Handling and safety of polonium contaminated lead-bismuth capsules in a hot cell

R.W. Bosch, W. Claes, R. Fernandez
SCK•CEN, Boeretang 200, B-2400 Mol, Belgium
rbosch@sckcen.be

Abstract

During the irradiation of the so-called ASTIR experiments in BR2 polonium is formed due to neutron irradiation of lead-bismuth. The irradiated lead-bismuth capsules will be dismantled and further tested in a hot cell. During this dismantling and testing small amounts of polonium can be released in the hot cell. In this paper the approach how to deal with polonium in a hot cell environment to guarantee safe and reliable operation is described. This approach consists of two parts: First, an estimate is made how much polonium can be set free in the hot cell and second, safety measures are foreseen to minimize polonium release and to assure containment of the polonium in the hot cell.

Polonium can be set free in the hot cell in three ways:
1. During cutting of the capsules, the gas plenum (containing a small amount of Po) on top of the lead-bismuth comes free.
2. During melting of the lead-bismuth to take out the specimens.
3. During testing in the LIMETS2 mechanical test facility.

Calculations show that the total amount of polonium that is set free is small compared to the amount of α-aerosols that is allowed to be released. In the safety approach we mainly focus on leak tightness of the α-box, proper ventilation and filtering, temperature control of the hot cell and the use of a cooling down period.

Keywords: lead-bismuth, polonium, Liquid Metal Embrittlement, irradiation experiment

1. Introduction

In the nuclear energy sector one of the main candidate designs for the accelerator driven system (ADS) uses liquid lead or lead bismuth eutectic both as a coolant and as spallation target. When a solid metal - liquid metal couple is formed, conditions for brittle failure due to Liquid Metal Embrittlement (LME) can be present. Therefore the sensitivity to LME is investigated for the construction materials used in the various lead alloys. One of the initiatives for this is the ASTIR experiment with the objective to determine the separate and possibly synergetic effects of a lead-bismuth environment and neutron irradiation [1]. For this experiment lead-bismuth filled capsules containing tensile samples are irradiated in the BR2 MTR. During the irradiation of these experiments, polonium is formed due to neutron irradiation of lead-bismuth. Afterwards the irradiated lead-bismuth capsules will be dismantled in a hot cell. During the dismantling and testing of the irradiated samples, small amounts of polonium can be released in the hot cell. Figure 1 shows a picture of the hot cell set up used to test tensile specimens in liquid lead alloys and a tensile specimen after testing. This test was carried out with a non-active Eurofer97 sample in lead-lithium.

In this investigation we describe our approach how to deal with polonium in a hot cell environment to guarantee safe and reliable operation. This approach consists of two parts:
- An estimate is made how much polonium can be set free in the hot cell. Reason for this is to try to properly define the polonium problem and to put it to its right proportion.
- Safety measures are foreseen to minimize polonium release and to assure containment of the polonium in the hot cell.

