State of development of the heavy coolant quality support and control system for NF BREST-OD-300

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Abstract. Liquid lead has been chosen as the coolant for nuclear power plants with inherent safety in Russian Federation. Its physical and chemical properties offer distinct advantages over other types of coolants in FR with inherent safety, but this coolant also possesses certain technological challenges in the course of reactor operation. Heavy liquid metal technology management system for BREST-OD-300 reactor consists of a number of high-end technological devices designed to operate and maintain crucial parameters of lead coolant for decades. Development of these devices required innovative and creative approach as well as strong verification procedures. This presentation will give recent updates on the development of oxygen sensors, mass-exchange devices, hydrogen purification system, coolant filter, hydrogen sensors, which combined present Coolant quality control and management system.

1. Introduction
Liquid lead was selected in the Russian Federation as main coolant for natural safety fast reactors. Its physical and chemical properties provide certain advantages compared to other coolant types in natural safety reactors, however, its use is associated with certain process challenges in the course of NF operation.

The heavy coolant quality support and control system of NF BREST-OD-300 consists of a number of high-tech devices aimed at functioning and support of coolant’s key properties during decades of operation. Development of these systems required an innovational approach, as well as many years of works over their justification.

2. Heavy liquid metal coolant (HLMC) justification history
The liquid lead is suitable for its use to cool the nuclear reactor due to the following properties.

Lead has good nuclear and physical properties, has a small neutron-capture crossing allowing it being used as a coolant in reactors exploiting intermediary and fast neutrons. Lead weekly activates under the reactor conditions and is explosion-proof. Its steam pressure is low, boiling temperature is high (~ 1750 °C), allowing it having low pressure at reactor contour I. Lead is comparatively cheap and it can be produced in large quantities.

Besides, by its physical and chemical properties, lead is close to lead-bismuth eutectic alloy. The last has been successfully used as a coolant of nuclear reactors of transportation installations for many years. A lot of data about physical, chemical, thermal and physical and other properties of the alloy were accumulated. This coolant technology and means for its implementation have been developed.
The methodological and experimental bases created can be used for justification of the lead application as the power reactor coolant.

The above-stated supports development of BREST-OD-300 reactor, which is carried out under the control of Dollezhal R&D Institute of Power Engineering (NIKIET) with involvement of numerous experts from various scientific centers.

At the same time, to justify the possibility of lead use for cooling BREST-OD-300, a number of studies and development were required. Their main directions:

- detailed study of the lead coolant;
- development of the lead coolant technology applicable to the specific nuclear reactor with certain parameters and design.

This is due to the following reasons:

- the global practice lacks the experience of use of lead or its alloys at facilities, which scale and resource are similar to that of BREST-OD-300; the lead and bismuth coolant was used at relatively small power units, where equipment layout and coolant circulation contour were in general materially different from such of BREST-OD-300.

The works in the specified directions have been intensified since 1989 under justification of BREST reactors. Until 1999, main efforts were aimed at the proof of the principal possibility and identification of specific features of liquid lead handling under the conditions of the closed circulatory contour, elaboration of filling modes, launch and exploitation of experimental contours, review of certain issues of mass-transfer and mass exchange (mainly corrosion of structure steels, behavior of impurities), applicability of processes of the lead-bismuth coolant technology in liquid lead contours. Currently as a result of the series of estimate and experimental works performed, as well as the analysis of the experience of justification and application of a lead-bismuth coolant of many years, the lead coolant technology has been elaborated in general. The coolant technology is used to describe the whole set of organizational and technical events, processes and systems (means) of implementation thereof, performed and carried out in order to ensure given (required) contour purity and corrosion resistance of its construction materials upon the design, launch, repair and operation of the experimental stand or the reactor facility. The heavy coolant quality support and control system of NF BREST-OD-300 serves as main tool of the lead coolant technology implementation. Its creation is mainly based on the set of already existing and newly obtained or confirmed following study results.

3. Interaction of liquid lead and structural materials and oxygen

Many chemical elements and compounds, including components of structure materials, dissolve in lead. This may result in destruction of materials and contour insulation. The rate of dissolution (corrosion) of materials can be reduced efficiently if steels are covered with protective films based on iron, chrome oxides. Liquid lead actively reacts with oxygen. This may result in generation of slags (phases containing oxides of the coolant itself, components of structure steels, etc.), which may deposit on the contour surface, deteriorating its thermal and hydraulic properties [1].

