On immobilization of high-level waste in an Y–Al garnet-based cermet matrix in SHS conditions

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Abstract

A method of high-level waste (HLW) radionuclide immobilization in a long-life matrix based on Y–Al garnet, a material highly chemically resistant to natural environments, has been developed for the ultimate HLW isolation from the environment. Model systems containing Ce, Nd, Sm, Zr, Mo, 238U, and 241Am were used in the study as simulators of HLW radionuclides. An energy-saving technology of self-propagating high-temperature synthesis (SHS) was employed to synthesize the matrix material with fixation of HLW radionuclide simulator elements in the Y–Al garnet structure. The results of an X-ray phase analysis for the synthesized materials have shown that the simulator elements, as well as uranium and americium are incorporated strongly in the structure of Y–Al garnet predominantly forming the matrix’s major neof ormation fit for environmentally safe disposal. The produced synthetic mineral-like matrices feature high water resistance, the property confirmed by a very low rate (10−9–10−10 g/cm²·day) of americium leaching into water. Besides high strength of the americium fixation in the structure of Y–Al garnet, the latter’s carryover is small at high temperatures due to a short duration of the process.

The technically, economically and environmentally attractive novel HLW immobilization technique proposed herein may form the basis for the closing process of the spent nuclear fuel reprocessing.

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The new technology platform of nuclear power based on a closed nuclear fuel cycle (CNFC) suggests the need for new technologies to be created to reprocess spent nuclear fuel (SNF). The progressing accumulation of SNF reprocessing products (high-level waste) poses a major danger to human activities and the environment and hinders the evolution of nuclear power. The HLW formation requires the problem of the HLW conditioning with the absolute waste isolation from the biosphere to be solved. One of such possible ways is to immobilize HLW in matrix materials – highly durable analogs of natural minerals chemically resistant to natural water environments. The key to the effective application of such matrix materials is the relative simplicity of the chemical processes involved in the synthesis thereof, which may be decisive when it comes to the selection of the proper commercial technology.

No final decision has been so far made as part of the CNFC as to the preferred SNF reprocessing technology and concerning the selection of the matrix material for the HLW isolation.

The most common of the stable matrix materials are mineral-like oxide ceramic neof ormations obtained in solid-phase high-temperature chemical processes. These processes form the closing HLW handling phase.

As far as water-based treatment processes are concerned, the most promising of these appears to be the one with radionuclides of selected groups extracted from liquid HLW, fixed on sorbents and incorporated at a high temperature into a crystalline structure of synthesized mineral-like formations. The techniques used at the final HLW conditioning stage may include cold compaction followed by high-temperature baking (CCB), induction melting in a cold crucible (IMCC) or self-propagating high-temperature synthesis (SHS).

Stable matrix materials suitable for the HLW conditioning include analogs of long-lived natural minerals based on complex oxides of titanium, zirconium, aluminum and...
rare-earth elements (REE). The most common RREs are light lanthanides (Ln) with a high level of yield during nuclear fission. Along with other fission products, these can be used to form a conserving matrix for the actinide (An) immobilization. Table 1 presents the content of elements in cooled spent fuel [1] which, together with minor actinides, shape the composition of the An-RRE fraction during the HLW fractionation.

Synthesized analogs of long-lived minerals based on titanates, zirconates and aluminates are the most common matrix materials for the immobilization of An, Ln and other elements of the An-Ln HLW fraction which form mineral-like (ceramic) matrices. Primarily, these are titanate and zirconate pyrochlores (RRE, An, Ca, …) (Ti, Zr)2O7 [2,3], titanate and aluminum perovskites (Ca, RRE, An, …) (Ti, Al)O3 [4,5] и Y–Al garnets (Y, Ln, An, Ca, …)3Al2O12 [5], which isomorphically incorporate HLW actinides (237Np, 239Pu, 241Am, 242Cm) with the chemical properties and ionic sizes close to those of light Ln.

