovery of nuclides being included would involve no difficulties.

On this basis, the object of this work was to conduct experimental study on seeking of decisions, which would allow using 'reactor' palladium for immobilization of such long-lived radionuclides as I-129 and TPE. It is expected that incorporation of radionuclide oxides or slightly soluble iodine compounds into metal palladium matrix would allow to get a material presenting low lixiviation rate and suitable for a safe long-term storage. In authors opinion such materials may be also used as the targets for long-lived radionuclides transmutation.

Experimental Results and Discussion

The study of conditions for the synthesis of metalloceramic compositions based on palladium & europium oxide:

The materials to be used as matrices for TPE transmutation should meet the following requirements:

- To possess appropriate physical properties: high melting point, high heat conductivity, tow thermal expansion; to undergo no phase transformations, to be chemically and mechanically stable in the range of process temperatures; to absorb neutrons weakly; to generate no secondary nuclear waste in the form of radiotoxic products due to matrix activation;
- Matrix material should be compatible incorporated TPE and FP generated on

irradiation; the material should not react with target shell materials and reactor heat carrier.

By our opinion it is quite promising to create matrix compositions based on metal palladium incorporating TPE oxides.

When projecting this work it was supposed that incorporation of radionuclide oxides into metal palladium matrix would allow essentially decrease the leachability of these matrices thereby providing a higher degree of long-term storage safety.

In the first stage of studies the experiments on Pd- and Eu_2O_3-based product synthesis were conducted. The powders of metal palladium and europium oxide, obtained by oxalate precipitation technique followed by precipitate calcination, were use as initial materials. The foregoing data show that the powders of metal palladium and europium oxide are the system with practically identical dispersity ($D_{av.} \sim 0.35\mu$). Phase composition of europium oxide powder was completely consistent with initial product formulation, suggesting that Eu_2O_3 accounts for about 100% of the powder. The powder of metal palladium contained the main phase (Pd, 93%) along with the small amounts of palladium oxides (~3%) and palladium hydroxides (<1%) as well as unknown phase X (~5%) that could not be identified on X-ray picture. In addition metal palladium contains 2 foreign elements (S ~ 1%, Cl ~ 2<5%), the form of their occurrence remaining unclear.

A pressing plant was used for preparation of Pd-based pellets containing Eu_2O_3 as a filler. Along with the press this plant comprises HF generator, forevacuum chamber and a pump station. The press-molds were made of graphite AG-1500. Pressure operations were conducted under argon atmosphere. Weighted portion (3-4 g) of working mixture (metal palladium and europium or uranium oxides) was poured into press-mold (mold-mortise diameter = 11 mm). The mold was inserted inside the inductor. The chamber was evacuated by means of forepump and further filled with argon. Powder pressing was conducted for 1 hour at given temperature and pressure. 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 Tables I - III and in Fig 1.

Table I. Characteristics of the Pellets containing Metal Palladium and Europium Oxide.

No.	Eu_2O_3 content, %	Pellet mass, g	Ø, mm	h, mm	ρ,	S*10000, m^2
200	50	3.364	11	4.2	8.4	1.45
210	70	3.365	10.9	6.4	6.4	1.88

Table II. The Results of X-ray Diffraction Analysis for Specimens No. 200 and 210 (polished surface).

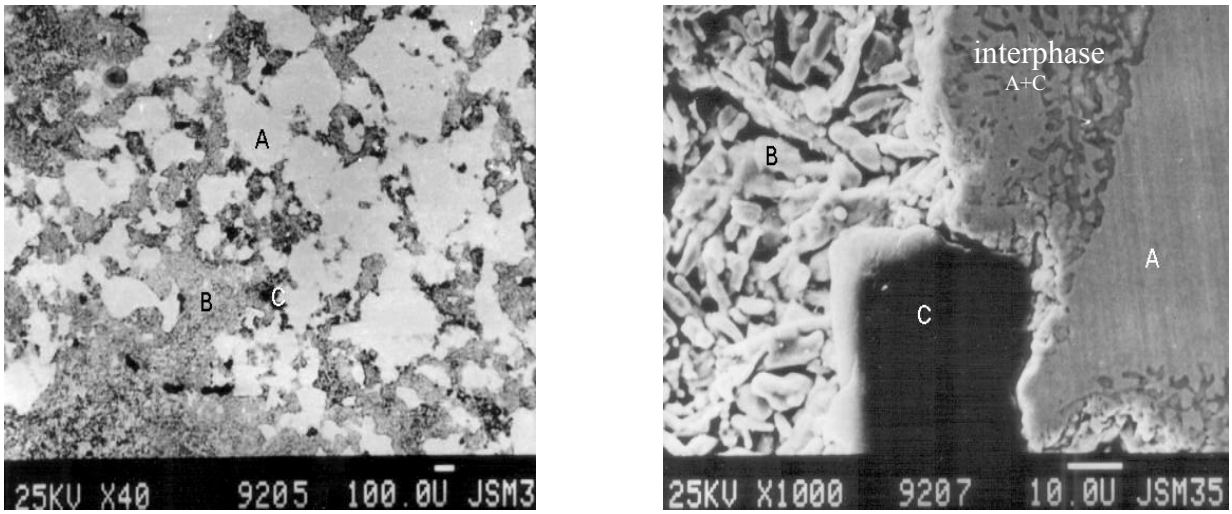
Phases	Analysis area, % (No. 200)-				Analysis area, % (No. 210)			
	Average, %	A	B	C	Average, %	A	B	C
Eu_2O_3	55	0 - 5	98	80 - 70	75*	0 - 5	95 - 90	55
Pd	40	100 - 95	1 - 4	0 - 10	20	100 - 95	5 - 10	5
X	~ 5	0	0	20	~ 3	0	0	40

