DEVELOPMENT OF MATRICES WITH THE PURPOSE IODINE-129 IMMOBILIZATION

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1. Introduction

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\(_{1/2}\) = 1.57×10\(^7\) years) and high mobility in different mediums.

There are several conceptions of \(^{129}\)I isolation: dissemination in ocean waters; transmutation; pumping of iodine-containing slurries in clayey geological formations by stratum hydroluperture technique; prolonged monitored storage or a final disposal of slightly soluble iodine-containing compounds. The possibilities for incorporation of slightly soluble iodine compounds and iodine-containing sorbents into cements, bitumen and easily melted glasses were being studied with the aim to improve the safety of iodine immobilization. It was shown that iodine lixiviation rate from the concrete (containing Ba(IO\(_3\))\(_2\) was 2.6·10\(^{-6}\) g/m\(^2\)-day, and from bitumen (equally with Ba(IO\(_3\))\(_2\)) – 8·10\(^{-7}\) g/m\(^2\)-day. Iodine lixiviation rate from phosphate glasses is of the same order of magnitude (2.6-6·10\(^{-6}\) g/m\(^2\)-day) [1]. Comparatively recent is a process proposed for the incorporation into easily melted phosphate glass of radioiodine caught by Ag-containing filters [2].

Along with the studies of Ag-phosphate glasses the experiments were conducted on iodine incorporation into Pb-borosilicate glass in the form of BiPbO\(_4\), which provides uniform iodine distribution throughout the matrix. Vitreous frits of composition B\(_2\)O\(_3\):SiO\(_2\):PbO = 30:10:60 (mole %) were mixed with BiPbO\(_4\) and melted at 520 °C for 30 minutes. [3]. French scientists examined the potentialities of ceramics of apatite structure application for radioiodine immobilization [4]. This material is produced by PbI\(_2\) sintering in orthovanadatophosphate medium [Pb\(_{0.4}(VO_4)_{1.6}(PO_4)_{0.4}\)] at 700°C and pressure of 25 MPa. Orthovanadatophosphate is not only involved in iodine-containing ceramics but, when sintering, it creates protection barrier about it as well. In Japan lead-vanadium iodine-apatite (Pb\(_{10}(VO_4)_{6}I_2\)) has been synthesized by hot pressing of stoichiometric amounts of PbO, PbI\(_2\) and V\(_2\)O\(_5\) at 500°C and pressure of 9 MPa [3]. Iodine, lead and vanadium lixiviation rate from this product within initial seven days were found to be 3.9·10\(^{-5}\); 1.55·10\(^{-5}\) и 1.61·10\(^{-4}\) g/cm\(^2\)-day, respectively. Contrary to Japanese scientists, Russian specialists suggested iodine incorporation into copper matrix in the form of CuI (40-85 mass.% CuI and 15-60% metal copper) [5]. Presently, the improvement of traditional cement materials is being continued along with searching of novel matrices for radioiodine immobilization.

For the synthesis of compounds suitable as materials for prolonged storage or final disposal of iodine-129 or manufacture of targets for subsequent transmutation of TPE radionuclides, it seems very promising to use fission products contained in irradiated fuel [6]. Again, for immobilization of J-129 one can use the "reactor" palladium, the accumulation of which in spent WWER is more than 1 kg per ton [7].

The object of this work was to conduct experimental study on synthesis matrices on the base of ‘reactor’ palladium for immobilization of iodine-129. It may be suggested that the incorporation of iodine-129 into Pd-based matrix would allow obtaining a material of lower leach rate which would be perfectly suitable for save long-term storage.

2. Experimental results and discussion

The conditions of PdI\(_2\) deposit manufacture from nitrate-acid solutions have been studied. A precipitate of PdI\(_2\) was obtained by mixing of solutions of KI and Pd\(^2+\) in nitric acid. (HNO\(_3\) concentration – 2 mole/l.) The value of Pd\(^2+\)/2I\(^-\) ratio varied during the experiments from 5 to 50% of palladium excess relative to stoichiometry of reaction.

\[
PdCl\(_2\)+KI\rightarrow PdI\(_2\)+KCl
\]

The sequence of solution mixing was also altered: PdCl\(_2\) solution was added to KI solution or KI solution was poured in PdCl\(_2\) solution. It was supposed that in the first case the precipitate yield (referred to iodine) could be noticeably lower due to formation of palladium iodide soluble complex resulted from the occurrence of iodide-ions excess at the initial stage of the process:
However the yield of palladium iodide precipitates was almost the same in the majority of these experiments (98.1 – 98.6%).

The specimens so obtained was transmitted for elemental, disperse and phase analyses. Electron-microscopic photos of the specimens are given in Fig. 1.

Fig. 1. Electron-microscopic photos of the PdI₂ specimens.

Within the limits of experimental error I/Pd ratio value for all specimens agrees with stoichiometric ratio for PdI₂. The other elements have not been detected, whereas the occurrence of non-analyzable elements in amounts below 2-6% is possible.