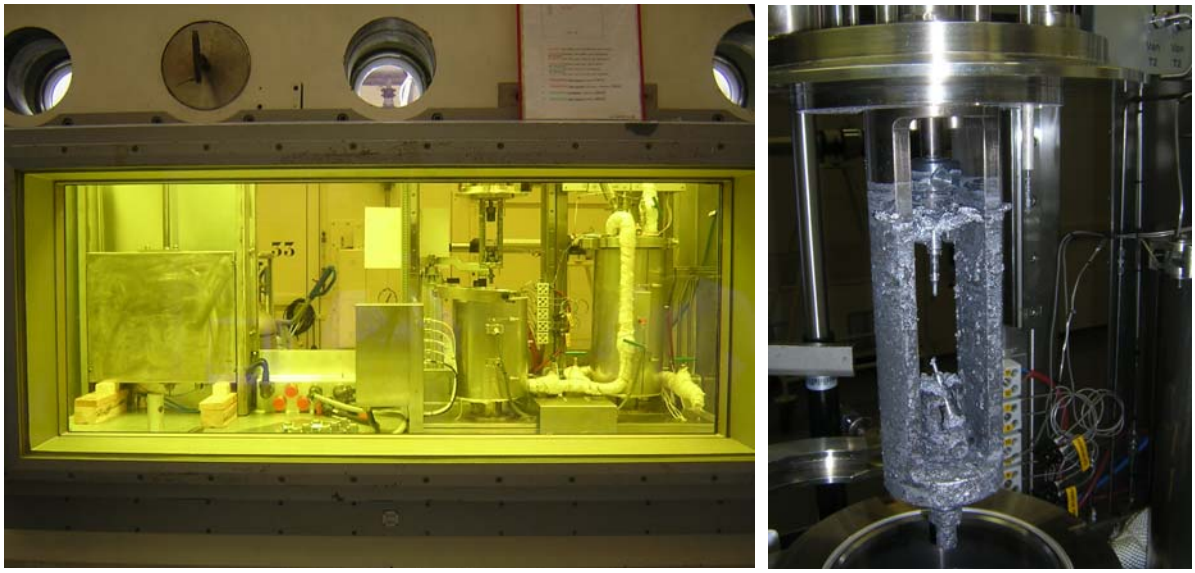

Figure 1 Hot cell with LIMETS2 (Liquid metal testing station) and tensile specimen after testing (non-active)

Polonium is a chemical element in the periodic table that has the symbol Po and atomic number 84. It is a rare and highly radioactive metalloid, polonium is chemically similar to tellurium and selenium. It occurs in uranium ores. Polonium has been studied for possible use in heating spacecraft and as an atomic heat source to power radioisotope thermoelectric generators via thermoelectric materials. According to Kershner [2] " *In ^{210}Po the technologist has found an almost unique alpha-emitting isotope* ". It has also been used in application to remove static electricity (for example in textile mills and brushed for removing dust from photographic films) [3]. It exists as a number of radio-isotopes with the most important for ^{210}Po. Polonium does exist in the environment as it is the last step in the Radium series i.e. the natural decay of U-238.
When lead-bismuth is bombarded with neutrons, ^{210}Bi is created, which then decays to ^{210}Po via β decay.

$$^{209}Bi + n \rightarrow {}^{210}Bi \underset{t_{1/2}=5days}{\overset{\beta-}{\rightarrow}} {}^{210}Po \underset{t_{1/2}=138days}{\overset{\alpha}{\rightarrow}} {}^{206}Pb$$

Some relevant properties of polonium are summarized in Table 1. For comparison we add the measured Radon activity in the environment in Belgium and the EC guideline for house interiors.

Table 1 Materials specifications Polonium 210 [4, 5]

Radioactivity	$166.2.10^{12}$ Bq/gr
Half life time	138.376 days
Atomic number	84
Atomic mass	210 gr/mol
Density	9.398 g·cm^{-3}
Melting point	254 °C
Boiling point	962 °C
Appearance	silvery
Maximum concentration in air	0.2 Bq/m^3
Maximum concentration in water	0.83 Bq/l
Radon gas (outside)	35-70 Bq/m^3 (Belgium)
Radon gas (in houses)	200 – 400 Bq/m^3 (EC guideline)

2 Polonium release in the hot cell

2.1 Capsule dismantling – cutting

When an irradiated lead-bismuth filled capsule is cut the gas on top of the lead-bismuth surface (the so called gas plenum) will be released in the hot cell. This gas will contain a certain amount of Po, based on the saturation vapour pressure of Po [5,6]. This amount can be estimated when the saturation vapour pressures of the volatile components are known and the concentration of Po in the lead- bismuth melt. The perfect gas equation of state and Raoult's law are used to calculate the concentration of Po in this gas plenum. Figure 2 shows the activity of Po in a 3 cc gas plenum as a function of temperature. It is clear that the Po activity is negligible. Also the temperature plays an important role in the amount of Po gas present. Notice that the saturation vapour pressure at low temperatures were obtained by extrapolation high temperature data obtained for T>200°C.