Quantity of oxygen in the coolant itself and the contour in general is a very critical factor responsible for good contour operation. Excess leads to contours slagging. Disadvantage - to dissociation of protective oxide coatings on structure materials and corrosion processes onset. Therefore, for successful operation of NF BREST-OD-300, it is necessary to regulate the coolant quality, i.e. to support the optimal quantity of impurities (oxygen, oxide compositions based on structure materials, etc.).

It is also necessary to take measures aimed at prevention of staining the gas space equipment and cleaning the gas circulating through the gas space of the reactor from lead evaporation products, metal corrosion and other impurities.

4. Impurities in a coolant

Impurities, their quantities, forms of existence and composition may and must have an impact on the processes of mass-transfer in contours with liquid lead, its properties, and the NF operation in general.
The following lead ore accompanying elements relate genetic (initial) impurities: Cu, Te, Bi, Ag, Au, Sn, As, Sb, Zn.

At this time, it is assumed that to fill in contour I of NF BREST-OD-300, lead containing very little impurities, which will have no significant effect on physical and chemical processes to take place in future in the circulation contour, will be used.

Composition, physical state and quantity of exploitation impurities depend mainly on the contour stage and conditions of operation.

In the course of the contour operation, after filling it with the coolant, majority of impurities are generated due to the interaction of the coolant and structure materials with air oxygen, which is usually associated with the contour insulation failure [1].

Additional impurities are generated from dissolution of the structure materials’ components. Dissolution may take place in case of direct contact of the coolant with the contour surfaces. In case of presence on the contour surfaces of oxide films, components diffusing into the coolant from the structure material through these films are dissolved.

Almost all impurities (mainly, Fe, and also Ni, Cr, Mn, Si etc.), getting to the coolant from the structure material due to dissolution or diffusion thereof through films, react with oxygen dissolved in the coolant or oxygen-containing compounds with formation of oxide phases of various composition. This results in that a part of oxygen is spent for thickening of oxide films at these steels, and the other part on oxidation of metal impurities excreted from steel to the coolant. Thus, gradual coolant deoxidation takes place in case of operation of any insulated contour. Various external and internal relatively to the contour oxygen sources are used for its compensation.

As was noted above, normal exploitation of the contour is possible only in case of support of strictly given range of oxygen concentration (activity) values in the coolant. If this condition is met, the mass-transfer process intensity is minimal.

The range of allowable (optimal) concentrations of dissolved oxygen is limited here with $1 \times 10^{-6} - 4 \times 10^{-6}$ (w.%) values. The low limit is determined with the iron oxide resistance at the temperature of 650°C, and the upper one - by the concentration of lead saturation with oxygen prior to crystallization at the minimum coolant temperature of 380°C. Maintenance of activity within this optimal range [2] excludes both oxygen impurity crystallization at cold contour areas and their filling, and the increased corrosion of contour structure materials under the conditions, when the coolant has no oxygen to form iron oxides and fixing defect oxide films on steels.

### 5. Coolant technology processes and methods

As a result of the calculation and experimental works, the following lead coolant technology methods were selected and used in further development:

- coolant and contour hydrogen cleaning;
- regulation of the coolant quality by its oxygen content using a solid-phase oxidizing agent;
- cleaning the coolant from solid phase impurities;
- cleaning the gas from particles and aerosols.

#### 5.1. Coolant and contour hydrogen cleaning

The method is based on the interaction between the coolant’s surface or flow and the contour with water and mixtures of hydrogen and water steam.

In the course of its application the coolant is cleaned from coolant oxides with pure Pb returned to the coolant. At the same time conditions for creation of Fe3O4 phase, i.e. the basis of protective oxide coatings are formed.

Use of mixtures of hydrogen and water steam for cleaning (at simultaneous reduction of oxygen content in the coolant) is most efficient if these mixtures are added directly to the coolant circulating flow. To do this, special devices (gas dispersers) are used to introduce the finely dispersed gaseous phase from the NF gas space to the coolant flow and the two-component “coolant-gas” flow is formed. During its circulation along the contour, the oxidizing and restorative gaseous phase is delivered to
local areas of the contour surface, including places of impurities, deposits concentration. When lead-based deposits interact with the restorative gaseous phase, partial or full hydrogen reconstitution of lead from these deposits take place with partial or full destruction of such deposits, correspondingly [3].