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. 2).

Fig. 2 The bar charts for PdI₂ powder grain size distribution.

In addition to elemental, disperse and phase analyses of palladium iodide the differential thermal analysis was carried out for thermal stability determination (Fig. 3).

Fig. 3. DTA-curves for PdI₂ specimen.

An endothermal spike for PdI₂ decomposition was observed in the course of specimen heat-treating, its origin lying at 400°C and the maximum occurring at 525°C. Reference data for decomposition temperatures
are generally given for maximum’s area. In our case the temperature corresponding to maximum is essentially higher than reference value for palladium iodide decomposition temperature (375°C). Normally palladium iodide contains 39.4 mass.% palladium. The thermo gravimetric data showed that the amount of palladium remaining after decomposition was as low as 33.1%. Thus, it may be suggested that the initial substance contained about 4-6% foreign admixture.

Substantial characteristic of iodine compounds intended for preparing of targets for $^{129}$I transmutation is chemical and heating stability.

Another objective of conducted researches was palladium iodide (PdI$_2$) solubility determination with the use of radiotracer $^{125}$I (half-life period 60 days). $^{125}$I was added as the “marker” during PdI$_2$ specimens synthesis. The value of PdI$_2$ solubility was found to be as low as 2.5 mg/l.

At the next stage of the work we prepared the specimens containing 50% palladium iodide being incorporated into metal palladium matrix.

A pressing plant was used for preparation of Pd-based pellets containing PdI$_2$ 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 palladium iodide) 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 1-2 and in Fig 4.

![Fig. 4. The results of electron-microscopic analysis for Pd+PdI$_2$ pellets. (Phase structure, specimen No. 301. Reflected electrons: 1- PdI$_2$, 2-Pd, 3- mixture: PdO, PdO$\cdot$H$_2$O, Na$_2$Pd$_3$O$_4$.
S/S$_0$: 1 - 62%, 2 - 23%, 3 - 15%. 1 consists of grains ~ 40 µ, borders concern to a phase 2.)](image)

In micrographs, presented in Figure 4 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 a phase 3 composition is more complicated and corresponds to the mixture of PdO, PdO$\cdot$H$_2$O, Na$_2$Pd$_3$O$_4$. It should be noted that palladium iodide is X-ray amorphous constituent of pellet material.

The results of X-ray morphological analysis for Pd+PdI$_2$ pellet.

<table>
<thead>
<tr>
<th>Phase number</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Average</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 2.
The results of X-ray diffraction analysis for Pd+PdI$_2$ pellet.
Iodine lixiviation rate for some specimens was determined. (The content of iodine and palladium in solutions were determined with using ICP mS procedure.)

Lixiviation tests were conducted in distilled water following common technique. Lixiviation rate (R) was calculated from the formula:

\[ R = \frac{M_t}{S \cdot t_n} \]

where: \( R \): lixiviation rate, kg/m²·day; \( M_t \): amount of an element being leached for \( t_n \) days, kg.

\( S \): specimen open surface area, m²

The results of lixiviation rate estimation are given in Table 3.

Table 3.
The rate of iodine and palladium lixiviation from Pd-base metalloceramic compositions.

<table>
<thead>
<tr>
<th>t, days</th>
<th>I, mg/l</th>
<th>Pd, mg/l</th>
<th>R, g/sm²·day</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>1.4</td>
<td>83.3</td>
<td>9.0·10⁻⁵</td>
</tr>
<tr>
<td>78</td>
<td>0.8</td>
<td>154</td>
<td>1.6·10⁻⁵</td>
</tr>
<tr>
<td>210</td>
<td>0.56</td>
<td>209</td>
<td>4.2·10⁻⁶</td>
</tr>
</tbody>
</table>

After being contacted with distilled water for 200 days they exhibited iodine lixiviation rate about (4 – 5)·10⁻⁸ kg/m²·day.

According the data shown in this table the content of palladium is increased in the course of experiment something in 2,5 times and at the same time content of iodine is decreased. This fact could be explained in the following way. In the presence of water [PdI₄]²⁻ is got out in solution but the part of iodine is retained in matrix of pallet with metallic palladium.

In the second set of experiments palladium iodide powder without complexes of [PdI₄]²⁻ is using. The pallets were manufactured with using cool pressing technique. The content of palladium iodide was 30, 50 and 70 masses % accordingly. For the purpose chemical stability comparison the pallets on the base of copper and palladium iodide were manufactured.

The results of determination of iodine leaching-out rate from the specimens are given in Fig. 5.

For 5. Leaching-out rate of iodine from the specimens on the base of palladium and copper.

Presented data point out to the large chemical stability of compositions on metallic palladium base. Initial leaching-out rates of iodine come to level 2·10⁻⁵ - 8·10⁻⁶ g/sm²·day.

