

Investigations of regularities in the accumulation of hydrogen-reduced slags in circulation circuits with lead-containing coolants*

Vladimir V. Ulyanov¹, Mikhail M. Koshelev¹, Vladlena S. Kremlyova^{1,2}, Sergey E. Kharchuk¹

1 JSC “SSC RF-IPPE n.a. A.I. Leypunsky”, 1 Bondarenko Sq., 249033 Obninsk, Kaluga Reg., Russia

2 Obninsk Institute for Nuclear Power Engineering, NRNU MEPhI, 1 Studgorodok, 249040 Obninsk, Kaluga Reg., Russia

Corresponding author: Sergey E. Kharchuk (skharchuk@ippe.ru)

Academic editor: Yury Kazansky ♦ Received 20 January 2021 ♦ Accepted 15 June 2021 ♦ Published 23 September 2021

Citation: Ulyanov VV, Koshelev MM, Kremlyova VS, Kharchuk SE (2021) Investigations of regularities in the accumulation of hydrogen-reduced slags in circulation circuits with lead-containing coolants. Nuclear Energy and Technology 7(3): 245–252. <https://doi.org/10.3897/nucet.7.74154>

Abstract

The paper presents a computational analysis of regularities in the accumulation of slags during the interaction of lead and lead-bismuth coolants with oxygen gas. Oxidation of lead-containing coolants will cause the formation of lead oxide, while the formation of bismuth oxide is unlikely. Dosed supply of oxidizing gas to lead-containing coolants makes it possible to oxidize, selectively, chromium and nickel to their oxides without the slag formation from solid lead oxide. Regularities were studied which are involved in the lead oxide formation during the interaction of lead-containing coolants with oxygen gas. It has been found that, in the process of interacting with oxygen gas, a lead-bismuth alloy is oxidized 1.7 times as intensively as lead, this being explained by the presence of bismuth in the alloy. Bismuth is oxidized more intensively than both lead and the lead-bismuth alloy. The inert gas overpressure during depressurization does not prevent air oxygen from entering the circuit, and the dependence of the nitrogen and oxygen flow into the circuit on the argon flow out of the loop is close to linear regardless of the circuit state (cold, without coolant; heated, without coolant; heated, with circulating coolant). Oxygen is a chemically active impurity and is absorbed by the circuit; it is therefore important to control nitrogen in the gas spaces of the reactor and research plant circuits with lead-containing coolants. This will make it possible to signal, in a timely manner, the ingress of oxygen into the circuit and to take measures required to avoid or reduce the scale of the slag formation from lead oxides.

Keywords

Lead-containing coolant, slags based on lead oxides, lead, lead-bismuth eutectic, oxygen gas, lead oxide activity, Gibbs energy, hydrogen-based cleaning from slags, oxidation pattern, backpressure ingress

Introduction

The choice of liquid metals as nuclear reactor coolants made by A.I. Leypunsky in the 1940s is explained by their unique properties. With a turbulent flow of liquids

in tubes, heat is transferred due to the turbulent mixing of the flow and by the molecular thermal conductivity of the coolant. Liquid metals have better molecular thermal conductivity as compared with other coolants. This leads to an increased share of heat transported by

* Russian text published: *Izvestiya vuzov. Yadernaya Energetika* (ISSN 0204-3327), 2021, n. 2, pp. 119–131.

means of thermal conductivity and provides better heat-transfer properties, which defines the advantages of liquid metals as coolants. Mercury was the first to be tested as coolant (the Clementine reactors in the USA and the BR-2 reactor in the USSR). Further on, sodium was selected as the coolant for civilian fast neutron reactors because of a shorter fuel doubling time, and lead-bismuth eutectic was selected as the coolant to be used in reactor plants for small-displacement ships and high-power plants, which has made it possible to achieve such specific weight and dimension parameters as are not possible in water-cooled plants (Fleitman and Weeks 1971, Weeks 1971, Antonovskiy et al. 1997, Pioro et al. 2019). Reactor plants were built for the K-27 nuclear submarine and its 27/VT ground prototype test facility, as well as the KM-1 reactor plants with a ground prototype test facility for nuclear submarines, projects 705 and 705K respectively (Zrodnikov et al. 2007, Beznosov et al. 2016). All these plants have a similar loop layout of the primary circuit equipment: the reactor core, the pump sets and the steam generators were connected through pipelines, and auxiliary pipelines were used for the leaking coolant discharge to buffer tanks from which the coolant was fed back into the main circulation line. This shared layout had variable design.