The study continues an earlier [6] laboratory research on high-temperature synthesis of matrices based on Y–Al garnet with incorporation of it into the structure of Ce, Nd, Sm, Zr, Mo, U and 241Am. The said elements, considered as model waste, simulate the elements of the An-RRE HLW fraction that are isomorphic to them.

Self-propagating high-temperature synthesis (SHS), a highly technically and economically attractive energy-saving technique, was used to synthesize the matrix at high temperatures with all simulator elements being simultaneously fixed within the structures of its neoformations [7]. The major advantage of the method is that it uses an out-of-furnace technology to implement a high-temperature solid-phase exothermic process in the metal-ceramic SHS mode. In the course of this process, following the priming, e.g. by electrical ignition, spontaneous chemical transformations take place during a short-term heat-up of the reaction mixture to temperatures of 2000–2500°C in the combustion wave propagating in the initial powder-like or precompacted charge.

The SHS charge formation diagram is shown in Fig. 1.

The metal-ceramic SHS charge includes energy-forming components: fuel – metallic powders of elements with a great affinity to oxygen (Al, Ti, Zr), and oxidizers – oxygen-rich oxides containing elements of metals with a relatively low affinity to oxygen (Fe2O3, MoO3, MnO2, CuO and others). The charge also includes structure-forming additives containing oxides of elements which, together with oxides of fuel elements, form the basis for the target SHS product formation. These oxides are largely TiO2, ZrO2, Y2O3, Al2O3, SiO2, CaO and Ln2O3. The elemental composition of the SHS charge depends on the specific target product to be formed, a mineral-like matrix (MLM) suitable for environmentally safe disposal.

Radionuclides of HLW may be added to the SHS charge in the form of HLW calcinates or in the form of sorption calcinates containing radionuclides extracted from liquid HLW, based, e.g., on Al2O3 and TiO2, as it is used in this study with the employment of simulator elements, uranium and americium-241.

The SHS charge formulation is calculated in accordance with the most probable nature of the interaction between the charge components using the yttrium-aluminum garnet formation chemical equation

$$\begin{align*}
x \cdot \text{Al} + 0.5x \cdot \text{MoO}_3 + (2.5 - 0.5x) & \cdot [(0.102 \cdot \text{CeO}_2 \cdot 0.122 \cdot \text{Nd}_2\text{O}_3 \cdot 0.224 \cdot \text{ZrO}_2 \cdot 0.121 \cdot \text{MoO}_3) \cdot \text{Al}_2\text{O}_3] + (\frac{x}{2} - \theta) \\
+ 0.1 \cdot \text{UO}_2 & + 0.1 \cdot \text{CaO} + (0.536 + 0.173x) \cdot \text{Y}_2\text{O}_3 \\
= [\text{Ce}_{0.235 - 0.03x} \cdot \text{Nd}_{0.610 - 0.122x} \cdot \text{Zr}_{0.56 - 0.122x} \cdot \text{Mo}_{0.303 - 0.061x} \cdot \text{U}_{0.1} \cdot \text{Ca}_{0.1} \cdot \text{Y}_{1.072 + 0.346x}] \cdot \text{Al}_2\text{O}_3 + 0.5x \cdot \text{MoO}_3.
\end{align*}$$

The experimentally determined value “x” in the equation corresponds to the establishment of the best possible energy conditions of the SHS process.

Apart from the presented chemical equation (option I), two more alike processes were investigated in the study: option II where Sm2O3 (An simulator) is added to the charge instead of uranium, and option III where 241Am is added to the charge for option I.

For synthesized specimens, the content of the HLW radionuclide simulator elements in the charge was about 10% wt; the content of uranium was about 3% wt; and the specific activity of 241Am in the MLM specimen was 8·107 Bq/g.