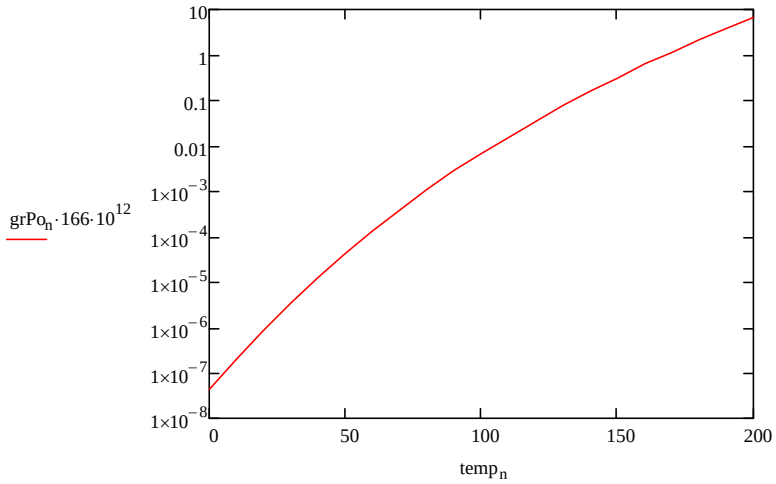

Figure 2 *Po concentrations in Bq in a 3 cc gas plenum in an irradiated lead-bismuth capsule as a function of temperature (°C)*

2.2 Capsule dismantling – melting

When PbBi is in the liquid phase, Po can be evaporated directly. Neuhausen has investigated the polonium release due to evaporation under conditions were the liquid PbBi is in contact with hydrogen (Ar/7%-H2) and water (water-saturated Ar) [7]. The release of Po for water saturated argon and hydrogenated argon is similar. The release at temperatures smaller than 900 K (= 627 °C) is small. Besides these measurements a quantitative assessment has been made based on Po release experiments from Tupper and Neuhausen [7, 8] and an updated equation again from Neuhausen [9]. These equations were used to calculate the activity release in Bq during capsule melting of 30 minutes. Figure 3 shows the two curves as a function of temperature.

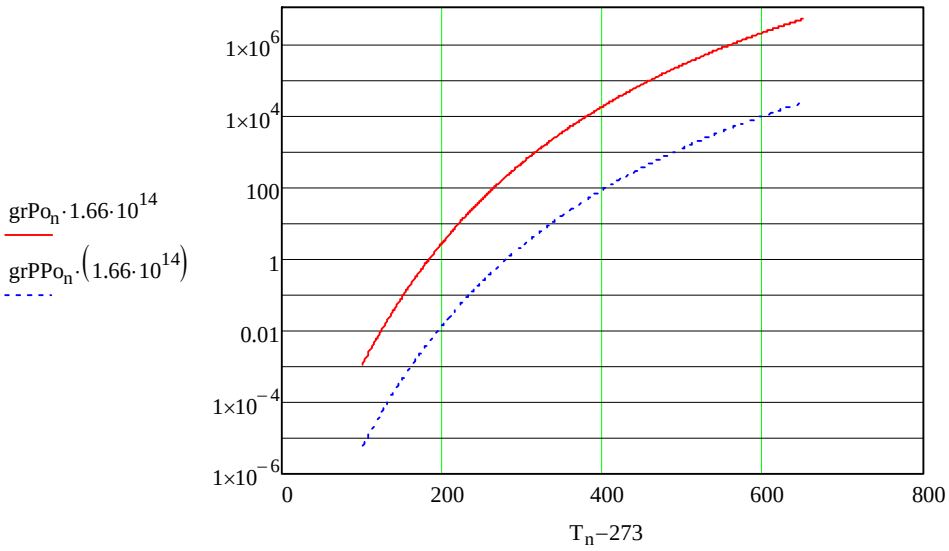

Figure 3 Activity release of Po (Bq) during melting as a function of temperature (°C) (red curve [5], blue curve [9]); melting time is 30 minutes.

During melting a certain amount of Po is set free, which depends on temperature and melting time. The lower the temperature and the shorter the melting time, the smaller is the release. A typical temperature to melt the PbBi so it can be removed from a capsule is 200 °C. Depending on which equation to use, the best scenario results in a release of ≈ 0.015 Bq and the worse scenario in ≈ 45 Bq.

2.3 Testing in LIMETS2

A tensile specimen that has been taken out of the irradiation capsule will not be cleaned completely. A small layer of lead-bismuth will stick to the sample. It is important that this layer will stay there as the interface metal-PbBi as it is formed under irradiation is of scientific interest. This means however that a small amount of Po will enter the LIMETS2 set-up it self. The PbBi in the autoclave and dump tank will contain Po that comes from this thin layer that sticks around the tensile specimen. During a test PbBi is liquid and so evaporation of the Po will take place.

