POLONIUM PROBLEM IN LEAD-BISMUTH COOLED NUCLEAR POWER INSTALLATIONS

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ABSTRACT

The IPPE experience in investigation of problem of high hazardous alpha-radioactive polonium generated in lead-bismuth eutectic (LBE) of naval liquid metal reactors has been considerably improved and applied to the safety research and development of generation IV small power LBE reactors and liquid metal targets for accelerator driven systems (ADS).

It was shown that polonium hazard appears in cases of primary circuit depressurization and heat exchanger failure, as well as while repair and maintenance works, fuel reloading and accidents with radioactive LBE spill.

The rules of polonium release from LBE into high temperature environment have revealed that it is precipitated in the form of intermetallic compounds of lead and bismuth polonides and is accompanied by unstable gaseous compounds of polonium hydride.

As far as generation IV small power LBE reactors concerned the main contributor of polonium hazard is Po-210 isotope, while that concerned LBE targets for the ASD it is isotopes of Po-210, Po-209, and Po-208.

Taking into account high radiation hazard of polonium along with potential danger of other volatile and gaseous nuclides accumulated in radioactive LBE one can conclude that a corresponding technology culture of polonium treatment and special means of radiation safety ensuring are required. In this connection the analysis of LBE purification from Po-210 isotope using alkali melts in air and inert gas atmosphere was presented.

INTRODUCTION

Nuclear disasters occurred on Fukushima and Chernobyl NPPs, as well as those occurred earlier on Three Mile Island, Windscale and in Urals which caused radioactive contamination of wide areas and significant social costs, give rise to deep concern of the world community in view of prospects of nuclear power development and necessity of further improvement of safety systems related to the innovative nuclear technologies.

In the Russian regulatory document on radiation safety NRB-99/2009 [1] limitation is given to permissible radiation doses for personnel of NPP and inhabitants. Max annual permissible dose values for inhabitants and personnel are, respectively, 1 mSv and 20 mSv.

Social accessibility of the newly created reactors requires comprehensive safety analysis of proposed designs including analysis of incredible severe accidents. Forecast of radiological consequences of reactor operation and possible accidents should be based on the quantitative data on the sources of radioactivity and mechanisms of its release to the environment and on chemical forms of radionuclides.

Now reactors with heavy liquid metal coolants (lead and lead-bismuth) are considered among other options as applied to the new generation NPP. These reactors are capable of realizing inherent safety principles to a considerable extent.

If lead-bismuth coolant (LBC) is used in the reactor, attention is paid to high hazard caused by polonium produced in lead-bismuth during reactor operation. Heightened level of awareness about polonium-caused hazard is valid to a considerable extent. Po-210 is practically absolute α-emitter ($E\alpha$ = 5.3 MeV). As regards polonium-210, the following annual limit on intake (ALI) and permissible annual average volumetric activity in the air (PVA) and in potable water (PAW) are indicated in NRB-99/2009:

for personnel: $ALI_{pers.} = 6.7\cdot10^{3}$ Bq/year; $PVA_{pers.} = 2.7$ Bq/m^3;

for inhabitants: $ALI_{inhab.}=2.5\cdot10^{2}$ Bq/year; $PVA_{inhab.} = 3.4\cdot10^{-2}$ Bq/m^3;

$ALI_{нас.}=1.1\cdot10^{2}$ Бк/год; $PAW^{water} = 0.11$ Bq/kg.

In order to prevent impermissible polonium contamination, sufficiently high technological culture of radioactive lead-bismuth coolant handling and special radiation safety measures are required. Polonium is produced in the reactor as a result of nuclear reaction on bismuth nuclei:

$$^{209}Bi + n \longrightarrow {}^{210g}Bi \xrightarrow[T_{1/2}\,=\,5.013\text{ days}]{\beta^-} {}^{210}Po \xrightarrow[T_{1/2}\,=\,138.8\text{ days}]{\alpha} {}^{206}Pb$$

Pb-Bi eutectic is also considered as target coolant in the accelerator driven systems (ADS) designed as spallation neutron source. With protons energy E_p=(0.8-1.5) GeV and current value (1-10) mA specific activity of Po^{210} in the target of this ADS may reach $4 \cdot 10^{11}$ Bq/kg value. In addition to Po^{210}, Po^{209} ($T_{1/2}$=102 years), Po^{208} ($T_{1/2}$=2.9 years), as well as some short lived polonium isotopes can be produced in the target in (p,xn) and (α,xn) reactions as a result of protons beam effect on lead and bismuth nuclei.