In option III, the SHS process was implemented in a safety box of the KNZh-2 type accommodated inside a hot laboratory room for activities of radiation hazard class I. The front panel of the box was additionally clad with lead plates, and the windows were covered with lead glass. Inside the box, laboratory equipment was laid out as shown in Fig. 2. A graphite crucible of the diameter 60 mm with a graphite lid was used as the reaction vessel. The SHS charge was being thoroughly mixed, placed in the crucible, dried at a temperature of 120–130°C, and pressurized manually. A portion of

<table>
<thead>
<tr>
<th>Element</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Y</th>
<th>Zr</th>
<th>Mo</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of radioactive atoms</td>
<td>–</td>
<td>24</td>
<td>–</td>
<td>14</td>
<td>–</td>
<td>1</td>
<td>70</td>
<td>–</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>Total number of atoms</td>
<td>68</td>
<td>149</td>
<td>59</td>
<td>186</td>
<td>14</td>
<td>23</td>
<td>48</td>
<td>320</td>
<td>248</td>
<td>1115</td>
</tr>
</tbody>
</table>
the Al and Mg powder mixture was being placed onto the charge surface and ignited using a piece of burning thermite wire. The duration of the SHS process was 1–2 min.

After the process was initiated, the graphite crucible was closed with the graphite lid and a lid of a heat-insulating material (fireclay), following which the reaction unit (see Fig. 2) was covered tightly with a glass cap. In the course of the process, escape of a gas-aerosol phase from beneath the graphite lid and into the glass cap was observed. There was no visually observed release of aerosol in the form of smoke from beneath the cap and into the working volume. Several minutes after the end of the process, the atmosphere inside the cap was turning fully transparent due to the aerosol precipitation on the cap’s inner surface.

In the course of the process in option III, when 0.14 wt % of AmO₂ was added to the SHS charge, the extent of the ²⁴¹Am carryover from the reacting charge and into the gas-aerosol phase was measured and found to be 0.025% wt.
The quantity of the carried over americium was determined through the washing of the cap’s inner surface with hot nitric acid solution.

The resultant SHS product represented a crystallized material having cavities and caverns. The experimentally determined specific surface of this material was equal to 20 m²/g.

The results of an X-ray phase analysis of a specimen synthesized in accordance with option I using the presented chemical equation are shown in the diffractogram in Fig. 3. It can be seen that the specimen’s major phases are target yttrium–aluminum garnet (Y₃Al₅O₁₂) and elementary molybdenum. The presence in the diffractogram of minor quantities of phases, identified as CeO₂ and Y₂O₃, may be explained by the complexity of their identification with such a small content.

It follows from the diffractogram that the synthesized matrix material does not practically contain independent phases of simulator element oxides, including uranium, zirconium, and RRE oxides that have entered the Y–Al garnet structure while isolating themselves from the environment.

The longevity of matrix materials is estimated experimentally by measuring the rate of leaching into water of biologically significant radionuclides as specified in GOST [8]. The study involved a research into the water stability of the americium-241 containing matrix material synthesized in accordance with option III.

According to GOST [8], the ²⁴¹Am leaching rate was calculated using the formula

\[ R = \frac{A}{A_0 \cdot S \cdot t} \]

where \( R \) is the leaching rate, g/cm²·day; \( A \) is the activity of \(^{241}\text{Am} \) that has passed into water for the given time interval, Bq; \( A_0 \) is the specific activity of \(^{241}\text{Am} \) in the SHS product, Bq/g; \( S \) is the area of the specimen surface contacting the solution, cm²; \( t \) is the duration of the given holding time interval, days.

The results of measuring the rate of the americium-241 leaching into distilled water at 20–25°C are illustrated by the diagram in Fig. 4.

Conclusions

The obtained data prove that the synthesized matrix material is highly chemically stable, which is confirmed by very low rates of the actinide leaching from a specimen with a relatively large specific working surface (at a level of $10^{-9}$ to $10^{-10}$ g/cm²·day). In accordance with the existing requirements [9], the rate of leaching into water of another actinide (plutonium) shall not exceed $1 \times 10^{-7}$ g/cm²·day.

By many determining parameters, the method being developed for the HLW immobilization in the SHS mode is advantageously different from alternative solutions not being used commercially in conditions of growingly increasing quantities of accumulated high-level waste, due to the complexities involved in the implementation of the technology for processing high-level materials and stringent requirements to the quality of matrices.

References