Purification of Lead-Bismut Eutectic Used in Accelerator Driven Systems - 9411

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ABSTRACT

MYRRHA is an Accelerator Driven System (ADS) under development at Mol, Belgium. With the development of such ADS and also with the development of some GEN IV type reactors, new problematic waste types occur, needing a different waste treatment approach during operation and/or during decommissioning. One of the problems to be solved during the operation of the ADS MYRRHA is the removal of Polonium from the lead-bismut eutectic. This paper gives an overview of an exhaustive literature study concerning the Polonium removal techniques from a lead-bismuth eutectic melt that will be used as target and reactor coolant in the MYRRHA reactor. Five extraction techniques have recently been investigated: distillation, Polonium hydride stripping, alkaline extraction, rare-earth filtration and electrodeposition. None of these techniques has yet been applied at large scale. A detailed description of each extraction process is given. It shows that there is no ideal solution to the problem. The Polonium hydride stripping and electrodeposition methods can already be ruled out, the former for obvious safety reasons, the latter because no convincing results could be provided to date. The distillation process is rather simple and could also be coupled to the removal of Hg-194 from the gas plenum, but a pilot scale investigation would require working with Polonium. The other main drawbacks of the method are that it necessitates a large transfer area and that high temperatures are required. The alkaline extraction method represents the most extensively studied technique because of the possibility to develop it with Tellurium as Polonium surrogate. The main challenge of the technique will be to find a material that could adequately cope with the high temperature and the corrosivity of the alkali melt. The rare-earth filtration represents the most elegant technology but would still require a lot of research and development efforts since a broad expertise is needed in many fields.

INTRODUCTION

Accelerator Driven System – MYRRHA

One of the most important concerns for the nuclear energy is the radioactive waste management. Geological disposal is the solution of this problem. Nevertheless, a relaxation of the constraints on the geological disposal would be very welcome. This could be achieved thanks to the transmutation of minor actinides (Np, Am, Cm,...) and long lived fission products. The ADS MYRRHA will allow studying these phenomena.

An ADS (Accelerator Driven System) - sometimes also called a nuclear amplifier - is an alternative concept to the critical nuclear reactor. The idea was first proposed by Nobel prize laureate E.O. Lawrence in the 1950's and was revived by another Nobel prize laureate C. Rubbia in 1993 after recent major advances in accelerator technology.

The main advantage of an ADS is its non-critical fission core, i.e. a core that cannot on its own sustain the fission chain reactions. Instead, a neutron source placed at the center of the core provides primary neutrons which are then multiplied or amplified by the core. MYRRHA as an intense irradiation neutron source could also be used for nuclear fuel and material research for present day fission reactors (PWR, BWR) and the new generation reactors (Pb-cooled fast reactor, HTGR) presently called "Generation IV" reactors and for the fusion reactor. The purpose of MYRRHA is to serve as a multipurpose irradiation

facility for research to address ADS technological demonstration, waste transmutation studies of minor actinides and long lived fission products, radioisotopes production for medical & industrial applications and more. MYRRHA will have a proton beam power of 1.5 MW (600 MeV * 2.5 mA), a windowless liquid Pb-Bi spallation target, a sub-critical core (about 60 MW) made of MOX fuel with a plutonium content limited to 35 wt%, cooled with Pb-Bi and a K_{eff} value of 0.95.

Lead Bismut Eutecticum (LBE)

The use of heavy liquid metals like lead and lead-bismuth eutectic (LBE: 44.5 wt.%Pb-55.5wt.%Bi), as coolants for fast reactors offers several safety and economic advantages. These advantages arise from the following basic material characteristics: chemical inertness with air and water, high atomic number, high boiling temperature, low melting temperature and low vapor pressure at operating temperatures. However, several important technological issues still need be addressed. One of the most important issues is the radiological hazard associated with activation of LBE coolant upon neutron bombardment. Po-210, a toxic alpha-emitter of 138.38 days half-life, is formed from Bi-209 by neutron capture according to the following reaction:

$$^{209}Bi + n \longrightarrow {}^{210}Bi \xrightarrow[t_{1/2} = 5\ days]{\beta^-} {}^{210}Po \xrightarrow[t_{1/2} = 138\ days]{\alpha} {}^{206}Pb \qquad \text{(Eq. 1)}$$
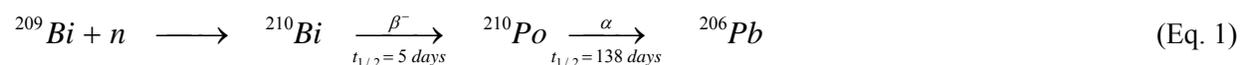
Most of the Polonium is retained in the LBE coolant during normal operating conditions and can cause problems during maintenance operations or if coolant leakage occurs. However, some polonium migrates to the cover gas in the reactor plenum and will diffuse outside the primary system when the reactor is opened for refueling or maintenance.

