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TECHNOLOGY OF REPROCESSING HIGH-LEVEL WASTES BY METHOD OF SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SPHTS) INTO MINERAL-LIKE MATERIALS

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ABSTRACT

To reduce the risk of propagation of transuranium actinides, carbon-14 and other radionuclides contained in high-level radioactive wastes (RW) of NPPs, Rosenergoatom Concern has made up a decision to develop a technology of self-propagating high-temperature synthesis with production as the result of a ceramic matrix suitable for long-term environmentally safe burial of high-level nuclear wastes in deep-seated geological formations.

The handling of high-level RW (HLW) requires consistent implementation of a defense-in-depth concept. At present time, there is a broad international consensus on the necessity of burying long-term HLRW in deep-seated geological formations.

The system of barriers in the HLW handling should contain:

- a physical and chemical form of conditioned (reprocessed) HLW (packaging);
- a container with conditioned (reprocessed) HLW inside;
- a leak-tight enclosure of subsurface storage rooms (interim storage);
- a combination of the safety features of the inherent (passive) and engineered barriers involved in burial in deep-seated geological formations.

Subjected to recycling (conditioning with transformation into ceramic packaging) are spent fuel spills, HLW from reprocessing of nuclear fuel, high-level graphite moderators of reactors.

The selection of the graphite HLW SPHTS reprocessing method is based on the following main conditions:

- excluding the formation of considerable amounts of gaseous products during reprocessing due to the presence of a considerable quantity of the biologically significant long-lived radionuclide of ^{14}C in graphite;
- producing the end target product characterized by a high chemical stability and ensuring reliable fixation of radionuclides in the matrix;
- simplifying the process, especially as to high-temperature chemical transformations;
- ensuring the shortest time of the interaction products being under the maximum process temperature.

The proposed method of reprocessing the graphite HLW that immobilize radionuclides into a thermally, chemically and radiation stable carbide and corundum matrix is based on the SPHTS process run as a chemical reaction based on the C+Al+TiO_2 system where the component of C is irradiated graphite of the RBMK reactor core moderators.

The submitted paper is a report on the results of the R&D activities for optimizing the SPHTS technology on a pilot plant using non-irradiated graphite and fuel spill simulators (HLW).

Keywords: HLW-graphite, SNF spillages, self-propagating high-temperature synthesis, ceramic matrix.

1. INTRODUCTION

1.1. During operation of the uranium-graphite reactors large amounts of the radioactive waste (RAW) is generated in the form of irradiated graphite. A main radionuclide responsible for graphite contamination is ^{14}C. Sometimes fragments of the spent nuclear fuel (so-called SNF spillages) and fission products in graphite are resulted from loss of the fuel element and channel tightness in case of accidents. Such areas of the graphite stack belong to a category of high-level activity (HLW-graphite) and require the appropriate management. Development of a technological process for handling the irradiated graphite containing the SNF spillages is provided for in a Program on removal of the SNF spillages from the stack, systems and components in the Beloyarsk NPP Units 1 and 2 shut down for decommissioning.

1.2. By now 12 Russian uranium-graphite reactors have been shut down for decommissioning, namely 10 production uranium-graphite reactors (PUGR) and two power AMB reactors of the Beloyarsk NPP first phase. There were incidents associated with loss of the fuel element tightness and ingress of uranium to the graphite stack in both production and power reactors. Usually, graphite radwaste generated from the graphite-fabricated items (blocks, bushings) during repairs of the stack are highly contaminated, deformed and fragmented (debris, grit, dust), and are in need of treatment. According to the safety regulations NP-002-97 [1] on the nuclear plant RAW management, the fine and dust-like solid radwaste shall be transferred to the monolithic form as transition to a stable, chemically and radiation resistant form is one of the main objectives of the RAW treatment. A long half-life of the contaminating radionuclides results in a specific problem connected with the necessity of long-term environmental isolation of the mentioned solid radwaste. For the purpose of reduction of the risk of spread of transuranic actinides, carbon-14 and other radionuclides contained in the NPP HLW, the Rosenergoatom concern decided to develop a technology of self-propagating high-temperature synthesis (SPHTC) obtain a ceramic matrix suitable for long-term and ecologically safe deep geological disposal of the high-level radwaste of nuclear industry.

1.3. For the high-level waste (HLW) management, the defense-in-depth principle is required to be consistently implemented [1]. Today there is a wide international consensus as to the necessity of deep geological disposal of the long-lived HLW [2].

In our opinion, a system of barriers for the HLW management should include:

- Physical and chemical form of the conditioned (treated) HLW-graphite (package);
- Cask to contain the HLW-graphite conditioned (treated);
- Leak-tight enclosure of the surface storage facility (which is a temporary one until a national geological disposal is established in the country);
- Set of protective properties of natural (passive) and engineered barriers to be used for the deep geological disposal.