The paper contains brief information about the experience gained in carrying out work under conditions of polonium contamination on nuclear submarine power plants and ground mounted prototypes with reactors cooled by lead-bismuth alloy; some results of basic research work performed in Russia (at the SSC RF – IPPE) and in other countries on polonium release from polonium containing media on the basis of lead heated under vacuum and in gas atmosphere; its chemical forms and laws of radiation environment formation.

EXPERIENCE GAINED IN CARRYING OUT WORK ON NPP UNDER CONDITIONS OF CONTAMINATION WITH POLONIUM-210

Experience has been gained during almost 40 years in operating nuclear submarine NPP and ground mounted prototype reactors with lead-bismuth coolant. Under normal operating conditions with the leak-tight primary circuit polonium imposes no hazard. The hazard arises if the primary circuit is unsealed, i.e. in cases of scheduled repair of the primary components, reactor refueling or accident resulting in radioactive coolant spill to the attended room. The main source of hazard in these cases is α-radioactive polonium aerosols in the air atmosphere of the working premises and surface contamination caused by aerosols deposition or α-activity transfer by contact.

A unique experience of work performed under polonium contamination conditions was gained primarily on the first reactor facility with lead-bismuth coolant of ground mounted prototype of nuclear submarine at the SSC RF – IPPE in Obninsk, on which numerous coolant spill accidents took place in the early operation stage. On this facility various procedures of maintenance and repair of polonium-contaminated components were carried out. It was in this stage that the basic organizational and technological measures were developed, as well as protective means against polonium for personnel, which were used later in the submarine reactor plants and made it possible to prevent personnel overexposure.

The most important measures are as follows:

- arrangement of the main primary components in the leak-tight enclosure under vacuum with respect to reactor compartment atmosphere,
- arrangement of controlled access areas and stringent radiation control areas in the work zones;
- assurance of local air exhaustion in the spill areas and areas with high surface α-contamination with simultaneous use of aerosol filters made of Petryanov fabric;
- removal of pieces of frozen radioactive alloy;
- decontamination of polonium-contaminated surfaces of the rooms and components;
- application of easily-removable protective polymer coatings on polonium-contaminated surfaces;
- prohibition on fire work (cutting and welding);
- use by personnel of work wear (gloves, boot covers etc.) and personal respiratory protective means (Petal type face mask with Petryanov fabric and pressure suits, if necessary).

Accident with the spill of 2000 kg of radioactive liquid metal into attended room occurred on one nuclear submarine (NS) in 1982. In the stage of post-accident work α-contamination of the air fluctuated within the wide range of values ($4\text{-}4 \cdot 10^3$ Bq/m^3) depending on the nature of the work performed. The highest activity level was observed when the alloy was chiseled causing intensive formation of radioactive aerosols.

Protective-accumulative coatings showed good results of locking polonium contamination, changing its physical and chemical condition and confining it within limited volume to prevent its spreading to the environment. Shielding and decontamination effect of these coatings is based on phenomena of sorption and solvability of sediments in dispersion medium and diffusion transfer throughout the coating volume. Duration of protective effect of the film is 250 - 300 days, its sorption capability being equal to $4 \cdot 10^6\text{-}4 \cdot 10^7$ Bq/kg.

The in-situ tests of coating were carried out in 1968 in the course of the long-duration repair work resulting in significant polonium release. It was revealed during these tests that application of 300 μm thick coating in highly contaminated rooms (up to $1 \cdot 10^5$ α-part./min.-cm^2) improves strongly radiation conditions by decreasing surface contamination down to permissible value. The applied coating can be used in the rooms at high temperatures of the air (up to 45°C) during 6 months and even longer without changing its properties, unless high humidity is present.

Spent coatings are easily removed from the surface causing no additional radioactive contamination.