Considerable experience in dealing with polonium-related issues has been gained since more than 30 years in Russia where several submarines were equipped with LBE-cooled nuclear reactors. A polonium technology was developed including special polonium filters for air cleaning, polonium-adsorbing adhesive films for decontamination of large surfaces, special respirators, and pressurized suits for maintenance of contaminated areas [1].

The polonium hazard can be significantly reduced by continuous online, or batch extraction from the reactor coolant because the rate of polonium release under any circumstances is proportional to its concentration in the LBE melt. It should be emphasized though that in spite of the experience gained by the Russians in dealing with polonium contaminated LBE, no publication describing industrially established and proven polonium extraction technology exists.

PROPERTIES OF THE CHALCOGENS

Polonium forms with Selenium and Tellurium the heaviest of the Chalcogens (or Group 16), which also contain Oxygen and Sulphur. Selenium and Tellurium are generally considered as the chemical analogues of Polonium. Polonium is the only element in the group that does not have stable isotopes. The three longest lived isotopes of Polonium, together with their modes of production and radiological properties are shown in Table I:

Table I: Production and radiological properties of long-lived Po isotopes

Isotope	Production	$T_{1/2}$	E (MeV)
^{208}Po	^{209}Bi (d,3n) or (p,2n)	2.898 y	5.11

| ^{209}Po | ^{209}Bi (d,2n) or (p,n) | 102 y | 4.88 |
| ^{210}Po | ^{209}Bi (n,) | 138.376 d | 5.305 |

Several atomic and physical properties of the three elements are as expected, as e.g. the trends to larger size, lower ionization energy and lower electronegativity. The trend to metallic conductivity is also noteworthy; indeed Po resembles its horizontal neighbours Bi, Pb and Tl not only in this but in its moderately high density and notably low melting and boiling point. It behaves as a typical metal. Selenium and Tellurium are considered as semiconductors.

The first saturated vapour pressures of Selenium, Tellurium and Polonium that have been reported are shown below in Table II with the vapour pressure and temperature respectively expressed in *Pa* and in *K*. The equations are reasonably accurate up to 750°C.

Table II: Saturated vapours pressures of Se, Te and Po

$$\text{Selenium:} \quad \log p_{Se} \ = \ 10.214 - \frac{4990}{T}$$

$$\text{Tellurium:} \quad \log p_{Te} \ = \ 9.725 - \frac{5960}{T}$$

$$\text{Polonium:} \quad \log p_{Po} \ = \ 9.36 - \frac{5378}{T}$$

If the physical properties of Polonium resembles those of elements in the same period (Tl, Pb, Bi) rather than those of the other chalcogenides, its chemistry shows nevertheless much similarity to that of Tellurium and at a lesser extent to that of Selenium. Parallel with this trend is the gradual emergence of cationic properties with Te, and these are even more pronounced with Po. Selenium, Te and Po combine directly with most elements, though less readily than do Oxygen and Sulphur to form binary chalcogenides. The most stable compounds are the selenides, tellurides and polonides (oxidation state: -2) formed with the strongly positive elements of Groups 1, 2 and the lanthanides. Polonium forms extremely stable derivatives with lanthanides, since these compounds do not decompose even at 1000°C. All chalcogens exhibit bivalency, with two covalent bonds and two lone pairs of electrons, but this state in Se and Te, particularly for the dihalides (oxidation state: +2), is unstable, the bivalent compounds disproportionating to the element and the tetravalent compound. The hydrides, H_2X, decrease in stability from Se to Po. Of specific interest, Lead polonide PbPo is formed when lead is heated (350°C) in Polonium vapour, and also appears in the condensate of metallic Polonium during its -decay. Lead polonide PbPo was reported to distil at 700°C.

Health hazards and handling problems

Most Selenium compounds are highly toxic, particularly hydrogen selenide. Great care should be taken in handling all selenides and soluble selenites or selenates. Tellurium compounds, apart from hydrogen telluride, are rather less toxic than those of Selenium, probably because of their rapid reduction in the body to elementary Tellurium. Polonium is far more dangerous than either Selenium or Tellurium because of its radioactivity. The three elements are absorbed essentially in the kidneys, spleen and liver, and these organs, in the case of Polonium, suffer irreversible damage because of their complete absorption of the alpha particle energy. For this reason, the maximum permissible body-burden for ^{210}Po is only 1.11 kBq, equivalent to a particle weighing 6.8 10^{-12}g. The maximum permissible concentration in air is 0.2 Bq.m^{-3}, and 0.83 Bq.l^{-1} in water [2, 3]. The maximum permissible concentration in air for

Selenium and Tellurium is 10^{-4} g.m^{-3}. The main hazard is the formation of volatile Po compounds forming -radioactive aerosols.