1.4. When selecting the HLW-graphite treatment methods, the developers were based on the following conditions:

- Exclusion of generation of noticeable amounts of the gaseous products in the process of treatment because of considerable amounts of the biologically significant long-lived ^{14}C radionuclide contained in the graphite;
- A final target product shall be of high chemical stability and provide reliable in-matrix fixation of the radionuclides;
- Simplicity of the technological process, in particular – in terms of performance of high-temperature chemical transformations;
- Minimization of time of exposure of the interaction products to the process maximum temperature.

The proposed HLW-graphite treatment method to immobilize the radionuclides into the thermally, chemically and radiation stable carbide-corundum matrix is based on a SPHTC-process according to the chemical reaction in the system $C+Al+TiO_2$ [3,4,5], where the component C is irradiated graphite of the RBMK reactor core moderators. The resulted final products of the treatment can be directly transported to the disposal.

The process includes crushing the HLW-graphite , its mixing with reagents, electrical initiation in the process, and then the following solid-phase, exothermic and spontaneous reaction takes place in the burning wave:

$$3C + 4Al + 3TiO_2 = 2Al_2O_3 + 3TiC \qquad \Delta H^0_{1700} = -373{,}6 \text{ kJ/g-at C.}$$

The process in the mode of SPHTC-compacting (product to be pressed after burning) results in a dense ceramic matrix. Strength of radionuclide fixation is linked to inclusion in the crystal lattice of the matrix. The TiC lattice includes ^{14}C; actinides, rare-earth element (REE) radionuclides, ^{90}Sr, etc. are included in the lattice of aluminates, yttrium-aluminum garnet generated during interaction of part of Al_2O_3 with the yttrium oxide (Y_2O_3), insignificant amount of which can be incorporated in the initial SPHTC charge.

2. RESULTS OF SPHTC-TECHNOLOGY ADJUSTMENT AT NIKIET EXPERIMENTAL FACILITY

On the basis of the existing equipment, and with support of the State Research Center - Physics and Power Institute and RADON, a process bay was established at NIKIET to implement a complete cycle of the simulating HLW-graphite treatment by the self-propagating high-temperature synthesis method, where basic process parameters were adjusted.

The facility is shown in Fig. 1.

The facility is comprised of three main units:

1) graphite preparation unit;
2) charging and mixing unit;
3) SHS-conditioning unit.

Below is a sequence of the main SPHTC technological processes:

- crushing of graphite blocks;
- pounding of graphite to the required size;
- mixing of the charge (C +Al +TiO2);
- feeding of the crucible;
- SPHTC-conditioning to be carried out:
  - outdoors; or
  - in the process box.

To implement the SPHTC-process in the environmentally isolated facility, a process box, whose picture and general view are given in Fig. 2, was developed, manufactured and tested at the required working pressure (up to 3 atm gauge).

Depending on SPHTC conditions, the upper part of the crucible was charged with the titanium powder (outdoor tests), or the fuse was remotely placed (tests in the process box), which were the process initiators.

2.1. Outdoor experiments

The Fig. 3 shows the outdoor SPHTC-conditioning stages in the Al crucible.

The SPHTC-process is based on spontaneous exothermic metal-thermal processes.

Peculiarities of the chemical SPHTC-based interactions are associated with the high temperature of interaction, when fast internal self-heating is due to release of the considerable amount of chemical energy. The chemical transformation is concentrated in the burning area that moves in the initial powder-like or pre-pressed charge. Speed of the burning wave propagation is 1÷5 mm/s, which determines short-term exposure of the interaction products to the maximum temperature (~2100 °C), when however the chemical transformations are fully implemented. In case of the chosen scenarios of HLW-graphite treatment processes in the metal-thermal SPHTC mode there is practically no stable gaseous products generation, which facilitates the development of the chemical reactors operating under the leak-tight conditions.

At selection of options for the chemical transformations, the developers were based on the necessity of synthesis of such final products, whose structure will reliably fix the elementary radionuclide ^{14}C contained in the waste, and actinide radionuclides and their fission products contained as oxides.

According to the proposed HLW-graphite treatment method, the waste radionuclides are incorporated into the matrix, which is a composite material composed of stable carbides to immobilize ^{14}C, and mineral-like aluminate-based phases to immobilize actinides, their decay and fission products.

The above components of the composite matrix being notable for thermal, chemical and radiation stability and longevity, are to reliably fix, in their structure, the actinides, REE elements and strontium. These matrixes are the first protective barrier that environmentally isolates the wastes.

The Fig. 4 shows three basic types of crucibles tested at the NIKIET facility made of:

- aluminum shell;
- asbestos-insulated tin shell;
- chamotte-insulated tin shell.