5.2. Solid oxidizing agent application
To regulate the oxygen content, namely, to increase its concentration in the coolant, solid oxidizing agents are used. The oxide material (PbO) is maintained within the limited circulation contour plot (reaction vessel), through which the coolant is passed. Here, the solidphase oxidizing agent contacting the coolant is dissolved with emission of oxygen, which then transported by the contour with coolant flow. By changing the temperature and (or) consumption of the coolant in the reaction vessel, the oxide dissolution rate may be controlled based on the contour needs in dissolved oxygen.

5.3. Coolant filtration methods and means
The most effective method to remove impurities from the coolant is filtration. This is especially effective to remove large particles (≥ 10 mcm) from the melt.

High-temperature conditions of filters operation (t ≥ 450 °C) and aggressive exposure of the lead coolant with slags make selection and justification of efficacy of filter materials the most important stage of studies.

Studies of fiber, granular and grainy materials for thermal stability of strength properties and chemical compatibility with the lead melt and slags were carried out, and candidate materials for coolant continuous cleaning filters were determined.

- Silica glass fabric.
- Carbon fabric, and combinations of carbon fabrics with silica and mullite silica glass fabrics.
- Mullite silica kaolin fabric.
- Needle-punched metal-fiber (metal-felt) fabric.
- Grainy granular material – αAl2O3-based spheres and abrasive grit made of Al2O3.

Above listed materials have passed material tests in the lead melt under static and dynamic conditions, as well as circulation stand at temperatures 450÷600°C based on the given resource of 360; 500 and 1000 hours.

The criterion of satisfactory compatibility of filter materials with the lead melt is absence of chemical reaction and destruction, as well as functional deterioration of properties and reduction of the material strength.

5.4. Coolant oxidizing potential control
Critical role of oxygen in assurance of normal operation of units with heavy coolants was mentioned above. Therefore, studies of almost all processes within the contours with lead coolant are carried out under the control of the oxygen impurity inside the coolant. Oxygen control is performed using oxygen sensors of thermodynamic oxygen activity. They function based on the galvanic concentration cell with a solid, oxygen ion conducting, ceramic electrolyte and the standard reference electrode. Zirconium dioxide is usually used as the solid electrolyte material stabilized with yttrium oxide (ZrO2 +Y2O3). Bi-Bi2O, Fe-Ft3O4, etc., are used at the reference electrode.

The electromoving force of the galvanic concentration cell reviewed is determined by the following ratio:

\[ E = \frac{RT}{4F} \ln \frac{p_{O_2}^\prime}{p_{O_2}^\prime} \]

R – gaseous constant, F = 96500 coulomb/mole, Faraday constant \( p_{O_2}^\prime \) and \( p_{O_2}^\prime \) - partial oxygen pressure over the reference electrode and liquid lead, correspondingly.
Relation of the e.m.f. of a cell (e.g. reference electrode Bi-Bi$_2$O$_3$) with the dissolved oxygen concentration and its thermodynamic activity is represented as follows:

\[
E(mV) = 131.2 - 1.54 \cdot 10^2 \cdot T \cdot (1 + 6.61 \cdot \lg (a_0))
\]

\[
E(mV) = -389 + 0.326 \cdot T - 0.09992 \cdot T \cdot \lg (C)
\]

6. State of development of the heavy coolant quality support and control system for NF BREST-OD-300

6.1. Oxygen activity sensor (OAS)

OAS structure has been designed. The production technology has been elaborated. Make-up samples were manufactured. The significant part of experimental studies with the use of make-up samples has been performed [4]. It was demonstrated that the sensor with three sensitive elements placed in one body is functioning, and its technical characteristics are in general consistent with those stated in the terms of reference.

The estimate justification of the oxygen activity control sensor (OAS) measurement error in the lead coolant was performed and OAS signal processing algorithms with three reference electrodes developed.

Primary transformers signal processing algorithms for a sensor with three sensitive elements were developed.

Stands and installations were equipped with the lead coolant used in BREST-OD-300 NF justification works, laboratory oxygen activity control sensors approved as the measurement equipment.

The OAS resource justification was performed based on the results of laboratory OAS exploitation with the total production of over 10,000 hours.