First we have to guess how much PbBi will stick to a tensile specimen. We assume a surface layer of 0.1 mm thick at the gage with length 10 mm of the tensile specimen [10]. The volume of PbBi at one specimen is $\frac{1}{4}\pi 10\left(2.6^2 - 2.5^2\right)$ = 4.00 mm^3, which means for 36 samples a maximum of 0.144 cm^3. From this volume the mole fraction x of Po in PbBi is then calculated. For the evaporation calculation a similar approach has been followed as in paragraph 2.2. Figure 4 shows the release in Bq for a test of 24 hours as a function of temperature. Again it is clear that the test temperature plays an important role whether a major amount or a very small amount of Po will be released.

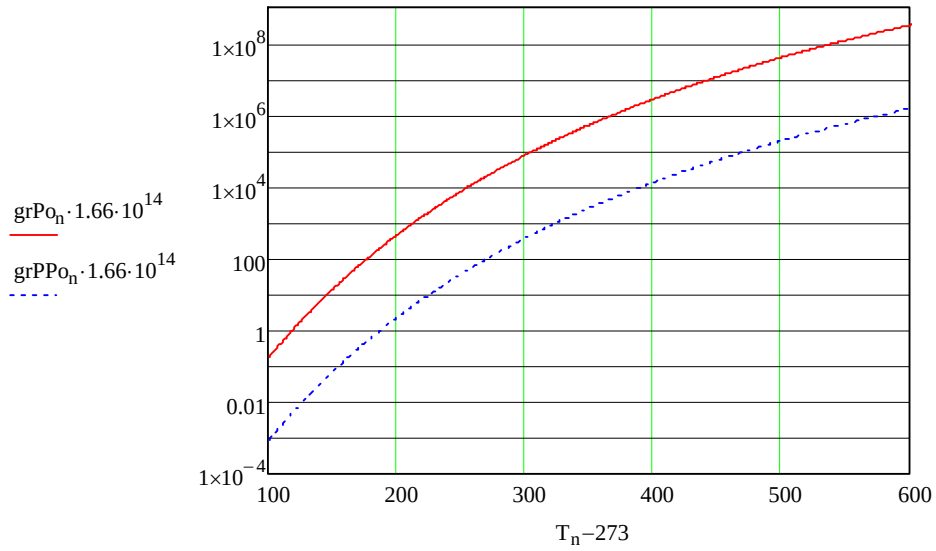

Figure 4 Release of Po (Bq) per hour as a function of temperature (red full curve [5], blue dashed curve [9])

Again the amount of Po that is set free is relatively small. During testing not all the samples will be put together in the LIMETS2. In fact they are tested one by one. Between the first test and last test can be a period of 4-6 months. That means that the last sample will contain much less Po due to radioactive decay then the first and so the release will be smaller.

3 Polonium hydride

Polonium can form the unstable gas compound polonium hydride. Polonium hydride has been reported to be volatile, albeit that it is not very stable and tend to decompose quickly. Pankrov reported that polonium hydride was released, when water reacted with polonium oxides [11].. Buogornio mentioned that polonium hydride can be formed in when water is blown through polonium contaminated lead- bismuth, part of a conceptual reactor, which he investigated for his Ph-D [12, 13]. Neuhaus stated that polonium hydride will most probably only be formed when it can react with atomic hydrogen [14]. Here we look at possible sources of polonium hydride formation in a hot cell. An estimate of the likelihood of formation and contamination of polonium hydride has been made and whether this could hamper the hot cell operation.