According to the results of study of the final product received in the open air with exhaust ventilation, compositions obtained with the high-volume heat-insulated crucibles (Fig. 5) are of the best appearance and mechanical strength, and do not show any flaws or thermal micro-cracks.

The main advantage of this SPHTC-process in the chamotte-insulated crucibles is slow cooling, which provides a minimum number of the thermal cracks in the final product as compared with all three tested crucibles, which explains, in particular, minimum heat losses in the process (heat of the exothermal reactions is neither lost in the form of radiation – like in the aluminum crucible, nor directed to melting of asbestos; instead it is used to support the synthesis reaction).

From this point of view, it would be useful to increase the crucible's capacity: the energy release is increased proportionally to the volume, i.e. to the third power, and the heat removal – proportionally to the surface, i.e. to the second power only.

Strength test results showed that strength of the carbide-oxide matrixes satisfies the requirements set forth to the solidified high-level radwaste. Inclusion in the charge of additives in the amount of up to 20% would allow to increase compression strength of the final product by a factor of 1.5, i.e. from 8.7 to 13.3 MPa.

2.2. Experiments in the process box

At testing it was noted that quality of the final products received at the leak-tight process box is distinctly better than that of the similar products received in the open-air environment; however, earlier it was considered that this factor had no influence upon the concerned SPHTC-process (Fig. 6).

According to the experiments performed to study the gas-release process, the SPHTC-process in the leak-tight box is not accompanied with any significant gas release, and when the box is completely cooled down, even little rarefaction is registered.

Estimations of entrainment of the biologically significant nuclides by the gaseous phase, based on the experimental data are given below:

- uranium entrainment	under 0.001 mass %;
- carbon entrainment	under 0.1 mass %;
- cesium entrainment	under 2.1 mass %.

Such low values are explained, in particular, by the fact that during the wave top-down burning being implemented in the SHS-process, the composite's upper layer, when getting cold, prevents intensive removal of the components from the reaction mix.

2.3. Problems to be resolved during future R&D

According to water-resistance tests (Fig. 7), water absorption of the carbide-oxide matrixes exceeds 30%, and values received for the radionuclide lixiviation rate (for Cs and for α-emitters) do not still meet standard (GOST) requirements to the high-level wastes. A task for improvement of the final product's water-resistance is inseparably linked to a task for reduction of the product's open porosity.

A main line of lixiviation reduction is in the field of use of the product's hot pressing (SPHTC-compacting).

A range of the immediate tasks associated with SPHTC-mode for graphite HLW treatment includes:

- approbation of technologies that use hot pressing of the product in the SHS-process (to reduce porosity);
- thorough studies of the process parameters, and characteristics of the product of the SNF spillage radionuclide immobilization;
- performance of a set of accurate experiments with the purpose of selection of the crucible's sizes and design, including those with actual reactor graphite of the Beloyarsk NPP.

At the meeting organized at Rosenergoatom concern in the 2003 year the following conception was agreed for the "emergency", "unscheduled-storage" graphite of the Beloyarsk NPP:

1) Graphite blocks are to be sorted to two groups: high-level with spillages; and medium- and low-level (as per categories established in SPORO-2002).
2) HLW is to be transported to the treatment site (e.g. to hot cells), and treated in the SPHTC-process mode; then the received packs are to be further placed in the cask and transported, first, to the temporary storage, and then – to the final disposal site;
3) the medium- and low-level wastes (graphite blocks, breakage) are to be conditioned by superficial soaking (F preservative, or inorganic phosphate preservative, or …), with packs being placed in thin-walled metal casks for temporary storage in the Beloyarsk first-stage rooms cleared from the contaminated equipment after its dismantling.

To minimize the treatment costs, it would be necessary to reduce the volume of the primary HLW-graphite , when mainly spillages are SPHTC treated, and the irradiated graphite is used only as one of the charge components. In this connection, thoroughness of the primary sorting of the unscheduled graphite to high-level radwaste (first of all – SNF spillages) and low- and medium-level graphite, considering the opportunity of the surface decontamination of the graphite blocks, takes on special significance.

According to the stated conception for the Beloyarsk emergency graphite removal, the pilot facility is assumed to be comprised of the following main parts (Fig. 8):

1) robotic facility (RF) for gripping, sorting and transferring of the graphite blocks (GB), graphite fragments and spillages from the storage sites to the high-level graphite RAW preparation unit;
2) HLW-graphite preparation unit;
3) component storage and charge preparation unit;
4) SPHTC-conditioning unit;
5) unit for final product packing for long-term storage.

3. FEASIBILITY EVALUATIONS OF SPHTC TECHNOLOGY BEING UNDER DEVELOPMENT

To provide an initial substantiation of the suggested HLW handling technology, the preliminary feasibility evaluations have been performed at the present R&D study with regard to development of a pilot plant for SPHTC conditioning of HLW-graphite of Beloyarsk NPP as compared with the possible options of irradiated graphite containerizing .