Risk of Polonium Contamination of the Secondary Circuit

In case of failure of steam generator tube and pressure decrease in the secondary circuit there is a possibility for liquid metal penetration to the secondary circuit and contamination of water with polonium. The major part of polonium remains in the alloy, condensate is saturated up to specific activity (10^3-10^4) Bq/kg, and the inner surface is contaminated by polonium absorbed from water.

Although only small portion of polonium brought with the alloy remains in water, it is this polonium that determines (in combination with steaming) radiation conditions in the turbine hall during operation. Filters provided to minimize oxygen and salt content in the secondary circuit decrease by an order of magnitude equilibrium water activity. Steaming over the secondary system path causes aerosol activity in the air of the turbine compartment with gaseous polonium compounds. Aerosol activity is continuously present and its concentration depends on steam leak rates. For instance, volumetric activity of polonium aerosols in the air in the area of the turbine ejector discharge reached 4 Bq/m^3 value with polonium activity ~$4 \cdot 10^9$ Bq/kg in the alloy.

Contaminated inner surfaces of the secondary circuit cause radiation hazard in case of components repair. Alloy remaining in the secondary circuit is a permanent source of water contamination. Neither simple replacement of water nor even decontamination of the inner surface would lead to the desired result. Decontamination of the secondary circuit is only possible upon removal of the alloy from it.

In the above mentioned accident in NS with large inter-circuit leak, there was almost no contamination of the secondary water by polonium (max value of alpha-activity in the main condenser of steam turbine plant did not exceed 5 kg/L) because of high pressure maintained in the secondary circuit.

Radiation Environment in the Course of Reactor Core Unloading

It was a specific feature of NS reactors with LMC that the core was installed in the reactor and removed from the reactor as consolidated block including also upper shielding plug and reflector. The first unloading of the core as consolidated block from the reactor of 27/VT test facility was carried out in October 1961. The core was removed using intermediate container and unloading sheath having no shielding slide valve at the bottom. The total time of the core removal from drawing it into the sheath to putting it on the bottom of the storage was 30 minutes. Decay heat in the core by the time of its unloading was 20 - 25 kW. Outlet temperature of the air provided for cooling unloaded core block did not exceed 100°C. In order to catch the alloy spilled from unloaded core block (activity $2 \cdot 10^{10}$ Bq/kg in terms of Po-210), special pan was provided along the path of its movement from reactor to the storage. Amount of the alloy spilled to the pan was within 800 cm^3. Unloading procedure was remotely controlled from shielded control board, no personal being present in the central hall and reactor cell. Upon unloading of the core block from the reactor, slide valve of the intermediate container failed to close because of malfunction of its hydraulic drive system. This resulted in the high Po-210 release to the air atmosphere of the central hall.

The total amount of polonium released to the special ventilation system in unloading procedure was ~ $5 \cdot 10^5$ Bq (deposition on the air duct being neglected). Volumetric activities of aerosols above the reactor and in the middle section of central hall during 30 minutes after unloading start were, respectively, 2370 and (207-925) Bq/m^3. In the next 30-minute period average activity of polonium aerosols in these points was much lower: 81 and (2-11) Bq/m^3. Three hours later, aerosols concentration decreased down to 7.8 and 0.4 Bq/m^3, and three more hours later, after closure of reactor cover, activity of aerosols in the air above the reactor reached background value (0.4 Bq/m^3). Upon completion of the core unloading procedure no excess contamination of room surfaces was revealed. Six hours after refueling polonium aerosols content in the air was below 0.4 Bq/m^3.

26 years later, in June 1987 the similar core unloading procedure was carried out using this reloading sheath on the other prototype facility in Sosnovy Bor. Decay heat of the core by the time of its removal was about 3 kW, and specific activity of the coolant was approximately 10^9 Bq/kg in terms of Po-210. Radiation environment in terms of Po-210 was much better than that in the first case. Concentration of Po-210 in the air of reactor cell and central hall did not exceed 4 Bq/m^3 value ($PVA_{pers.}$), and polonium release to the environment was within $4 \cdot 10^3$ Bq.

BIOMEDICAL MONITORING OF POLONIUM INGRESS INTO THE BODY OF PERSONNEL

From the early stages of development and operation of facilities with liquid metal coolants the problems related to high radiological hazard of polonium-210 required great attention of many specialists in radiobiology for the purpose of development of the efficient measures of radiation protection of personnel.