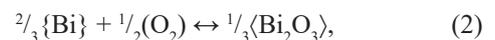
Lack of sufficient information on lead-bismuth coolants and the initially predominant concept that the cleanliness of the entire circulation circuit can be ensured through the coolant purification by removing lead oxides from free surfaces, led in 1968 to an accident at the K-27 nuclear submarine's portside reactor plant and a pre-emergency situation at the 27/VT ground prototype test facility (Yefanov et al. 2007). The damaged submarine was inactivated and a great deal of attention was given to investigating the physicochemical properties of the coolant, while a set of measures was developed to achieve the rated coolant quality and circuit surface cleanliness for addressing the lead-bismuth circuit serviceability problem. It was found that the key problem that led to the K-27 accident was frequent repairs of the steam generators, which were accompanied by the primary circuit depressurization and the continued formation of lead oxides due to the coolant interaction with atmospheric oxygen. The absence of an efficient primary circuit cleaning method led to slags being accumulated in excessive quantities and suddenly thrown into the core with an increase in the power level, this causing rapid deterioration of heat removal and further fuel melting.

By the time the reactor plants for project 705 and 705K nuclear submarines started to operate, an extensive experience had already been gained in handling of lead-bismuth coolants, so none of the nine reactor plants was decommissioned due to the excessive slag accumulation as the result of operation (Yefanov et al. 2007) with the total operating time of 80 reactor-years and cruising modes of about 20 reactor-years (Gromov et al. 1996). However, the operating conditions and design peculiarities of the reactor plants in question differed greatly from

the current requirements and concepts which suggest a tank-type layout and long-term operation while achieving the maximum installed capacity utilization factor. All this causes some experts to doubt that circuits with lead-containing coolants can be operated for a long time without slag accumulation, and that, therefore, the use of circuits with the above coolants can be expected, on the whole, to offer economic benefits (Mitenkov 2004, Poplavsky 2011). That is why the results of investigating the regularities in the accumulation of slags based on lead oxides in circulation circuits of plants with lead-containing coolants, as shown in the paper, are important to addressing the systemic problem of the safe and economically viable handling of lead and lead-bismuth coolants in the reactor plant conditions.

Computational study into the consequences of interaction between lead-containing coolants and oxygen gas

Lead and lead-bismuth coolants represent a complex thermodynamic system with respect to oxygen gas. With a small content of oxygen in the coolant, its properties are similar to strong scavengers (chromium or iron), and, in the saturation condition, the reaction with oxygen gas leads to the formation of solid lead oxide. Such property can be used for oxidizing, selectively, the coolant-contained impurities with a high affinity to oxygen which change from a dissolved state to a suspended state. However, uncontrolled interaction of lead-containing coolants with oxygen gas can lead to the formation and accumulation of slags based on the coolant oxides. This is confirmed by analyzing thermodynamically the reaction of the interaction of the coolant components with oxygen gas:



where $\{Pb\}$, $\{Bi\}$ are liquid lead and bismuth; (O_2) is oxygen gas; and $\langle PbO \rangle$, $\langle Bi_2O_3 \rangle$ are solid lead and bismuth oxides. Equations (2), (3) are practically meaningful for lead-bismuth eutectic, and only reaction (1) can take place in lead coolant (1). The driving force for the reactions is defined by the actual change of Gibbs energy, ΔG , for particular conditions of interaction also referred to as Gibbs free enthalpy (Wicks and Block 1965):

$$\Delta G = \Delta G^0 + R \times T \times \ln K, \quad (4)$$

where ΔG^0 is the standard Gibbs energy change (with the activities of solid and liquid substances equal to unity, and the oxygen gas pressure equal to $1 \cdot 10^5$ Pa), J/mol; T is

temperature, K; $R = 8.314 \text{ J}/(\text{mol}\times\text{K})$; and K is the constant of equilibrium defined by the ratio of the product of the activities of the resultants from reactions (1) – (3) to the product of the activities (pressures) of the initial reagents for the analyzed reactions. Value ΔG^0 for lead and bismuth oxides is determined by equations (Turovtseva and Kunin 1959)

$$\Delta G^0_{\text{form.PbO}} = -219003 + 100.4 \times T, \quad (5)$$

$$\Delta G^0_{\text{form.Bi}_2\text{O}_3} = -622411 + 313.8 \times T, \quad (6)$$

For reaction (3), value ΔG^0 is determined from the equation

$$\Delta G^0_{p,3} = \Delta G^0_{\text{form.PbO}} - \frac{1}{3} \Delta G^0_{\text{form.Bi}_2\text{O}_3}. \quad (7)$$