Polonium can form polonium hydride when it is in contact with water according to:

$$PoMe + H_2O \rightarrow PoH_2 + MeO \quad (1)$$

In this paper we look more specific at the direct formation of polonium hydride from the reduction of Po by water or protons (hydrogen ion H^+):

$$PoH_2 \leftrightarrow Po + 2H^+ + 2e^- \quad (2)$$

$$PoH_2 + 2OH^- \leftrightarrow Po + 2H_2O + 2e^- \quad (3)$$

Equations (2) and (3) are thermodynamically similar, but can take place at different reactions rates.
Three possible sources for polonium hydride are distinguished i.e. that are conditions were Po is in contact with water and/or hydrogen ions:

1. During cleaning and decontamination.

2. Reaction with water (humidity).
3. Reaction with hot water during testing in LIMETS2.

The thermodynamic calculations will consider equation (2) as this has been reported in the Atlas of Electrochemical Equilibria in Aqueous Solutions of Marcel Pourbaix [15]. To estimate whether PoH_2 will be formed the potential – pH diagram (also called Pourbaix diagram) of Polonium is used. The potential in this diagram is an electrochemical potential which means that it is the potential of an electrode or corroding surface measured against a reference electrode under open circuit conditions. The potential - pH diagram is constructed based on thermodynamic calculations and so contains no information about reaction rates. The diagram shows the region of stability of Po as a function of pH and potential and can be used to make an estimate whether PoH_2 will be formed or not. The region of PoH_2 is at the bottom left side of the potential – pH diagram (reproduced in Figure 5). That means that at very low potentials and low pH values Po is likely to be reduce to polonium hydride.

To obtain the potential and pH of a certain metal in a certain electrolyte a simple experiment can be carried out. Figure 5 shows the set-up of such an experiment. The metal to be investigated, for instance a stainless steel sample with a small layer of PbBi, is submerged in an electrolyte. This electrolyte in our case is the cleaning solution, tap water or demineralised water. The pH of the solution is measured with a pH electrode. The electrochemical potential of the stainless steel sample is measured with a reference electrode. This reference electrode has a fixed electrochemical potential that can be related the SHE (Standard Hydrogen Electrode) scale. The SHE scale is used for all potential – pH diagrams. Tests have been carried out with stainless steel, stainless steel with PbBi and PbBi in the cleaning solution, tap water and demineralised water. Tap water and demineralised water have been selected as we assume that the water present in air is somewhere in between these two compositions.

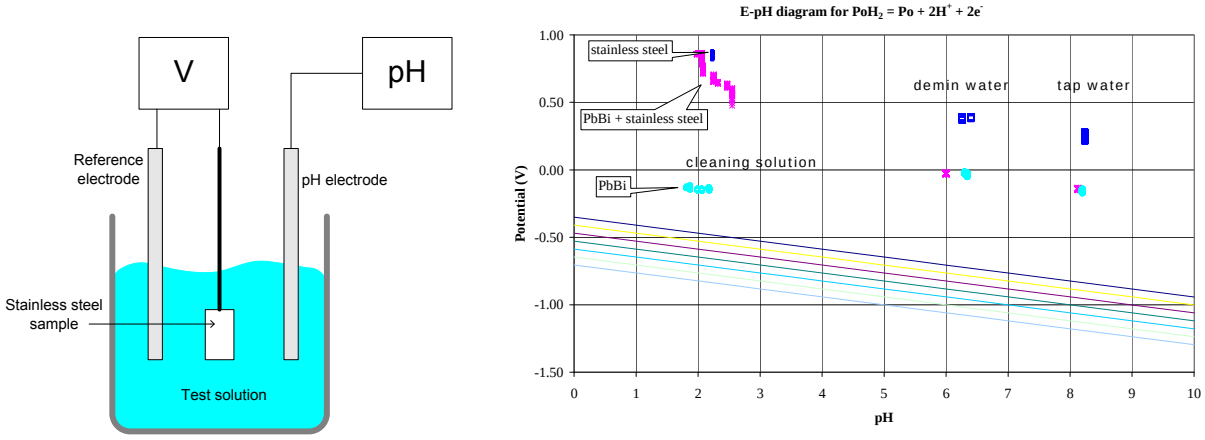

Figure 5 Principle of the potential pH measurement and the potential - pH diagram summarizing the test results

Based on these thermodynamic estimations, it is shown that formation of polonium hydride will not occur when it is in contact with aqueous solutions at ambient temperature even with low pH. In contact with hot water polonium hydride can however be formed. Water vapour that might be present in LIMETS2 can form polonium hydride at high temperature, albeit in small quantities. This polonium hydride will be released in the hot cell were it will decompose quickly due to its unstability and the lower temperature in the hot cell it self.