During further aging, leaching-out rates go down and come to 8·10⁻⁸ - 9·10⁻⁷ g/sm²·day depending on palladium iodide content. In the case of palladium based composition lower leaching-out rates are observed in comparison with copper based compositions.

Also we had executed the calculation of neutron physical characteristic of Pd-based matrix (from the point of view the behavior under irradiation) has been executed.

Considering that rather low \(^{129}\)I transmutation degree is expected achieved upon a single transmutation cycle (several percent), a complete \(^{129}\)I transmutation would need several cycles. So, it will be necessary to extract the \(^{129}\)I from irradiated target and again turn to reactor irradiation. Therefore it’s necessary to elaborate the simple target manufacturing and treatment technologies.
One of essential criterion for selection of matrices suitable for iodine transmutation is a low neutron capture by these materials for prevention of the losses of neutrons needed for transmutation. Also matrix irradiation should not be accompanied by generation of long-lived products of activation. There is only one radioactive nuclide of palladium in spent nuclear fuel: Pd-107 which has a half-life of 6.5×10^5 years and decays with radiation of soft beta-rays of 35 keV. One of possible “reactor” palladium usage that waives an radioactivity objection connected with its radioactivity is palladium usage as a basis for making containers and targets for long-term storage long-lived radioactive materials and irradiation in reactor (transmutation).

(Melting temperature (1552°C), mechanical strength and also chemical inertness permit to use palladium as target’s material.)

While estimation Pd container’s neutron physical characteristic from the point of view the opportunity of using for intrareactor it should be noted the following:

Container not must insert fair quantities of distortion in neutron flow in reactor channel.

The data for palladium isotopic composition in spent fuel and neutron-absorption cross-sections are presented in Table 4 below. (Data of JENDL 3.3. library have been used.)

Neutron-absorption cross-sections of Pd are notably higher in comparison with constructional materials of reactor active zone (zirconium iron or nickel). However container’s influence isn’t catastrophically and neutron flow reduction in immediate vicinity will average about 15 – 20 %.

In the nuclear fuel vicinity the capture cross-section (averaged on PWR neutron spectrum) will be about 32.4 b for Pd matrix and about 16.6 b for iodine. Far from fuel, in by water coolant-moderator it should be as 42.0 b and 26.7 b accordingly.

This means to the significant effect of (that) neutron capture reaction rate competition between Pd and iodine. So iodine irradiation as Pd compound can require increase the irradiation exposition in 3 or more times.

Table 4.

<table>
<thead>
<tr>
<th>Nuclide mass</th>
<th>Half-life</th>
<th>Content in spent fuel after 30 years, weight (%)</th>
<th>Neutron-absorption cross-sections, barns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thermal neutrons</td>
</tr>
<tr>
<td>^{102}Pd</td>
<td>Stable</td>
<td>0.0</td>
<td>2.97</td>
</tr>
<tr>
<td>^{104}Pd</td>
<td>Stable</td>
<td>15.8</td>
<td>0.46</td>
</tr>
<tr>
<td>^{105}Pd</td>
<td>Stable</td>
<td>27.5</td>
<td>17.9</td>
</tr>
<tr>
<td>^{106}Pd</td>
<td>Stable</td>
<td>26.4</td>
<td>0.27</td>
</tr>
<tr>
<td>^{107}Pd</td>
<td>6.5×10^5 years</td>
<td>15.9</td>
<td>1.8</td>
</tr>
<tr>
<td>^{108}Pd</td>
<td>Stable</td>
<td>10.9</td>
<td>7.6</td>
</tr>
<tr>
<td>^{110}Pd</td>
<td>Stable</td>
<td>3.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

While palladium irradiation some long-lived nuclides (silver, gadolinium) could be accumulated. According rough estimate during one year of irradiation it could be accumulated about 0.1% atoms of silver and gadolinium that give a few curies per gram of palladium. Accordingly neutron physical characteristic of Pd are severely limited but inestimable advantage connected with simple reprocessing of Pd-based targets after irradiation (TPE transmutation) give grounds to consider this material as very promising.

The experimental results clearly showed the feasibility of obtaining metalloceramic compositions based on metal palladium and iodine compounds. And the studies are being conducted now in searching for optimum conditions of pressing and protective coating application.

3. Conclusion

Substantial characteristic of iodine compounds intended for final disposal or preparing of targets for ^{129}I transmutation is chemical and thermal stability.

Relaying on correlation of various iodine compound characteristics, the authors of [8] concluded that an unambiguous choice between these materials was very difficult to do. None of compounds being considered fulfills all design requirements.

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. (It is evident that the use of natural palladium is impossible due to its high cost and deficiency).

"reactor" palladium contains long-lived radioactive isotope $^{107}$Pd (half-life $6.5 \times 10^5$ years) and its presence doesn't expect for possibility its use in traditional areas.

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 [6, 9]. These preliminary experimental results allow conclusion that the use of ‘reactor’ palladium as a material for I-129 immobilization seems to be quite justified.

References