The activities of lead and bismuth in lead-bismuth eutectic (Gromov and Shmatko 1996) are computed in accordance with the following dependences

$$\lg a_{\text{pb}} = -98/T - 0.32, \quad (8)$$

$$\lg a_{\text{Bi}} = -64/T - 0.23. \quad (9)$$

With equilibrium $\Delta G = 0$, so, for reaction (3), the value of the standard Gibbs energy change will be expressed by the equation

$$\Delta G^0 = -R \times T \times \ln [a_{\text{pbO}} \times a_{\text{Bi}}^{2/3} / (a_{\text{Bi}_2\text{O}_3}^{1/3} \times a_{\text{pb}})]. \quad (10)$$

By converting (10), using (7) – (9), one can obtain the relationship between a_{pbO} and $a_{\text{Bi}_2\text{O}_3}$ as a function of temperature in the equilibrium state (see Fig. 1). It can be seen that equilibrium can be reached in a temperature range of 350 to 650 °C with a much greater activity of PbO as compared with the activity of Bi₂O₃. Practically, this means that there will be 1×10^3 to 1×10^7 molecules of PbO for each molecule of Bi₂O₃ in the solution. If there are conditions for the solid PbO formation, the activity of Bi₂O₃ in the solution is approximately 10 times as small as the saturation.

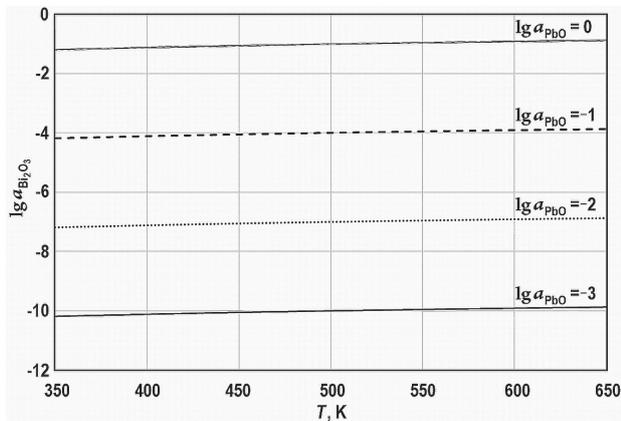


Figure 1. Equilibrium dependence of the lead and bismuth oxide activities on the lead-bismuth coolant temperature.

Therefore, there are no thermodynamic grounds for the formation of solid Bi₂O₃ in lead-bismuth eutectic, and reaction (1) is of prime importance in analyzing processes of oxidation by oxygen and slag accumulation not only for lead but also for lead-bismuth coolant. The driving force for the lead oxide formation reaction (1), which fits a negative value of ΔG , increases as the lead oxide activity decreases. Equation (4) for reaction (1) is transformed as

$$\Delta G = \Delta G^0_{\text{form.PbO}} + R \times T \times \ln [a_{\text{pbO}} / (a_{\text{pb}} \times P_{\text{O}_2}^{1/2})], \quad (11)$$

where P_{O_2} is the partial pressure of oxygen in the reaction area, atm; a_{pb} is the activity of lead (for lead coolant, $a_{\text{pb}} = 1$); and a_{pbO} is the activity of lead oxide often referred to as thermodynamic activity of dissolved oxygen.

Fig. 2 presents dependence (11) with a variable value of a_{pbO} , a constant value of a_{pb} , a temperature of 420 °C (the average mixed core inlet temperature in the most elaborated BREST-type reactor design with lead-containing coolant (Dragunov et al. 2015)), and a partial oxygen pressure of $0.21 \times 10^5 \text{ Pa}$ corresponding to that of air. It can be seen that an increase in the lead oxide activity in lead-containing coolants from 1 to 1×10^{-6} leads to a growth in the probability of the oxidation process to take place since the Gibbs energy magnitude decreases.