Permanent radiological and medical monitoring of personnel involved in the work was provided. According to the results of this monitoring, no cases of carrying incorporated polonium in personnel bodies in the amount exceeding permissible values specified in the national regulatory documents on radiation safety in effect at that time have been revealed during the whole period of operation of facilities with liquid metal coolants.

For instance, in the accident on NS in 1982 with the spill of about 2000 kg of radioactive alloy directly to the reactor compartment, concentration of radioactive aerosols in the air of the compartment did not exceed 37 Bq/m^3. Polonium content in the critical organs of NS personnel determined by unbiased results of analysis of bioassays was within 10% of corresponding permissible value. Analysis of consequences of severe radiation accident that occurred on the other NS in 1968 resulting in 7 injured crewmen showed that radiation damage was caused by gamma-radiation of radioactive noble gases (krypton and xenon) released from unshielded gas system piping. Polonium content in bioassays of injured personnel was within permissible limits.

Based on the results of medical monitoring of the staff carried out by medical specialists during many years, conclusion was made on that radiation-hygienic conditions and sickness rate of staff of NS with liquid metal cooled reactors were similar, in principle, to those of not only NS with water cooled reactors, but also services ashore positioned in the area of NS deployment, where there was no radiation effect. By now, there is no reason to believe that reactors with lead-bismuth coolant impose higher radiological risk as compared to that caused by the other type NPPs and that these reactors cannot be used in civilian nuclear power. Besides, up-to-date reactors with LMC are designed as monoblock units thus eliminating practically the possibility of radioactive coolant spills.

STUDIES ON MECHANISMS OF Po-210 RELEASE FROM POLONIUM-CONTAINING MEDIA

Over a period of years work was carried out at the IPPE on a synthesis of data published in Russia and in the other countries on polonium release from polonium-containing media [3], and both experimental and analytical studies were made in this area.

It is well known that polonium may exist in either elementary chemical form or in the form of chemical compounds, such as polonium oxide, intermetallic compounds, polonium hydride etc. These forms have different fugitiveness depending on temperature of medium, type and density of gas atmosphere above polonium-containing liquid metal and some other parameters.

Table 1: Pressure of saturated vapor of polonium and its compounds (Pa) as a function of temperature

T, °C	PbPo			Po		γ	Po (eff.)	
	1	2	3	4	5		6	7
300	$2.34·10^{-4}$	$2.84·10^{-4}$	$8.20·10^{-4}$	0.94	0.92	$1.01·10^{-4}$	$0.95·10^{-4}$	$0.92·10^{-4}$
400	$1.82·10^{-2}$	$2.01·10^{-2}$	$4.72·10^{-2}$	23.3	17.7	$5.73·10^{-4}$	$1.34·10^{-2}$	$1.02·10^{-2}$
500	0.452	0.483	0.955	252	262	$2.08·10^{-3}$	0.523	0.544
550	1.68	1.76	3.26	667	527	$3.51·10^{-3}$	2.34	1.85
600	5.40	5.56	9.68	1580	1260	$5.60·10^{-3}$	8.85	7.06

1 – Abakumov (PbPo);
2 – Neuhausen (Po, eff.); 3 – Buongiorno (Po, eff.);
4 – Abakumov (Po); 5 – Ohno (Po);
6 – Abakumov (Po, eff.); 7 – Ohno (Po, eff.)
$\gamma(T)$ - factor of chemical activity of Po in LBC;
$p_{sEFF}(\text{Po}) = p_s(\text{Po})\,\gamma$ - effective pressure of saturated vapor

In Pb-Bi eutectic

$$\lg \gamma_{\text{Po}}(T) = 1.079 - \frac{2908}{T}$$

It is shown in one of the earliest publications concerning studies on polonium carried out in Mound Laboratory (USA, 1956) [4], that fugitiveness of polonium from its dilute solution in bismuth is significantly lower (by about three orders of magnitude at 400°C) than elementary polonium vapor pressure related to the same its content in bismuth. This shows that within the temperature range under study (450-850)°C polonium is present in bismuth as chemical compound with lower fugitiveness, apparently, intermetallic compound PoBi.