The feasibility evaluations were made in consideration for three options of graphite blocks (GB) processing and conditioning.

Option 1 (use of a new SPHTC technology) – processing of GB that involves separation of HLW-graphite fraction, its grinding, processing based on SPHTC technology, packing into concrete shielded containers for further storage and disposal in near-to-ground disposal sites. MLW (LLW)-graphite fraction is not subject to processing and is sent in metal containers to long-term storage and disposal, also in near-to-ground disposal sites.

Option 2 – processing of GB that involves separation of HLW-graphite fraction, its grinding and packing into special containers for long-term storage and further disposal in underground storage facilities. MLW (LLW)-graphite fraction after grinding and packing in metal containers is directed to interim storage and then to disposal in near-to-ground disposal sites.

Option 3 – processing of GB that involves waste grinding and packing in concrete shielded containers for long-term storage and further disposal in underground storage facilities.

The findings of the expert feasibility evaluations of processing HLW-graphite being stored in "unauthorized" way at BNPP using SPHTC-technology conditioning are given in Table 1 below.

Table 1 . A comparison of the options of BNPP-stored HLW-graphite conditioning

Name	Measuring unit	Option 1	Option 2	Option 3
1. Total amount of graphite, including (received):	t	1637	1637	1637
- HLW;	t	27.3	27.3	
- MLW (LLW)	t	1609.7	1609.7	
2. Transfer cask for RW:				
– steel containers;	pc	-	376	-
– metal containers;	pc	1937	1937	-
– concrete containers	pc	223	-	1263
3. Capacity of containers to be stored in:				
– near-to-ground disposal sites;	m^3	2308	1973	-
– deep geological disposal sites	m^3	-	40	4585
4. Duration of :				
– conditioning period;	yr	2.2	2.2	2.2
– storage filling in;	yr	2.2	2.2	2.2
– storage service life	yr	47.8	47.8	47.8
5. Updating of expenditures	times	1.19	1	3.06

Certain advantages of option 2 as compared to the suggested SPHTC technology (≈ 19% in terms of total costs) can be explained, first of all, by inadequate optimization of this technology at the present stage of its development. It should be also noted that option 2 implies storage of some amount of HLW in a deep geological disposal. At the moment there are no plans in Russia to construct such disposal sites. Therefore, option 1 involving the use of a new SPHTC technology is considered as a reasonable solution.

4.CONCLUSIONS

4.1. Results of the SPHTC-technology adjustment at the NIKIET facility confirm the possibility of resolving the problem of HLW-graphite management (first of all – for the Beloyarsk damaged reactor graphite where SNF spillages are contained).
4.2. Based on the results of the preliminary feasibility evaluation of the different options of container-based storage, it is recommended to proceed to the more detailed development of the suggested SPHTC-conditioning technology for HLW-graphite of BNNP.
4.3. The Russian R&D program in the area of SPHTC-technology includes the following activities:

- a number of the process parameters are to be perfected, including use of the SPHTC-compacting technology at the NIKIET and ISMAN pilot facilities,
- a set of the SPHTC-product characteristics is to be studied at the RADON facilities;
- treatment modes are to be adjusted with the use of the irradiated reactor graphite at the pilot facility in hot cells of IRM;
- a pilot facility for Beloyarsk NPP is to be established for HLW treatment by the SPHTC- method.