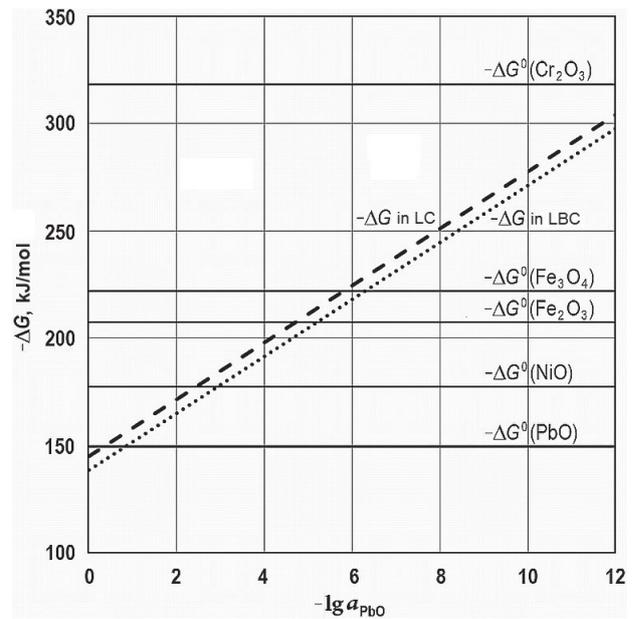


Figure 2. Actual Gibbs energy change as a function of the dissolved lead oxide activity in lead coolant ($-\Delta G$ in LC) and in lead-bismuth coolant ($-\Delta G$ in LBC) during oxidation by atmospheric oxygen gas at a temperature of 420 °C.

It can be seen in the figure that, in certain conditions, the Gibbs energy changes during oxidation of lead-containing coolants and standard Gibbs energy changes during iron, nickel or chromium oxidation coincide. This means that oxidation of lead-containing coolants and oxidation of a metal contained in structural steel are equally possible at coincidence points. For instance, oxidation of lead

coolant with $a_{\text{PbO}} \geq 1 \times 10^{-6}$ and oxidation of iron with the formation of solid iron oxide ($a_{\text{Fe}} \approx a_{\text{Fe}_3\text{O}_4} \approx 1$) have similar thermodynamic grounds. A major increase in the activity of dissolved lead oxide in lead-containing coolants will cause deeper oxidation of an iron impurity to iron oxide. In this case, achieving a thermodynamic equilibrium will require the following conditions to be fulfilled: with $a_{\text{PbO}} \gg 1 \times 10^{-6}$, $a_{\text{Fe}_3\text{O}_4} \approx 1$, but $a_{\text{Fe}} \ll 1$. The formation of solid nickel oxide can occur with the lead oxide activity being $a_{\text{PbO}} \geq 1 \times 10^{-2}$.

Metal impurities in the circulating coolant originate largely from structural materials and most of such impurities (Fe, Cr, Ni, etc.) can be oxidized with the formation of respective solid oxides in conditions of oxygen-undersaturated lead-containing coolant, that is, without the formation of solid lead oxide. Therefore, it can be expected that, by providing a moderate amount of dissolved lead oxide, it is possible to oxidize, selectively, impurities of metals to their oxides in a solid phase through removing impurities from the circuit without the formation of slag based on lead oxide.

It follows from equation (11) that oxidation of lead-containing coolants is thermodynamically grounded at up to very small partial pressures of oxygen. For instance, the formation of solid lead oxide in lead coolant at a temperature of 420 °C is possible with an oxygen pressure of not less than 3.02×10^{-18} P. Therefore, in the event of depressurization of a circulation circuit with lead-containing coolant, atmospheric oxygen gas will interact with the coolant through reaction (1) and will lead to the saturation state with the subsequent formation of solid PbO. The composition of the slags formed during operation of circulation circuits with lead-bismuth coolant is shown in Table 1 (Martynov et al. 2005). Recalculating the content of oxygen as that of lead oxide shows that PbO accounts for 33 to 55% of the weight. The rest are the coolant and structural steel components. A difference was observed only for slags from the 27/VT facility which contained slightly less than 2 wt. % of magnesium, which can be explained by the experiment in protection of the test facility's structural materials by a corrosion-resistant film of magnesium-zirconium alloy. Mg with a higher affinity to oxygen than Pb and Bi was introduced into the coolant

but its presence led to the generation of hydrogen thanks to the chemical interaction with moisture which was present in the primary circuit due to the continuous steam generator leakage. This was the reason for terminating the experiment but the magnesium introduced into the coolant was gradually slagging in the form of magnesium oxide forming insoluble slag not reduced by hydrogen.

Experimental studies into the processes of lead-containing coolant interaction with oxygen gas

The authors happened to deal with studies in chemistry of lead-containing coolants, in which experiments were conducted in lead-bismuth eutectic and, believing its properties to be close to those of lead, the obtained results are generalized for both coolants (Askhadullin et al. 2011, Salayev et al. 2020). No reliable data were found as to if such generalization was comprehensively admissible, so, taking into account that there was no sufficient information on oxidation of lead and bismuth in air (Belousova et al. 2004) and there was no data on comparative oxidation of lead-containing coolants, a decision was made to study the regularities involved in comparative oxidation of lead-containing coolants.