* - monoclinic modification

Table III. The Results of X-ray Morphological Analysis for Specimens No 200 and 210 (polished surface).

No. 200	Al	S	Cl	Pd	Eu	No. 210	Al	S	Cl	Pd	Eu
Average**	0.7	0.6	0.3	40.6	57.6	Average	0.5	0.3	0.4	17.9	70.9
A	0	1	0	95 - 100	5 - 0	A	0	0.6	0.3	97.4	2.5
B	0.9	0	0	1 - 4	84	B	0.8	0	0	6 - 12	78.4
C*	0.3	0.3	1	0 - 10	55 - 70	C*	0	0	2	0 - 10	30 - 50

* - the phase non-identified by X-ray analysis.
** - measurement area ~ 5 mm^2



a

Specimen # 200. Reflected electrons: A-Pd: S/S_0=0.5, B-Eu_2O_3, C-X phase: S/S_0=0.07, L_C=40x80μ, S/S_0 - relative area of phase.

b

Specimen # 210. Secondary electrons: C-X phase. L_B=3x7 μ (Size of Eu_2O_3 crystallites), Interphase: solid solution (Pd-Eu_2O_3)

Fig. 1. The results of electron-microscopic analysis for pellets with Eu_2O_3.

At micrographs presented in Fig. 1 three phase (A, B, C) are clearly seen which are non-uniformly distributed throughout the pellet surface (micrographs *a* and *c*). The data given in Table II shows that the phase A (white areas) comprises mainly metal palladium whereas the phase B (gray areas) is constituted of europium oxide. The phase C is the most likely to be a solid solution of Pd- Eu_2O_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.

In the next stage of our studies we obtained under analogous conditions several specimens of metalloceramic compositions made of palladium and mixture of uranium and cerium oxides (V_{Ce}/V_{Ce+U} = 0.3 (mole); V_O/V_{Ce+U} = 2.11 (mole)), this mixture being prepared by plasma-chemical technique.

The lixiviation rate was determined for all specimens. Lixiviation tests were conducted in distillated water following common technique. Lixiviation rate (R) was calculated from the formula:

$$R = M_n/S \cdot t_n,$$

where: R: lixiviation rate, $kg/m^2 \cdot day$
M_n: amount of an element being leached for t_n days, kg
S: specimen open surface area, m^2

The results of lixiviation rate estimation are given in Table IV.

Table IV. The Rate of Europium and Uranium Lixiviation from Pd-base Metalloceramic Compositions.

Specimen number	Pellet composition	t, days	R, $kg/m^2 \cdot day$
200	Pd -50% (Eu_2O_3)	200	$1x4 \cdot 10^{-4}$
210	Pd -70% (Eu_2O_3)	110	$2x4 \cdot 10^{-5}$
220	Pd -50% (UO_2 -Ce_2O_3)	510	$1x4 \cdot 10^{-5}$
230	Pd -% (UO_2 -Ce_2O_3	510	$2x10^{-5}$

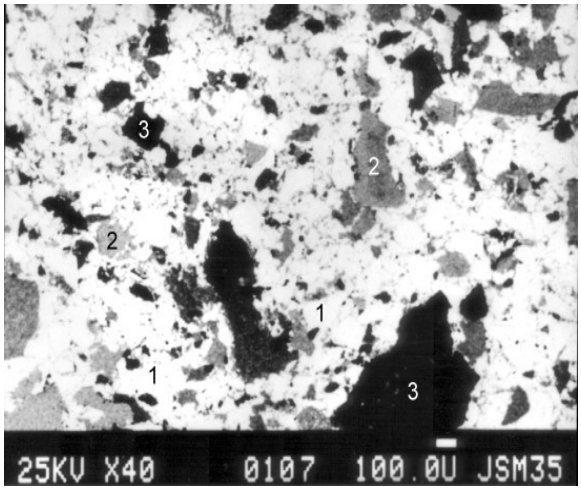
The synthesis of metalloceramic compositions based on palladium & palladium iodide:

^{129}Iodine holds a particular place among other long-lived fission products. In spite of its rather low specific activity (180 mCi/g) this radionuclide presents a serious threat for biosphere because of very large half-life value ($T_{1/2} = 1.57x10^7$ years) and high mobility in different mediums. There exist several concepts of I-129 isolation: the dissipation in World's ocean waters, transmutation, pumping of iodine-containing pulps into clay structures by stratum hydro-rupture technique, long-term monitored storage or final disposal in the form of slightly soluble compounds.