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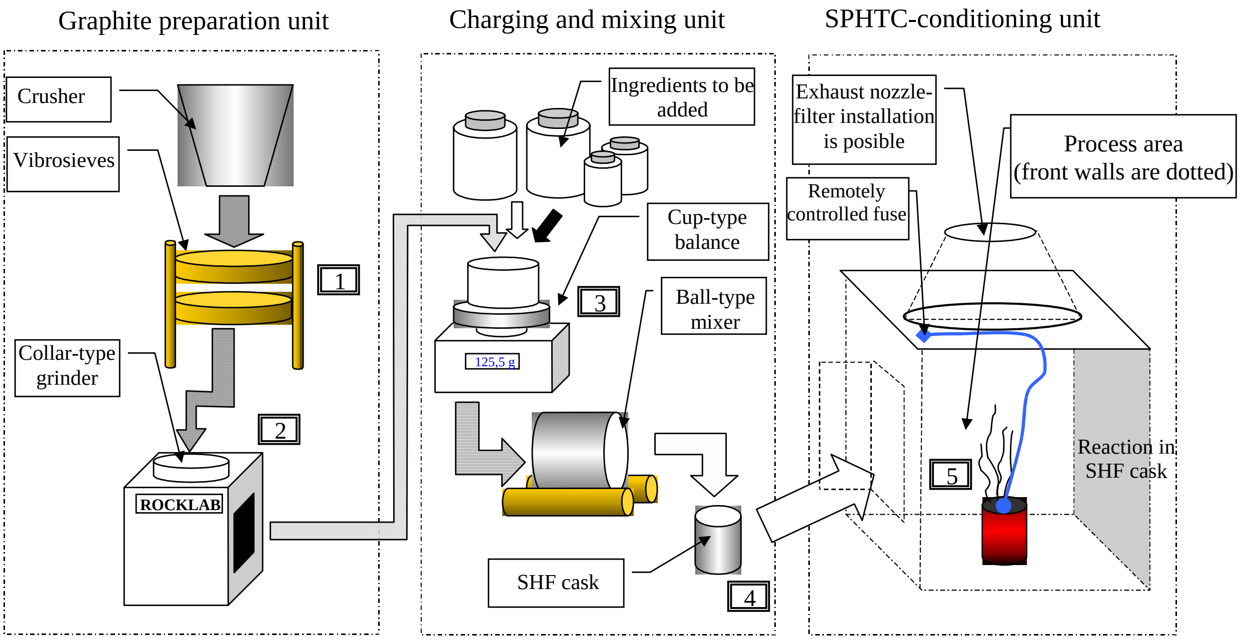
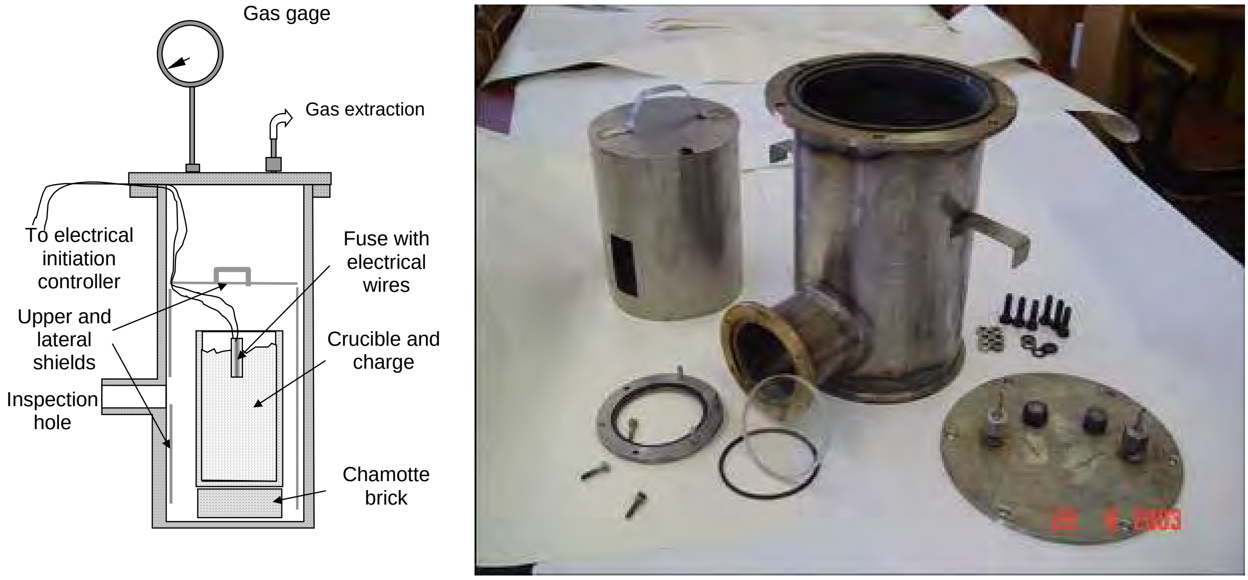


Fig.1. NIKIET SPHTC-Facility



a) Layout

b) Implementation (knocked-down)

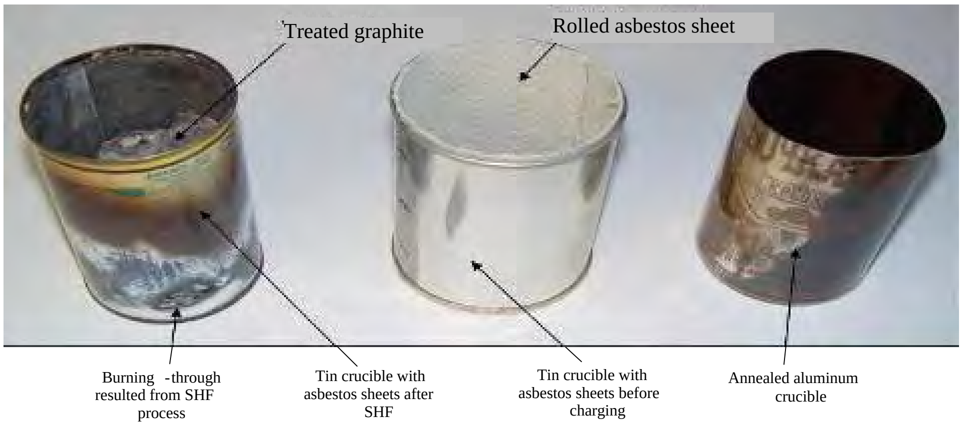
Fig.2. Process Box at the NIKIET Test Rig

a) before start b) initiator's ignition c) charge burning d) burning wave atop

e) wave's displacement f) end of burning (t=2'40") g) cooling down (t=4') i) getting cold (t=22')