The regularities of the lead and lead-bismuth eutectic oxidation were investigated on a facility the layout of which is shown in Fig. 3. The key part of the facility is reaction cell 5 inside of which there is alundum crucible 6 with the tested metal and alloy samples. The reaction cell is equipped with thermocouple 7 of the chromel-alumel type with an accuracy of ± 1 °C and is accommodated in electrical furnace 4 which allows one to control the temperature to keep it in the limits of 20 to 700 °C. Compressor 1 allows air to be blown through the reaction cell, and gate valve 2 and gas flow meter 3 allow monitoring the flow rate of gas mixtures through the reaction cell. The metal sample weight was measured using a laboratory balance with an accuracy of ± 0.01 g.

Table 1. Composition of slags formed during operation of test facilities

Place of slag formation	Content of elements in slag, wt. %					
	O	Pb	Bi	Fe	Cr	Ni
TT-2M test facility, pipeline dead-end	2.4	51.6	46.4	4×10^{-4}	3×10^{-4}	3×10^{-4}
SVT-3M test facility, internal wall of flow-through pipeline	3.5	55.9	39.5	4.2×10^{-1}	1.5×10^{-1}	9.5×10^{-2}
VNIAM's pump testing facility, internal wall of pump tank	3.9	51.9	42.1	2.6×10^{-2}	2.4×10^{-2}	1.2×10^{-3}
VNIAM's pump testing facility, internal wall of pressure pipeline	6.5	76.0	14.2	2.6×10^{-2}	1×10^{-2}	1.2×10^{-2}
27/VT prototype test facility, core inlet header	3.6	63.4	24.8	1.8	8.6×10^{-2}	7.0×10^{-2}

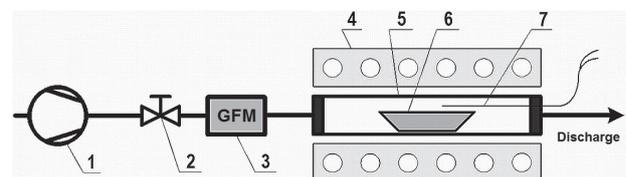


Figure 3. Layout of the facility to investigate the regularities involved in oxidation of lead-containing coolants: 1 – compressor; 2 – gate valve; 3 – gas flow meter; 4 – furnace; 5 – reaction cell; 6 – crucible with sample; 7 – thermocouple.

The experiments were conducted in two phases: oxidation of lead and an alloy with equal mass fractions of lead and bismuth was compared at stage 1, and oxidation of lead, bismuth and an alloy with equal mass fractions

of lead and bismuth was compared at stage 2. Lead S0 (GOST 3778-98) and bismuth Vi1 (GOST 10928-90) were used.

Experimental procedure at stage 1:

1. the initial lead sample and the crucible are weighed, and the lead sample surface area is determined;
2. the lead sample is placed in the crucible in the reaction cell, and temperature is increased to 535 ± 5 °C;
3. the compressor is switched on, and the reaction cell is air blown for the specified time (1, 1.5, 1.5, 3, 14, 2 h);
4. the compressor is switched off, and the reaction cell is cooled;
5. the lead sample is weighed;
6. steps 2 through 5 are repeated;
7. steps 1 through 5 are repeated with the lead and bismuth alloy sample.

The obtained regularity is presented in Fig. 4.

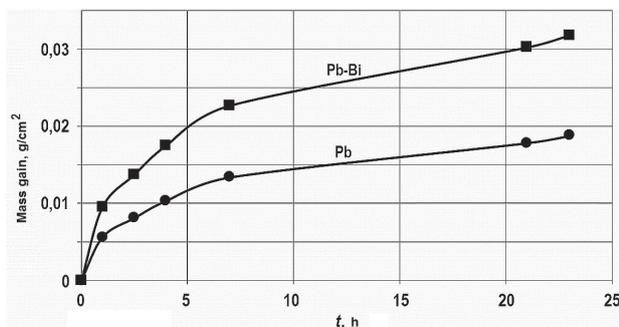


Figure 4. Regularity of the lead and lead-bismuth eutectic oxidation in air at $T = 535$ °C.

It can be seen that the lead and bismuth alloy, as applied to the experiment conditions, is oxidized in air approximately 1.7 times as fast as lead. A bismuth sample was also tested to identify the reason for the detected regularity at the experiment's stage 2.

Experimental procedure at stage 2:

1. the initial lead (bismuth, alloy and bismuth) sample and the crucible are weighed, and the lead sample surface area is determined;
2. the lead sample is placed in the crucible in the reaction cell, and temperature is increased to 420 ± 5 °C;
3. the compressor is switched on, and the reaction cell is air blown for 19 h;
4. the compressor is switched off, and the reaction cell is cooled;
5. the lead sample is weighed;
6. steps 1 through 5 are repeated at 535 ± 5 °C.