Laboratory experiments with heating polonium-containing specimens of $Pb_{83}Li_{17}$ eutectic performed by Feuerstein and his colleagues at FZK, Karlsruhe [5] showed that within the temperature range (300-800)°C the rate of polonium sublimation under vacuum was lower by about three orders of magnitude than that calculated for elementary polonium. The researches had a guess that polonium was present in lead-lithium eutectic as lead polonide having much lower vapor pressure than that of elementary polonium within the temperature range under study. Owing to the inert gas atmosphere polonium sublimation rate was decreased additionally by three orders of magnitude. So, the real measured polonium sublimation rate was by about six orders of magnitude lower than that calculated for elementary polonium evaporation under vacuum. The effect of shielding by gas medium was also observed in the experiments with evaporation of lead and bismuth from pure (Po-210 free) eutectic.

Very similar results were obtained in the experiments made by Tupper in the USA [6] with lead-bismuth eutectic. He draw a conclusion on that the extent of polonium hazard in radioactive lead-bismuth eutectic was often overestimated and the value of activity of Po-210 released from the alloy within the temperature range (300-800)°C was not a restraint for the use of lead-bismuth alloy as reactor coolant.

Later on, in 2003-2006 period the similar studies were conducted in Japan [7] and in Switzerland [8] confirming in general the above conclusion. Results of some studies are compared in the Tables 1, 2, and 3.

Table 2: Polonium activity in vapor phase (Bq/m3) per unit of molar fraction in Pb-Bi eutectic

T, ºC	IPPE	Ohno	Tupper	
			1	2
300	$1.70 \cdot 10^{9}$	$7.24 \cdot 10^{8}$	-	
400	$1.13 \cdot 10^{11}$	$8.60 \cdot 10^{10}$	-	
500	$2.44 \cdot 10^{12}$	$2.94 \cdot 10^{12}$	-	
550	$8.61 \cdot 10^{12}$	$1.26 \cdot 10^{13}$	$2.46 \cdot 10^{13}$	$1.25 \cdot 10^{13}$
600	$2.56 \cdot 10^{13}$	$4.46 \cdot 10^{13}$	-	

1 – evaluation by formula developed at IPPE: $$a^{\text{п}} / x^{T} = \lambda \cdot N_A \cdot \frac{P_{\text{эфф}}(T)}{R \cdot T}$$

2 – evaluation by Ohno [7] formula: $$\log\left(a^{\text{п}} / x^{T}\right) = 22.8 - 7985/T$$

Table 3: Mass flow rate (g/cm2·s) of polonium leaving Pb-Bi eutectic per unit of molar fraction in Pb-Bi eutectic

T, ºC	argon gas (1 atm pressure)			under vacuum		
	IPPE	Neuhausen	Tupper	IPPE	Tupper	
					1	2
300	$4.28 \cdot 10^{-11}$	$2.53 \cdot 10^{-10}$	-	$4.28 \cdot 10^{-8}$	-	
400	$3.03 \cdot 10^{-9}$	$9.59 \cdot 10^{-9}$	-	$3.03 \cdot 10^{-6}$	-	
500	$7.06 \cdot 10^{-8}$	$1.40 \cdot 10^{-7}$	-	$7.06 \cdot 10^{-5}$	-	
550	$3.26 \cdot 10^{-7}$	$4.17 \cdot 10^{-7}$	$2.78 \cdot 10^{-7}$	$3.26 \cdot 10^{-4}$	$1.07 \cdot 10^{-4}$	$7{,}35 \cdot 10^{-5}$
600	$8.30 \cdot 10^{-7}$	$1.10 \cdot 10^{-6}$	-	$8.30 \cdot 10^{-4}$	-	

1 – direct experiment
2 – evaluation made proceeding from P_{eff} (550 ºC) = $3.65 \cdot 10^{-11}$ Pa with Po molar fraction $x^T = 7.5 \cdot 10^{-11}$

Also, attention should be paid to another feature of polonium, i.e. its capability of forming unstable gaseous compound - polonium hydride. In the experiments with humid air flowing over polonium-containing specimens at room temperature gaseous polonium compound was formed and the only possible cause of this was hydrolyses reaction of polonium binary compound:

$$PoMe + H_2O \rightarrow PoH_2 \uparrow + MeO$$

Yield of PoH_2 increased with the increase of the air humidity. This interesting result gives a reason to a considerable extent for the constant value of α-activity in the air of reactor cell (~40 Bq/m^3) observed during several days after NS accident. Apparently, there were interaction of humid air with loose oxide film on the surface of frozen coolant containing polonium intermetallic compound, formation of polonium hydride and its sublimation to the atmosphere of the room.