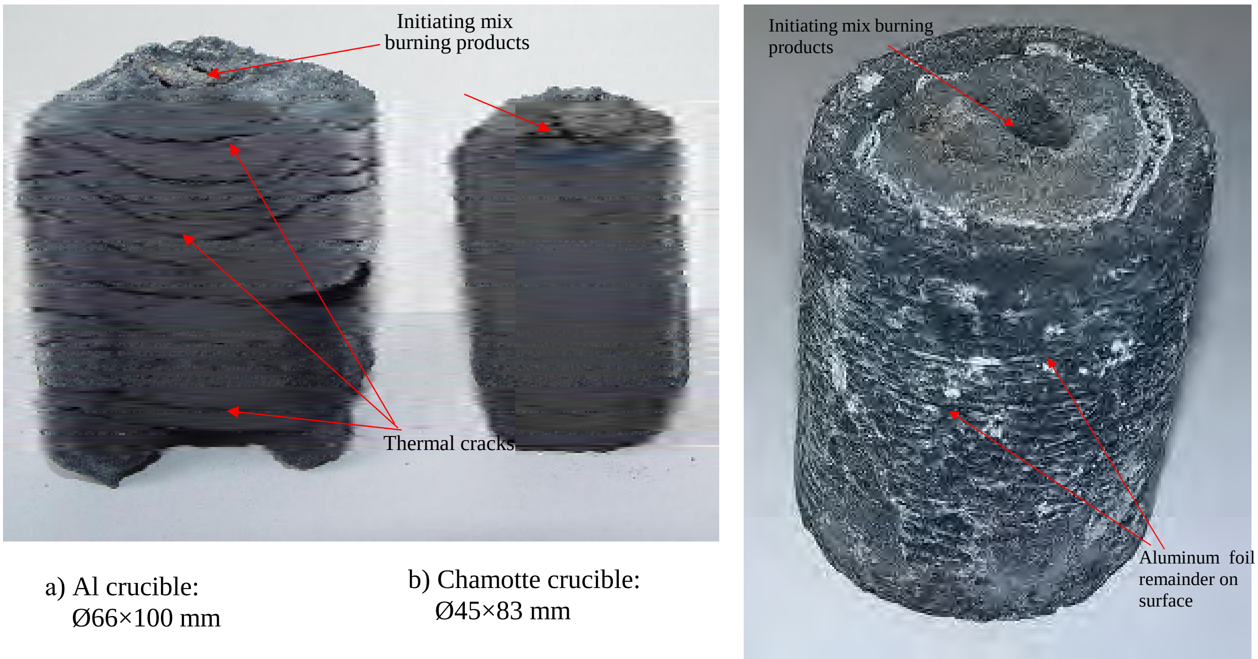
Fig. 3. Outdoor SPHTC in Al Crucible

1) Tin + asbestos 2) Al;