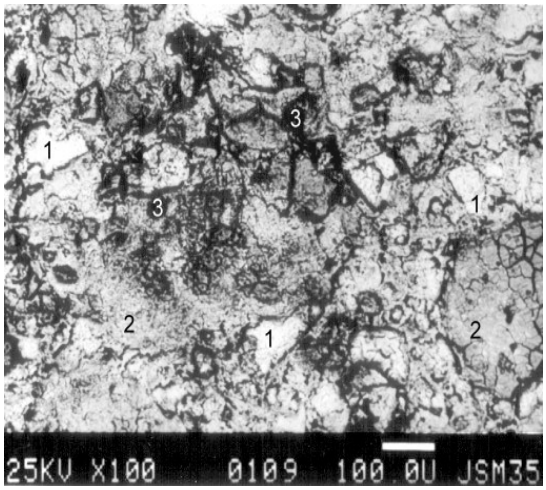
Taking into account high iodine mobility in various media, the use of its slightly soluble compounds as the form for iodine final disposal seems to be the most promising.

As it was already noted in Introduction, the literature cites slightly soluble palladium iodide, which is quite suitable for long-term storage and/or final disposal of iodine radionuclides.

We prepared the specimens containing 50% palladium iodide being incorporated into metal palladium matrix. The results of X-ray morphological and phase analyses of these specimens are shown in Fig 2 and in Tables V and VI. (Specimen No. 302 had additional Pd- coating, obtained by electrochemical deposition.)



Phase structure, specimen No. 301.
Reflected electrons:
1- PdJ_2, 2-Pd, 3- mixture: PdO, $PdO*H_2O$, $Na_2Pd_3O_4$.
S/S_0: 1 - 62%, 2 - 23%, 3 - 15%. 1 consists of grains ~ 40 μ, borders concern to a phase 2.



The composite structure, specimen No. 302. Secondary electrons:
1,2,3 - areas of various structure, as well as in specimen No. 301. (Pd- coating smooths the contrast of the image in comparison with the specimen No. 301.)

Fig. 2. The results of electron-microscopic analysis for Pd_PdI_2 pellets.

In micrographs, presented in Figure 2 one can clearly see three phases (1, 2, 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 XRM). Phase 2 comprises metal palladium, whereas phase 3 composition is more complicated and corresponds to the mixture of PdO, $PdO \cdot H_2O$, $Na_2Pd_3O_4$. It should be noted that palladium iodide is X-ray amorphous constituent of pellet material.

Iodine lixiviation rate was determined for these specimens. After being contacted with distillated water for 200 days they exhibited iodine lixiviation rate about $9.05 \cdot 10^{-8}$ kg/m^2·day.

Table V. The Results of X-ray Morphological Analysis for Pd+PdI_2 Pellet.

Phase number	Composition, %				
	Na	Al	Si	Pd	I
1	0	1,1	0	28-32	68-72
2	0	0	0	98.5	<0.05
3	1.5	0	0.3	75-88	<0.5
Average	0.3	0.8	0.3	52	46

Table VI. The Results of X-ray Diffraction Analysis for Pd+PdI2 Pellet.

Composition	Pd	PdO	$PdO \cdot H_2O$	$Na_2Pd_3O_4$	X	PdJ_2
%	25	1-3	1-3	1-3	3-5	65

The experimental results clearly showed the feasibility of obtaining metalloceramic compositions based on metal palladium and containing oxides or iodine compounds.

However it should be noted that all these results must be considered as preliminary ones, and the studies are being conducted now in searching for optimum conditions of pressing and protective coating application.

CONCLUSION

In last sixties palladium cost was about 5 times less than platinum one. Possibly, just this made palladium the most promising from all platinum group metals and opened him a large field of technological applications. At present an interest in this element is growing due to the prospects of hydrogen power development.

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 ^{107}Pd (half-life $6.5 \cdot 10^5$ years) in "reactor" palladium would exclude the possibility of its use in common industry.

Various techniques can be used for palladium recovery from spent fuel. But it must be understood that no matter how effective a technology may be, it would not find industrial application if there is no consumer's steady demand for this product.

Here again the first step on the road of eventual 'reactor' palladium use may be its utilization when reprocessing radioactive wastes. In this case the presence of palladium radioactive nuclide would not be an interfering factor; moreover there would not be any need of palladium profound decontamination from other fission products.
These preliminary experimental results allow conclusion that the use of 'reactor' palladium as a material for I-129 and TPE immobilization seems to be quite justified.

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