After the experiment is over, all tested metal samples were reduced by hydrogen in the same manner (Ivanov et al. 2015), which made it possible to determine the mass of the oxygen absorbed by the samples from the mass of

the water removed. The obtained values converged with the sample weighing results with an accuracy of up to ± 0.01 g which confirmed these to be valid. The experiment temperatures were selected with regard for the known data on the most elaborated BREST-type reactor design with lead-containing coolant (Dragunov et al. 2015): the average mixed coolant temperature at the core inlet is 420 °C, and that at the steam generator inlet is 535 °C.

Table 2 presents the results from the experiment's stage 2. It can be seen that the lead-bismuth alloy is oxidized more intensively than lead due to containing bismuth. And bismuth is oxidized by far more intensively than both lead and the lead-bismuth alloy. The intensity of oxidation was estimated from the absorbed oxygen weight reduced to the area of the melt and atmospheric oxygen interaction surface. As applied to the reactor plant conditions, in the event of depressurization during the core refueling, one can expect, when comparing the lead-oxygen interaction surface area in the laboratory facility and on the BREST coolant free surface, that the primary circuit will absorb 13 kg of oxygen gas, an equivalent of 185 kg of solid lead oxide, for 19 h of the interaction with air.

Table 2. Regularity of oxidation for lead, bismuth and an alloy composed of equal mass fractions of lead and bismuth at temperatures of 420 and 535 °C for 19 h

Sample type	Specific weight of absorbed oxygen at 420 °C, g/cm ²	Specific weight of absorbed oxygen at 535 °C, g/cm ²
Lead	1.09×10^{-2}	3.64×10^{-2}
Alloy with equal mass fractions of Pb and Bi	1.95×10^{-2}	4.87×10^{-2}
Bismuth	2.27×10^{-2}	6.17×10^{-2}

Given the fact that the circuit depressurization is inevitable for certain operations, e.g., during the core refueling, there are proposals to reduce the ingress of air into the circuit by keeping an inert gas overpressure in the circuit, that is, by organizing a leakage from the circuit and into the atmosphere. Solutions of the kind have been implemented in a number of applications, e.g., in control of the polyatomic liquid evaporation front (Cercignani 1991), but Knudsen effect and the presence of thermal diffusion and pressure diffusion (Theoretical Foundations 1994) suggest that ingress of atmospheric gases is possible in this case due to backpressure.

The ingress due to backpressure was experimentally estimated at the TT-2M test facility (Fig. 5) by loosening the flange gasket in the specially organized dead-end gas pipeline with a gas flow meter using which the circuit leakiness was achieved with the controlled argon leakage from the circuit.

Temperature was variable during the experiment, with or without the coolant in the circuit, the argon overpressure in the gas circuit was 1×10^4 to 5×10^4 Pa, and the gas phase composition change was observed in all modes. A Kristall-5000 chromatograph was used to monitor the composition of the gas mixture in the circuit. The nitrogen flow into the circuit was determined from the change of

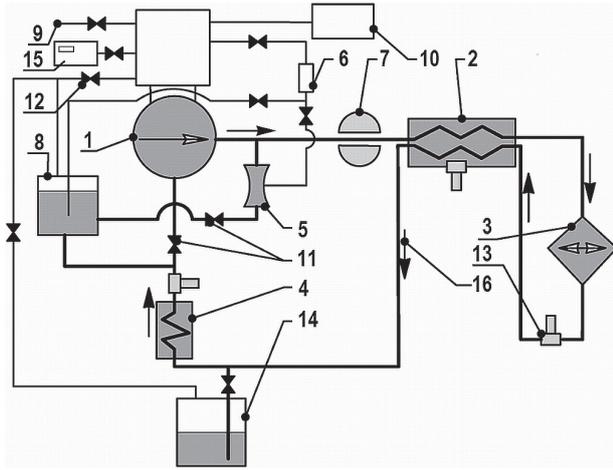


Figure 5. Layout of the TT-2M test facility circulation circuit: 1 – circulation pump; 2 – recuperative heat exchangers; 3 – core simulating heater; 4 – steam generator simulating chiller; 5 – ejector for gas mixture injection into coolant; 6 – water evaporator; 7 – coolant flow meter; 8 – coolant volume change compensator; 9 – gas circuit connection to gas supply and vacuum system; 10 – gas composition monitoring system; 11 – liquid metal valves; 12 – gas valves; 13 – oxygen activity sensors of zirconium dioxide; 14 – coolant storage and melting tank; 15 – gas flow meter; 16 – coolant flow direction.

the nitrogen concentration in the circuit and the total gas pressure and with regard for the fact that the total volume of the circuit was 430 l of gas during normal conditions. The obtained results are summarized in Table 3.