3) Tin + shamotte

Fig. 4. Crucible Types

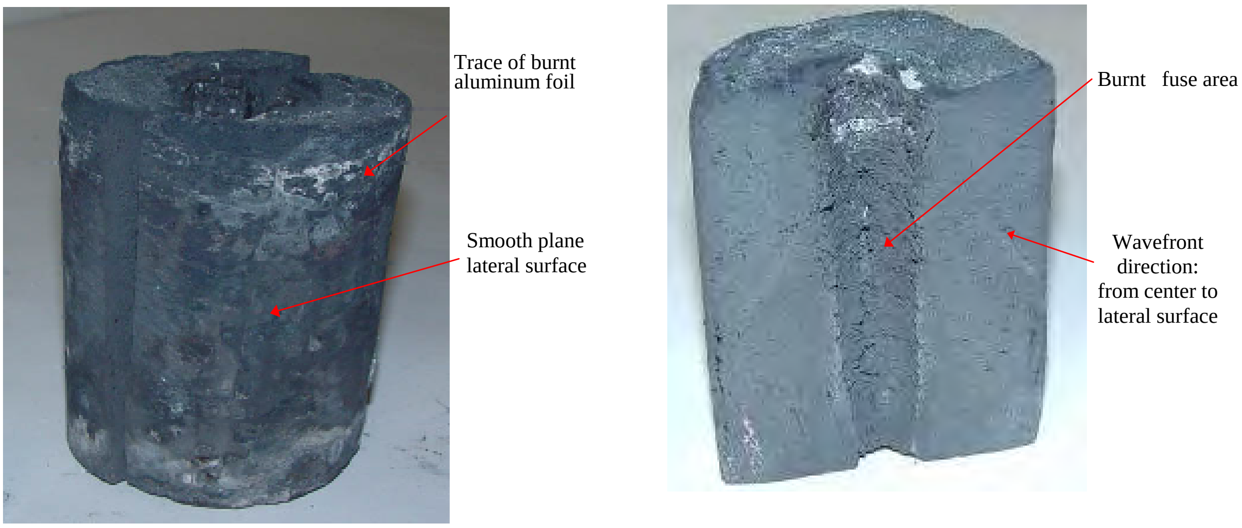


a) Al crucible:
Ø66×100 mm

b) Chamotte crucible:
Ø45×83 mm

c) Major chamotte crucible:
Ø77,5×106 mm

Fig.5. Carbide-Corundum Composites (outdoors)



a) Outer surface

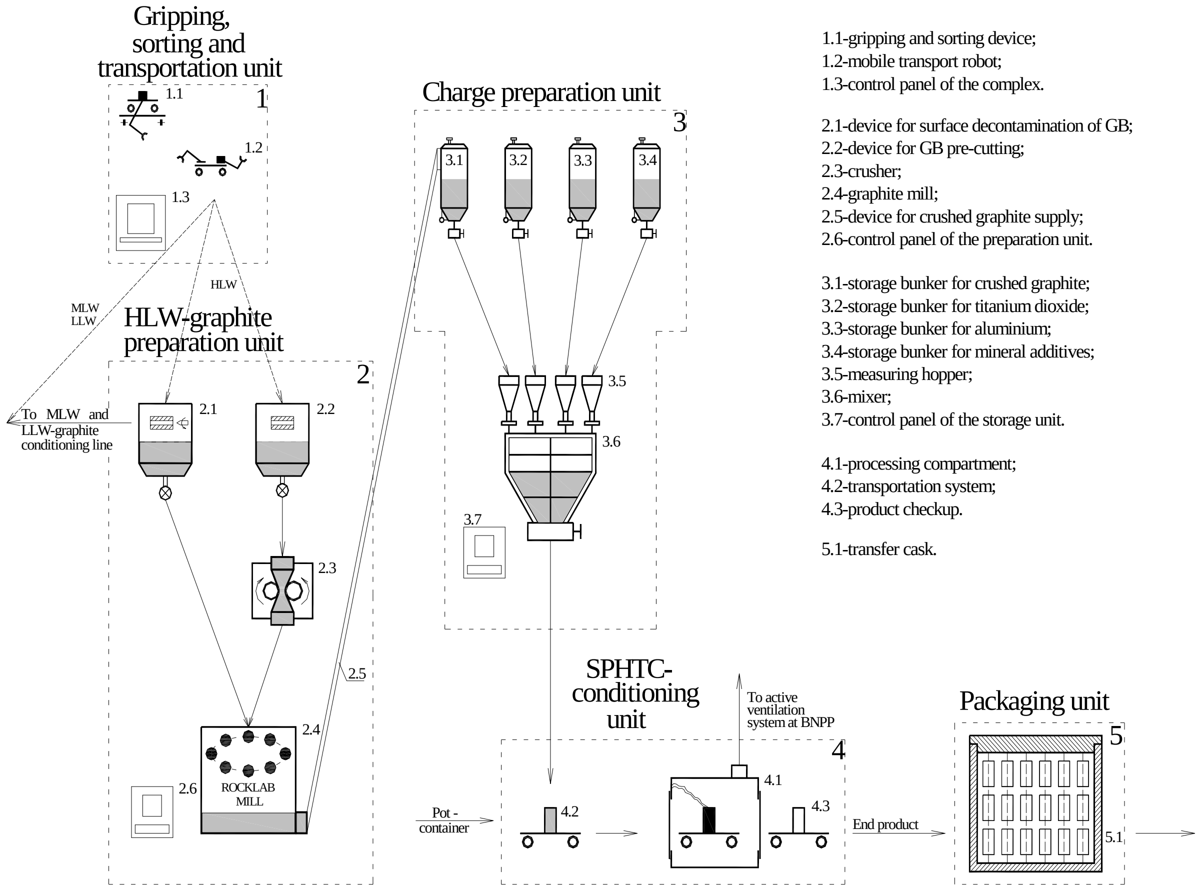
b) Cross section

Major chamotte-insulated crucible with central fuse

Fig.6. Carbide-Corundum Composites (in box)

