Encapsulating of high-level radioactive waste with use of ceramic coatings

(Program of investigations)

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It is known that high-level radioactive waste (HLW) constitute a real danger to biosphere, especially that their part, which contains transuranium and long-lived radionuclides resulting during reprocessing of nuclear fuel industrial and power reactors. Such waste contain approximately 99 % of long-lived fission products and transplutonium elements among which the key products are

- ^{90}Sr, ^{93}Zr, ^{134}Cs, ^{99}Tc, ^{129}I and others;
- ^{241}Am, ^{243}Am, ^{242}Cm, ^{244}Cm and daughter products of their decay;
- U, Pu, Np (residual amount).

At present the concept of multibarrier protection of biosphere from radioactive waste is generally acknowledged. The main barriers are the physicochemical form of waste and enclosing strata of geological formation at places of waste-disposal.

Applied methods of solidification of HLW with preparation of phosphatic and borosilicate glasses do not guarantee in full measure safety of places of waste-disposal of solidified waste in geological formations during thousand years.

One promising way to improve HLW handling safety is placing of radionuclides in mineral-like matrixes similar to natural materials.

The other possible way to increase safety of HLW disposal places is suggested for investigation by experts of Russian research institutes within the framework of the present program is to introduce an additional barrier on a radionuclides migration path by coating of HLW particles.

The objective of the Program is carrying-out of investigations on the development of method of HLW encapsulating with use of protective ceramic coatings and study of the prepared capsules properties with substantiation of safety of their disposal in geological formations.

To realize the aim the Program will provide the performance of a wide circle of researches:

- **Analysis of composition and properties of HLW being subject to solidification and encapsulation**

  In virtue of analysis of activity and chemical composition of waste will be choose the forms (oxides or other stable compounds) and methods of preparation of waste for granulation.

  Fulfilment of this stage will allow to develop process of preparation of granules of specified types of waste appropriate for protective coatings deposition.

- **Analysis of published and experimental data on properties of coatings.**

  During fulfilment of this task shall be collected and analysed the data on the properties of protective coatings including

  - coefficients of diffusion of key fission products;
  - irradiation and corrosion behaviour;
  - strength and thermal strength of coatings.

  This will allow to justify irradiation and corrosion resistance of capsules for HLW disposal and their mechanical and thermal strength.

- **Designing, manufacture and mounting of lab-scale equipment for preparation of simulators and coating deposition on them.**

  Fulfilment of this task will allow to create the experimental installation with the control system and registration of key parameters of technological processes for research on encapsulation of HLW.

- **Investigation of coating deposition conditions on HLW simulators.**

  During fulfilment of this stage will be

  - manufactured HLW simulators;
  - determined conditions of coatings deposition;
  - developed capsule design requirement;
  - selected and justified capsule design.

  Completion of the task will allow to develop the paperwork of capsule for HLW and process of such capsules preparation.

- **Preparation and investigation of characteristics of encapsulated HLW prototypes.**

  The fulfilment of this Program part will allow to test the flow chart of HLW capsules preparation, to manufacture enlarged batches of HLW simulators and experimental batches of capsules, to study their characteristics including structure, chemical composition of coatings, deviation from stoichiometry, density, closed and open porosity as well as geometry of capsules and deviation from requirements.

- **Development of computation models and computer programs for investigation of processes during storage and disposal of encapsulated HLW.**
  During this task fulfilment will be:
  - laid down edge conditions of fission products mass transfer through capsule layers including estimation of heat source power in a capsule;
  - estimated fission product release through ceramic coatings at long-term storage.
    Solution of this task will allow to predict capsule storage duration, when protective properties will be kept.
- **Calculations for selection and substantiation of encapsulated HLW characteristics**.
  During this task fulfilment will be refined granules requirements, capsule requirements and design.
  Solution of this task will allow to refine capsule geometrical dimension, to lay down the final capsule requirements and to estimate their storage duration.
- **Complex analysis of the investigation results and preparation of the initial data for pilot installation design**

The protective barriers must meet the following key requirements:

- low permeability including low coefficients of diffusion of gaseous and solid fission products;
- high radiation and chemical resistance including in ground waters;
- high mechanical strength.

Based on the experience of development and operation of High-Temperature Gas-Cooled Reactors (HTGR) uranium/thorium - graphite fuel elements with BISO and TRISO-type coated fuel particles, **pyrocarbon and silicon carbide** in many respects **meet these requirements**. Coatings from these materials prepared by chemical vapour deposition in a fluidized-bed are characterized by a low porosity and gas-permeability, low diffusion coefficients of radionuclides at temperatures from 500 to 1300°C [1 - 3]. Sr and Cs effective diffusion coefficients in SiC (density 3.2 g/cm^3) at 1400°C, for example, are $<5\cdot10^{-17}$ and $<6\cdot10^{-21}$ m^2/s, resp. [3], and diffusion coefficient of Cs in pyrocarbon (density 1.85-1.90 g/cm^3) at temperature 1200°C is $\sim10^{-15}$ m^2/s and more exactly can be described by equation $\boldsymbol{D = 1.88\cdot10^{-2}\, exp\text{-}(60754/RT)}$ in a temperature range of 1000 - 1500°C [2].

In addition silicon carbide has excellent mechanical, thermal and chemical properties, in particular, it is a good corrosion resistant material. Silicon carbide, e.g., is not dissolved in inorganic acids even at the boiling temperature; concentrated alkalis poorly react with it.

Presence of free silicon in the reaction-bound SiC slightly reduces its corrosion resistance both in acids and in alkalis (Table 1).

Table 1. Silicon carbide corrosion resistance [4].