Table 3. Dependence of the nitrogen flow into the circuit on the argon flow out of the circuit, temperature and coolant presence

Nitrogen flow into circuit, l/h	Argon flow out of circuit, l/h	Temperature, °C	Coolant in circuit
0.013	0.4	19	Absent
0.051	1.7	240	Absent
0.085	2.5	320	Present
0.175	5.5	19	Absent

The dependence of the nitrogen flow into the circuit on the argon flow out of the circuit is close to direct proportionality, and the nature of the argon outflow from the circuit and the ingress of nitrogen into the circuit did not practically change independent of the test facility operation mode (cold, without coolant; heated, without coolant; heated, with circulating coolant):

$$Q_{N_2} = 0.032 Q_{Ar}, \quad (12)$$

where Q_{N_2} , Q_{Ar} are the nitrogen flow into the circuit and the argon flow out of the circuit respectively, l/h. At a temperature of 19 °C, the content of oxygen grew with the increase in the nitrogen content in the gas circuit in ratios close to the nitrogen and oxygen ratio in air. At the same time, the volume fraction of oxygen decreased and stabilized at a level of 0.02%vol. at a temperature of 240 °C

following a short-term increase. The nature of the oxygen content change in the circuit with the coolant circulation in it and a temperature of 320 °C did not change as compared with the circuit without coolant at a temperature of 240 °C. Its volume fraction did not exceed 0.02%vol., which indicates that oxygen is absorbed by the circuit materials and the coolant at elevated temperatures.

Therefore, the ingress of air into the circuit due to backpressure has been confirmed. And the estimated argon ingress is more reliable than for oxygen, due to the oxygen absorption by the coolant and the circuit surfaces in the heated condition. A comparison of the argon and oxygen ingress into the cooled circuit has confirmed that these gases are capable to penetrate leaky joints and enter the circuit by backpressure. This allows estimating the ingress of oxygen gas into the circuit from air if the nitrogen ingress is known:

$$Q_{O_2} = (Q_{N_2} \times C_{O_2}) / C_{N_2} = (Q_{N_2} \times 20.95) / 78.08 = 0.27 \times Q_{N_2}, \quad (13)$$

where Q_{N_2} , Q_{O_2} are the nitrogen and oxygen flows into the circuit, l/h; and C_{O_2} , C_{N_2} are the content of oxygen and nitrogen in air, %.

It follows from relation (13) that the increase in the content of nitrogen in the gas circuit proves reliably that atmospheric oxygen enters the circuit, including in the event of its absorption by the coolant and the circuit surfaces.

Conclusions

Regularities have been investigated which are involved in the accumulation of hydrogen-reduced slags in circulation circuits with lead-containing coolants. Lead oxide will form in lead-containing coolants in contact with oxygen gas, and the bismuth oxide formation has no thermodynamic grounds. While providing a moderate amount of dissolved lead oxide in a controlled manner, it is possible to selectively oxidize impurities of metals to their oxides in a solid phase by removing impurities from the circuit without solid lead oxide formation.

In the event of depressurization, the oxidation of a lead and bismuth alloy is 1.7 times as intensive as that of lead which is explained by the presence of bismuth in the alloy. Bismuth is oxidized more intensively than both lead and lead-bismuth alloy. As applied to the conditions of the BREST reactor plant during the core refueling, the formation of 185 kg of solid lead oxide can be predicted.

An inert gas overpressure during depressurization does not prevent atmospheric oxygen from entering the circuit, in which case nitrogen monitoring in the circuit will make it possible to signal the ingress of oxygen into the circuit and, accordingly, to take measures required to avoid or reduce the scale of slag formation. It is therefore important to control nitrogen in the gas spaces of the reactor and research plant circuits with lead-containing coolants.