CONCLUSION

1. Experience gained in operating reactors of NS and ground mounted prototypes has shown that handling of radioactive lead-bismuth coolant requires high technological culture and special measures for assurance of radiation safety. Under normal operating conditions with leak-tight primary circuit, there is no hazard imposed by polonium. This hazard appears when the work is carried on the reactor with unsealed primary system (during repairs of the circuit components, reactor refueling and in case of accident with the spill of radioactive coolant to the attended room). Owing to research work and strict radiation control in the period of mitigation of consequences of accidents with coolant spills sufficient knowledge was gained and the main organizational and technical measures were developed, as well as protective means for personnel against polonium in order to prevent overexposure of the people.

2. Overview and synthesis of data on polonium release from polonium-containing media published in Russia and in other countries, as well as our own experimental results have shown that within (300-600)°C temperature range polonium is mainly present in lead-bismuth eutectic as lead polonide. This is the reason for that the rate of polonium evaporation from liquid metal surface to vacuum within this temperature range is lower by a factor of almost 1000 than the calculated value for elementary polonium dissolved in Pb-Bi eutectic. Polonium sublimation rate is significantly decreased if there is cover gas above the liquid metal surface. So, the real measured rate of polonium sublimation to the cover gas or air atmosphere was by about six orders of magnitude lower than that calculated for elementary polonium with the same molar content in the liquid metal under vacuum.

3. Radiological and medical control of personnel of nuclear power plants with LBC carried out during many ears on a regular basis has not revealed any cases of carrying incorporated Po^{210} in the people bodies in the amount exceeding permissible values specified in radiological and sanitary regulatory documents of Russia. Methods and equipment for personal and collective protection against polonium developed in the course of assimilation of these nuclear power plants reliably provided personnel radiation safety and environment protection.

REFERENCES

[1] Radiation Safety Standards NRB 99/2009, *Sanitary Rules and Standards. San P i N 2.6.12523-09.*

[2 Concept of safety ensuring. “Use of lead-bismuth coolant in nuclear reactors and accelerator-driven systems”, *Nuclear Engineering and Design,*Vol. 173, 1997, pp. 207-217.

[3 Harvey V.Mover, “POLONIUM”. Oak Ridge, Tennessee, USA, July, 1956.

[4] H.Feuerstein, J.Oschinski and S.Horn, „Behavior of Po-210 in molten Pb-17Li”, *Journal of Nuclear Materials*, North-Holland, 1992, pp. 191 -194.

[5] R.B.Tupper, B.Minuskin, F.E.Peters and Z.L.Kardos, “Polonium hazards associated with lead-bismuth used as a reactor coolant”, *Proceedings of International Conference on Fast Reactors and Related Fuel Cycles Current Status and Innovations Leading to Promising Plants*; . Kyoto, Japan, 1991, Vol. IV.

[6] I.V.Petryanov, I.B.Borisov, S.L.Churkin, L.I.Borisova and I.A.Starostina, “Formation of gaseous polonium fraction and its release from solid specimens”, *Reports of USSR Academy of Science*, Moscow, Vol. 322, 1992, No. 3, pp. 557-559.

[7] Shuji OHNO, Yuji KURATA, Shinya MIYAHARA, Ryoei KATSURA and Shigeru YOSHIDA, “Equilibrium Evaporation Behavior of Polonium and Its Homologue Tellurium in Liquid Lead-Bismuth Eutectic”, *Journal of Nuclear Science and Technology*, Vol. 43, 2006, No.11, p.1359-1369.

[8] Handbook on Lead-Bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-Hydraulics and Technologies, *ISBN 978-92-64-99002-9*, Nuclear Energy Agency Organization for Economics Co-operation and Development, 2007.