Parameter	GOST 50926-96	SHF-2003
1. Chemical stability (**lixiviation rate**) g/($cm^2\cdot$day): **Cs-137** **Sr-90** **Pu**	**$<1\cdot10^{-6}$** **$<1\cdot10^{-6}$** (90 days) **$<1\cdot10^{-7}$**	**$(1\div4)\cdot10^{-5}$** **$(3\div4)\cdot10^{-5}$** (28 days) **$1.7\cdot10^{-6}$**
2. **Volumetric homogeneity:** - structure - uniformity in micro-components, %	**Homogeneous** **±10**	РФА – **homogeneous**
3. **Thermal stability, °C**	**>550 °C**	**> 2000 °C**
4. **Radiation stability** (paras 1 and 2): **-β and** γ Gy **-α** disintr./s	**1·108** **1·1018 - 1·1019**	
5. **Mechanical strength,** kN/cm2: **- compression**	**>0.9**	**0.87(1.43)-1.33(1.5)** In parallel with (at right angle to) fibres
6. **Thermal constants:** **-α**, 1/°K **-λ** (20-500 °C), W/(m·K)	**<9·10-6** **1-2**	
7. **Gas release**	**Not allowed**	None

Fig. 7. Study Results



1.1-gripping and sorting device;
1.2-mobile transport robot;
1.3-control panel of the complex.

2.1-device for surface decontamination of GB;
2.2-device for GB pre-cutting;
2.3-crusher;
2.4-graphite mill;
2.5-device for crushed graphite supply;
2.6-control panel of the preparation unit.

3.1-storage bunker for crushed graphite;
3.2-storage bunker for titanium dioxide;
3.3-storage bunker for aluminium;
3.4-storage bunker for mineral additives;
3.5-measuring hopper;
3.6-mixer;
3.7-control panel of the storage unit.

4.1-processing compartment;
4.2-transportation system;
4.3-product checkup.

5.1-transfer cask.

Fig. 8. SPHTC-Facility for Beloyarsk NPP

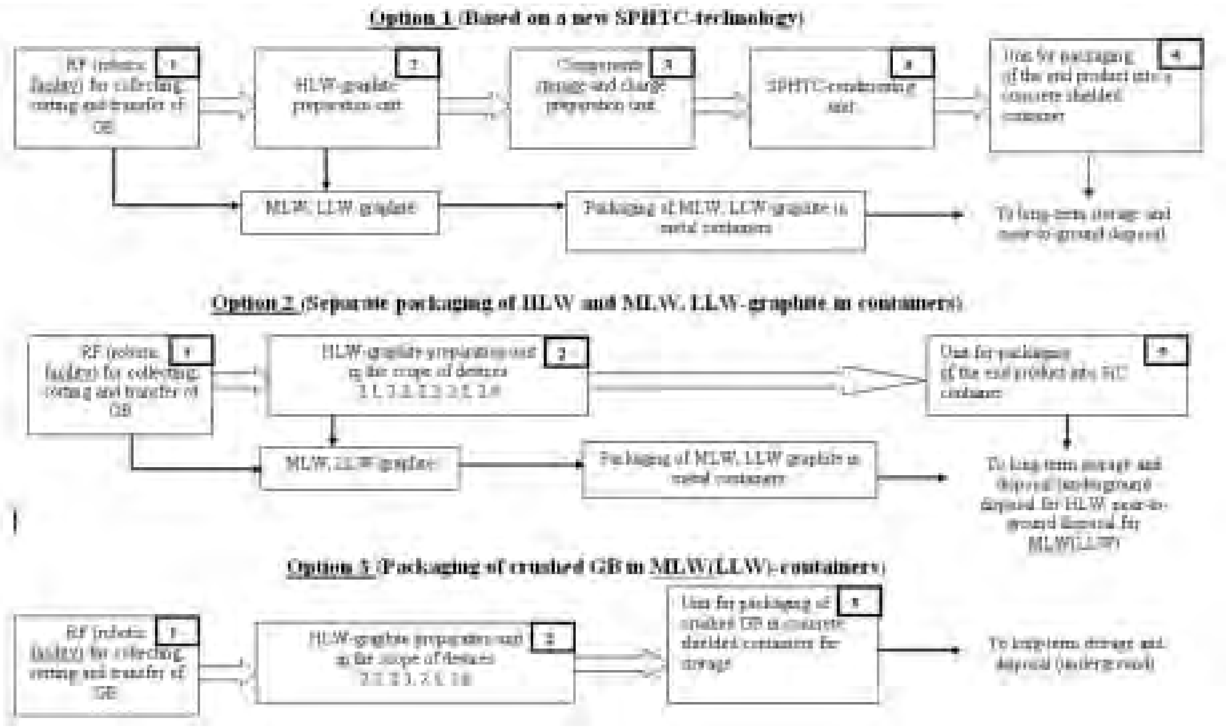


Fig. 9. The schematic diagrams of graphite processing options
($\boxed{5}$ *- the number of the plant unit as per Fig. 8)*