4 Safety considerations

4.1 Leak tightness of the α-box

Special precautions have been taken during the construction of the alpha-box regarding leak tightness. The leaking rate is ≤ 0.6 Vol%/hour, according to class 3, which allows testing of α-contaminated samples.

4.2 Proper ventilation and filtering

A HEPA filter can only capture particles. If we assume that part of the polonium can exist as a volatile gas (Po or PoH_2) then an activated coal filter has to be used to decrease the amount of Po that will be released to the environment. Therefore an activated coal filter will be mounted in the hot cell after the HEPA filter.

The total filter chain between the inside of the hot cell and the outside environment consists of 3 HEPA filters and an active carbon filter:

1. A HEPA filter in the α-box.
2. A activated carbon filter in the α-box
3. A HEPA filter on top of the hot cell
4. A large HEPA filter in the filter house at the end of the ventilation chain.

Figure 6 shows a picture of the HEPA and carbon filter as they will be mounted in the hot cell.

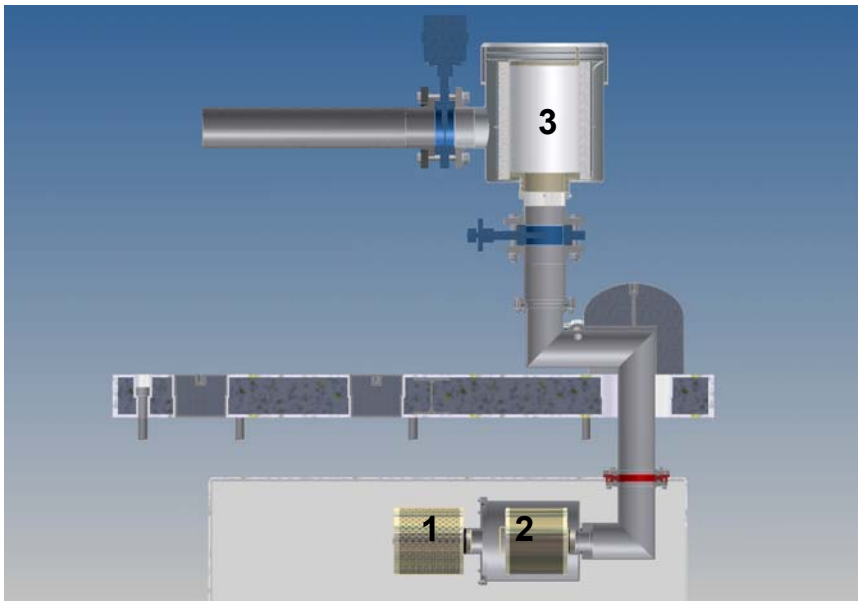

Figure 6 Filter systems in hot cell 12, (1) HEPA filter, (2) activated carbon filter and (3) HEPA filter.

4.3 Temperature control of the hot cell and LIMETS2

The temperature in the hot cell is also a safety issue. Therefore the following actions are foreseen.

1. High temperature alarm on the autoclave temperature.
2. High temperature alarm in the hot cell, visual and audio warnings at 45 °C.
3. High temperature alarm in the hot cell at 55°C, automatic shutdown of all heating devices in the hot cell.

4.4 Using cooling down period to decrease the total amount of Po.

The half life time of Polonium is 138 days. To reduce the Po activity a cooling down period can be foreseen. For instance for the long irradiation period of 10 cycles a cooling down of 320 days can be foreseen to reduce the Po activity by a factor of 5 .
Besides the Po activity, a cooling down period of minimum 3 months is foreseen to get rid of the short life time activity products.

4.5 Shielded storage of Po contaminated PbBi and samples in the hot cell.

The Po-contaminated lead-bismuth will be stored in the hot cell for a sufficient amount of time to let the Po decay. A simple but adequate storage system has been designed. It consists of small containers (maximum 5 kilo) that can be placed in cylinder shaped spaces that are submerged in the hot cell floor. These spaces are surrounded by lead blocks to shield for radiation. On top are lead plugs (for the also present γ-activity from other nuclides) with covers of magnetic materials (ferritic stainless steel) that can be removed with a magnet.