References

- Antonovskiy GM, Vorontsov VYe, Votintsev IS (1997) Half a century in nuclear engineering. KiTizdat Publ., Nizhny Novgorod, 303 pp. [in Russian]
- Askhadullin RSh, Ivanov KD, Shelemetyev VM, Sadovnichy RP (2011) Estimating the intensity of oxidation processes for structural steels of the primary circuit in nuclear power plants with heavy coolants. *Izvestiya vysshykh uchebnykh zavedeniy. Yadernaya energetika* 4: 121–128. [in Russian]
- Belousova NV, Denisov VM, Istomin SA (2004) Interaction of liquid metals and alloys with oxygen. Yekaterinburg. Institut Metallurgii UrO RAN Publ., 288 pp. [ISSN 5-7691-1531-9] [in Russian]
- Beznosov AV, Bokova TA, Bokov PA (2016) Technologies and key equipment of the loops of reactor plants, and industrial and research facilities with lead and lead-bismuth coolants. Litera Publ., 2016, Nizhny Novgorod, 488 pp. [in Russian]
- Cercignani C (1991) Numerical study of the strong evaporation of a binary mixture. *Fluid Dynamics Research* 8(5–6): 175–187. [https://doi.org/10.1016/0169-5983\(91\)90041-G](https://doi.org/10.1016/0169-5983(91)90041-G)
- Dragunov YuG, Lemekhov VV, Moiseyev AV, Smirnov VS (2015) Lead-cooled fast neutron reactor (BREST). *Problemy mashinostroyeniya i avtomatizatsii* 3: 97–103. [in Russian]
- Fleitman A, Weeks JR (1971) Mercury as a nuclear coolant. *Nuclear Engineering and Design* 16(3): 266–278. [https://doi.org/10.1016/0029-5493\(71\)90015-X](https://doi.org/10.1016/0029-5493(71)90015-X)
- Gromov BF, Orlov YuI, Toshinsky GI, Chekunov VV (1996) Nuclear power plants with bismuth-lead coolant. *Atomnaya energiya* 81(5): 340–347. <https://doi.org/10.1007/BF02408176> [in Russian]
- Gromov BF, Shmatko BA (1996) Physicochemical Properties of Lead-Bismuth Melts. *Izvestiya vysshykh uchebnykh zavedeniy. Yadernaya energetika* 4: 35–41. [in Russian]
- Ivanov II, Shelemetyev VM, Ulyanov VV, Teplyakov YuA (2015) Kinetics of reducing orthorhombic and tetragonal lead oxides to lead using hydrogen. *Kinetika i kataliz* 3: 1–5. <https://doi.org/10.1134/S0023158415030076> [in Russian]
- Martynov PN, Gulevich AV, Orlov YuI, Gulevsky VA (2005) Water and hydrogen in heavy liquid metal coolant technology. *Progress in Nuclear Energy* 47(1–4): 604–615. <https://doi.org/10.1016/j.pnucene.2005.05.063>
- Mitenkov FM (2004) Reflections on the experience. Izdatelstvo po Atomnoy Tekhnike Publ., Moscow, 400 pp. [in Russian]
- Pioro I, Duffey RB, Kirillov PL, Pioro R, Zvorykin A, Machrafi R (2019) Current status and future developments in nuclear-power industry of the world. *Journal of Nuclear Engineering and Radiation Science* 5(2): 27. <https://doi.org/10.1115/1.4042194>
- Poplavsky VM (2011) State and development trends of fast reactor technology. *Izvestiya vysshykh uchebnykh zavedeniy. Yadernaya energetika* 1: 5–15. [in Russian]
- Salayev SV, Askhadullin RSh, Legkikh AYu, Niyazov S-AS (2020) Results of investigations on expanding the methodological capabilities for determining the physicochemical state of liquid metal coolants based on lead. *Izvestiya vuzov. Yadernaya energetika* 1: 98–106. <https://doi.org/10.26583/npe.2020.1.10> [in Russian]
- Theoretical Foundations (1994) Theoretical Foundations of Refrigeration Engineering. Part 2. Heat and Mass Transfer. Kolos Publ., Moscow, 288 pp. [in Russian]
- Turovtseva ZM, Kunin LL (1959) Analysis of Gases in Metals. Izdatelstvo AN SSSR Publ., Moscow-Leningrad, 390 pp. [in Russian]
- Weeks JR (1971) Lead, bismuth, tin and their alloys as nuclear coolants. *Nuclear Engineering and Design* 15(4): 363–372. [https://doi.org/10.1016/0029-5493\(71\)90075-6](https://doi.org/10.1016/0029-5493(71)90075-6)
- Wicks CW, Block FE (1965) Thermodynamic properties of 65 elements, their oxides, halides, carbides and nitrides. Metallurgiya Publ., Moscow, 240 pp. [in Russian]
- Yefanov AD, Ivanov KD, Martynov PN, Orlov YuI (2007) Lead-bismuth coolant technology at nuclear power plants of generations 1 and 2. *Izvestiya vysshykh uchebnykh zavedeniy. Yadernaya energetika* 1: 138–144. [in Russian]
- Zrodnikov AV, Dragunov YuG, Vasilenko VA (2007) Problems and approaches to the management of spent nuclear fuel of liquid metal cooled reactors of nuclear submarines. *Izvestiya vysshykh uchebnykh zavedeniy. Yadernaya energetika* 1: 13–22. [in Russian]