Corrosion environment	T,°C	*Δl,* μm/year	
		Pyrolitic SiC	Reaction-bound sintered SiC (12%Si)
98 % H_2SO_4	100	0.6	18
50% NaOH	100	0.6	<350
53% HF	25	<0.1	2.5
85% H_3PO_4	100	<0.1	3.0
70% HNO_3	100	<0.1	0.2
45% KOH	100	<0.1	<350
25% HCl	70	<0.1	0.3
10% HF+57%HNO_3	25	<0.1	<350

Such low solubility in the most spread acids in the nature - hydrochloric and sulfuric – gives solid grounds for supposing good corrosion resistance of silicon carbide in subsoil water containing salts of these acids.

Oxidation of SiC by oxygen and water vapour begins at temperatures above 400°C. It is known [5 - 7] that silicon carbide oxidation rate in dry oxygen is lower than of silicon. Addition of moisture increases both of silicon and of silicon carbide oxidation rates. However formed thermodynamically stable SiO_2 film passivates silicon carbide surface and prevents its further oxidation. Based on the data of [5 - 7] preliminary estimation of the maximum corrosion rate of an ampoule made of the reaction-bound sintered silicon carbide shown that oxide film 0.6 μm in thickness will be formed on its surface at temperature 250°C for one year.

Irradiation could effects on silicon carbide in conditions of storage. Swelling of pyrolitic, reaction-bound sintered and single-crystal SiC (fig. 1) at temperatures below 1000°C at least up to fast neutron fluence 5 10^{25} n/m^2 is practically identical [3].

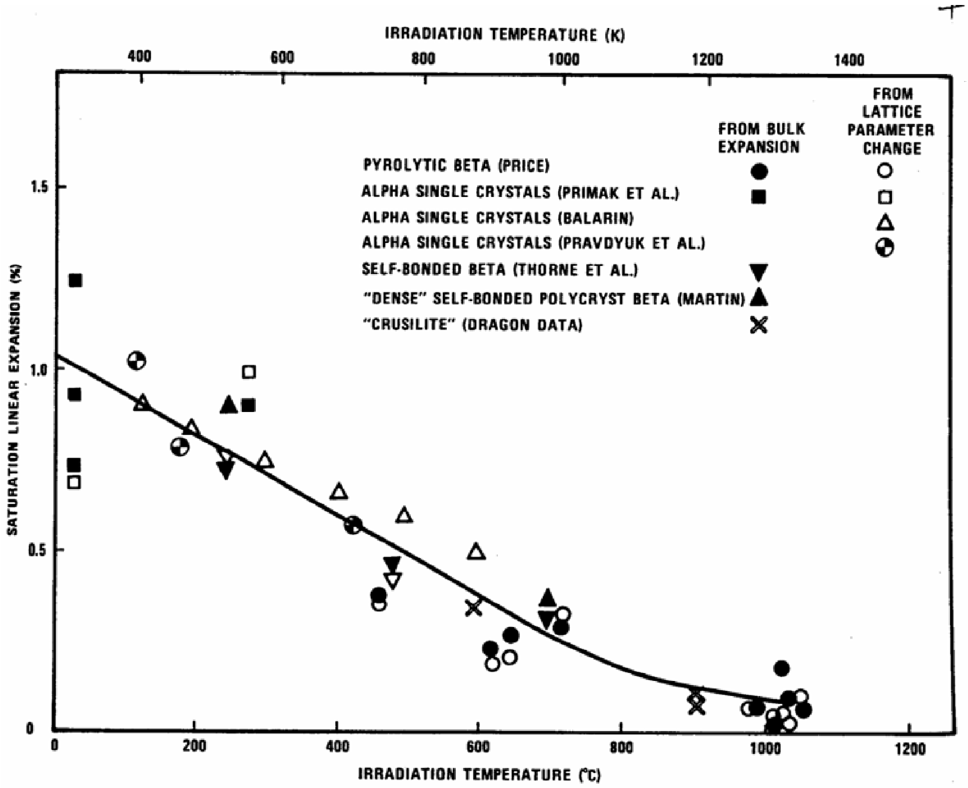

Fig. 1 Irradiation-induced expansion of SiC as a function of irradiation temperature (fluences between $3\cdot10^{24}$ and $5\cdot10^{25}$ n/m^2) [3]

We have shown also high chemical stability of LTI-pyrocarbon coatings in oxidative mixture consisting 98% H_2SO_4 and 60% HNO_3 at room temperature by lack of changes in morphology, macro- and microstructure of such coatings.

All these factors have predetermined a choice for investigations of:

- **Pyrocarbon** and **silicon carbide** materials as protective coatings on a granulated waste;
- **Silicon carbide** as a material of the container and/or a matrix together with glasses for creation of composites with coated waste granules.

The following materials will be considered as waste:

- separate fractions of fission products and transuranium elements;
- other products containing long-lived radionuclides (high-level radioactive sorbens formed during purification of liquid waste, pulps, calcites).

It is supposed to consider various encapsulating processes of fractionated HLW, for example

- conversion of HLW solutions into a solid aggregative state (calcites, granules of glass, sorbent, etc.);
- heat treatment of granules;

- deposition of protective coatings;
- placement of coated HLW granules or composites on their base in containers.

The latter are intended to be an additional barrier precluding radionuclides release during storage and disposal in geological formations.

The Program is calculated for 2.5 – 3 years.

Participation of experts in the fields of high-level radioactive waste processing and their disposal, CVD of ceramic coatings on fuel kernels, powder metallurgy, designing and material science from the leading russian institutes is foreshadowed for carrying-out of the Program.

The cooperation with interested foreign partners is proposed for joint realization of this Program, for example, in the form of an ISTC Project.

References

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