4.6 Alpha-monitoring system

An alpha-detector is installed in the hot cell. This alpha-detector (Silicon PIPS detector [16]) can measure the alpha/beta surface contamination. Monitoring of the alpha activity in the hot cell is carried out at two locations: (1) an air-filter through which a continuous air stream is maintained by a small ventilator, (2) a predefined surface in the hot cell with fixed dimensions. On a daily or weekly basis measurements are carried out and stored in a log book. This monitoring will start before alpha contaminated samples are brought into the hot cell. This should allow us to determine which operation causes an increase in alpha activity. Any increase in alpha activity is due to Po-210, which is the only alpha emitter present besides the natural background radiation.

5 Conclusions

- Polonium can be set free in the hot cell in three ways:
    - During cutting of the irradiated lead-bismuth capsules.
    - During melting of the capsules to get the tensile specimens out.
    - During testing of the polonium contaminated tensile specimens in the LIMETS2.
- The amount of polonium that can be set free has been calculated based on saturated vapour pressures and evaporation rates of Po from literature data. It is shown that during dismantling and testing the amount of Po that is set free is small.
- As the amount of knowledge on polonium is limited a certain redundancy regarding safety has been built in. For example all calculations were carried out assuming there is no cooling down period. In practice a cooling down period of > 3 months is foreseen.
- Safety considerations:
    - Leak tightness of the α-box
    - Proper ventilation and filtering
    - Temperature control of the hot cell and LIMETS2
    - Using cooling down period to decrease the total amount of Po.
    - Shielded storage of Po contaminated PbBi and samples in the hot cell.
    - Installation of an alpha monitoring system to follow and verify whether polonium and polonium compounds are set free in the hot cell.

6 References

1. Van den Bosch J., Al Mazouzi A., Benoit P., Bosch R., Claes W., Smolders B., e.a.- TWIN ASTIR: an Irradiation Experiment in Liquid Pb-Bi Eutectic Environment.- IWSMT-8.- Taos, United States, 16-20 October 2006.
2. C.J.Kershner, Properties and fabrication of ^{210}Po fuel forms, Symposium on Materials for Radio-Isotope Heat Sources, Nuclear Metallurgy, Vol. 14, 1968.
3. Handbook of Chemistry and Physics 79th ed. 1998-1999 CRC press 1998, p. 4-22.
4. Nuclides 2000, An Electronic Chart of the Nuclides, version 1.00, European Commission 1999.
5. *Properties of irradiated LBE and Pb*, Lead-Bismuth Hand Book 2006.
6. A.S. Abakumov, Z.V.Ershova, Radiokhimiya, 16 (36), 1974, p. 397.
7. J. Neuhausen, Y. Köster, B. Eichler, Radiochim. Acta 92, 2004, p. 917.
8. R.B. Tupper, B. Minuskin, F.E.Peters, Z.L. Kardos, Polonium hazards associated with lead-bismuth used as a reactor coolant, International Conference on Fast Reactors and Related Fuel Cycles, Current status and innovations, Vol. IV, October 28 – November 1, 1991, Kyoto, Japan.
9. J. Neuhausen, *Reassessment of the rate of evaporation of polonium from liquid eutectic lead bismuth*, TM-18-05-01, PSI, 2005.
10. D. Sapundjiev, S. Van Dyck, W. Bogaerts, Corrosion Science 48, 2006, p. 577.Dani
11. D.V. Pankratov et.al. *Polonium Problem in Nuclear Power Plants with Lead-Bismuth as a Coolant*, in Proceedings of the conference "Heavy Liquid Metal Coolants in Nuclear Technology", Obninsk: SCC RF – IPPE, 1999. – Volume 1, p. 101.
12. J. Buongiorno, Conceptual Design of a Lead-Bismuth Cooled Fast Reactor with In-Vessel Direct-Contact Steam Generation, Ph-D thesis, 2001, Massachusetts Institute of Technology
13. J; Buongiorno, C. Larson K.R. Czerwinski, Speciation of polonium released from molten lead bismuth, Radiochim. Acta 91, 2003, p. 153.
14. J. Neuhausen, Volatile Elements Release, Topical Day on Heavy Liquid Metal Technology, SCK•CEN, Mol, Belgium, 8 November 2005.Lecture topical day
15. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE Cebelcor, 1974, p. 572.
16. SPAB-15 Alpha/Beta Probe for Radiagem™ , Canberra Product information 2007.