The reference installation for OAS verification, including design, trial operation and preparing to attestation of the oxygen TDA reproduction method.

To complete the development it is required to:

- Carry out the methodological attestation of the method of the oxygen TDA level reproduction in the lead melt.
- Carry out attestation of OAS and OAS measurement channel as the measurement equipment.
- Complete OAS resource tests.

6.2. Mass exchange device

The material, shape and size of the solidphase source of dissolved oxygen for mass exchanged (ME) devices were selected - lead oxide granules. The granules manufacture method has been refined. Kinetics of the lead oxide granules dissolving in the lead coolant at various temperatures and rates of the coolant was studied. The method of MA oxygen efficiency calculation has been calculated.

It was experimentally proved that using lead oxide granules in MA serves as a feed of the lead coolant with already dissolved oxygen, excluding formation and accumulation within the contour of solid phase lead oxides, which may lead to generation of a large amount of slags.

Estimate and experimental studies of physical and chemical and hydraulic characteristics of filling of lead oxide granules were performed under the conditions of filling in MA of NF BREST-OD-300 [4].

MA make-up samples were tested on circulatory non-isothermal stands with a heavy liquid-metal coolant. Resource tests of lead oxide granules in the lead melt for over 1,000 hours have been completed.

Justified recommendations as to the structure of the MA reaction vessel containing filling of lead oxide granules, and the nominal consumption of the lead coolant through MA to provide for characteristics meeting TR requirements, have been given.
It was experimentally demonstrated on the circulatory non-isothermal stand that MA application allows maintaining the exact oxygen concentration in the coolant within the stated range of the automated control system.

6.3. *Hydrogen cleaning (HC)*

The HC process comprising the process chemistry and thermodynamics has been studied. The HC conduction procedure has been established [5].

The makeup of the HC device has been designed. The gas disperser (GD) is used to make up the finely-dispersed gaseous phase, which may be transported by the coolant at low flow rates of the hydraulic contour, including the plots with coolant’s low flow rates. Process control means and methods have been determined.

HC start and end criteria have been established. The basis for carrying out hydrogen cleaning is achievement of nitrogen concentration in the gaseous space of 4% vol. The hydrogen cleaning will be carried out after the hydrogen production rate has achieved 350 h.p.

HC duration and frequency have been determined. The duration of one hydrogen cleaning depends to the amount of slags within the circulatory contour and may be equal to 24 to 100 h. It is supposed that under the exploitation conditions of the NF BREST-OD-300 and taking into account its structural peculiarities (coolant nor drained from the first contour), the hydrogen cleaning mode will be significantly rare. This is due to a good startup (initial) preparation of the coolant, presence of the non-slag dissolved oxygen concentration control system to protect steel from corrosion, to prevent from penetration of oxygen to the circulatory contour surfaces, availability of systems of early diagnostics of insulation failure by air and inter-contour insulation failure.

The experimental GD sample with the full-scale working part (Ø 200 mm) has been designed, manufactured and tested under the BREST works performed.

Currently, it has been experimentally proved the ability of provision of the state of gaseous bubbles obtained, which allows for transporting with the low-rate flow of the coolant of NF BREST-OD-300 even at long low plots.

6.4. *Coolant filter*

As of now, the filter TR has been developed; lab samples obtained and thermal resistance tests of filter materials made of steel EP302 carried out; the filter make-up sample designed, manufactured and tested; the estimate and experimental justification of filter hydraulic properties performed at the make-up stand (the mechanism of work and pressure fall using the filter materials); materials for the memo and technical specifications for filter prepared; the filtering material for the coolant filter test sample manufactured.

7. *Conclusion*

The work on justification of the lead coolant justification in many aspects rely on previously carried out studies and experiments to justify the lead-bismuth coolant technology for transportation NPP, which have been performed since 60-s of the last century. Works on justification of the lead coolant itself were started at the end of 80-s. This continuation makes it possible to conclude that there is sufficiently full justification of the lead coolant technology as such. In the course of development of NF BREST-OD-300 a number of factors appeared such as scale, layout, mode parameters, resource, which required significant amount of additional studies in justification of the coolant technology methods proposed for NPP of new generation. The significant part of these studies has been completed by now. The remaining R&D studies mentioned in this Report are expected to be completed during coming years. The coolant quality support and control system under review has been included in the project documents of NF BREST-OD-300.
8. References

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