Properties of Polonium and lighter homologues in molten lead-bismuth eutectic

The use of molten lead-bismuth eutectic (LBE) as a heavy liquid metal coolant of fast-spectrum nuclear systems has been deemed preferable to pure Lead due to its lower melting point (125°C versus 327°C), which greatly simplifies coolant handling as well as the reactor design and operation. However, LBE does display several disadvantages with respect to Lead. The coolant is more costly (Bismuth is relatively rare), the solubility of steel is larger in Bi than in Pb, and production of radioactive Po-210 occurs due to the neutron activation of Bi. In MYRRHA, the primary system is sealed and separated from the secondary system. As a result, Po is well retained in the LBE during normal operation conditions and can create a problem only if a coolant leakage occurred. Some Po migrates to the cover gas in the reactor plenum and can diffuse outside the primary system if the reactor is not perfectly tight. Also, during maintenance activities for which access to submerged structures is required, Po is an issue. Polonium-210 may limit access to the surfaces on which it deposits, thus increasing maintenance costs and/or collective doses. The Po hazard can be significantly reduced by an extraction system from the reactor coolant because the rate of release under any circumstance is proportional to the Po concentration in the LBE melt. Even small rates of Po extraction can result in considerable reduction of the Po concentration in the LBE.

Early experiments from Feuerstein *et al.* [4] investigated the evaporation behaviour of Po-210 in molten Lead-Lithium eutectic (Pb-(Li-17)). They found that Polonium evaporates in the form of an intermetallic compound PbPo. Because of the low vapour pressure of Lead polonide, evaporation rates were small, about three orders of magnitude smaller than if Polonium would have formed an ideal solution with the eutectic. Abakumov and Ershova measured the vapour pressure of Lead polonide as a function of the temperature in the range of 640 to 850°C:

$$\log p_{PbPo}\,[Pa] \;=\; 9.06 - \frac{7270}{T\,[K]} \tag{Eq. 2}$$

Gromov *et al.* [5] established later that the evaporation rate of Po and PbPo under vacuum was three orders of magnitude larger than under atmospheric pressure. Yefimov *et al.* [6] confirmed that Po vapour pressure over melt Lead-Bismuth in the temperature range of 300 to 600°C was about three orders of magnitude less than for an ideal solution. They suppose that if Tellurium was used instead of Polonium as a chemical analogue, it would form PbTe rather than Bi_2Te_3 because of its larger thermodynamic stability. This reasoning is contradicted by other data [7] which are in favour of the Bi_2Te_3 formation. Nevertheless, the kinetics would certainly favour the formation PbTe given the supposed very low concentration of Tellurium in LBE.

The assumption that Po would rapidly form a stable compound with Lead was visually and analytically confirmed [8] at the Idaho National Engineering and Environmental Laboratory. They used Tellurium as chemical homologue of Polonium, which they mixed (at 0.01 wt% concentration) with LBE. It preferentially formed PbTe as observed from the SEM technique.

The evaporation behaviour of Po and its lighter homologues Se and Te dissolved in LBE has been studied by Neuhausen *et al.* [9] at various temperatures in the range from 209 to 1057°C under Ar/H$_2$ and Ar/H$_2$O atmospheres using -ray spectroscopy. Within short term (one hour) experiments, measurable amounts of Polonium are evaporated only at temperatures above 700°C. Long term experiments reveal that a slow evaporation of Polonium occurs at temperatures around 600°C resulting in a fractional loss of the melt of around 1% per day. Evaporation rates of Selenium and Tellurium are smaller than those of Polonium. The

volatility increases in the order Se<Te<Po. They observed that the presence of water did not enhance the evaporation within the error limits of their experiments. In the temperature range of interest for technical applications like liquid metal spallation targets (200-450 °C) no release has been observed within the experimental errors.

Ohno *et al.* [10] made an experimental study on the steady-state evaporation of LBE to acquire essential and fundamental knowledge about the vaporization of LBE. The investigated temperature range was from 450 to 750°C. The vapour mass ratio [Bi/Pb] was equal to 3 on average (compared to 1.25 in the liquid pool), with a standard deviation of 0.6.

POLONIUM ENRICHMENT IN LEAD AND LBE

Gromov *et al.* [5] calculated the accumulation of Polonium isotopes (208, 209 and 210) in LBE target after one year of operation with a 20 MW beam and found a total activity of 1.11 PBq for Po-210, 1.85 TBq for Po-209 and 0.13 TBq for Po-208 for a coolant mass of more or less 10 tons. Khorasanov *et al.* carried out the same kind of calculations for a fast reactor using Lead as coolant [11]. They propose the use of isotope Pb-206 as coolant to reduce the production of the most radiotoxic isotopes of Pb, Bi and Po and to avoid disposing a large amount of spent Lead.

Similar coolant activation calculations (1 kg Polonium for 100 tons of LBE) were carried out with respect to the MYRRHA design [12] and focused mainly on the production of the Po-210 isotope and its evaporation in the cover gas. This cover gas contamination by Po-210 has been investigated further in a subsequent document [13], which also concerned the assessment of an accidental release of the cover gas.

A report of the PDS-XADS (Preliminary Design Studies of an Experimental Accelerator-Driven System) European project [14] described the work done for the assessment of radiotoxicity in the target of XADS. The results show that the major risk associated with proton beam irradiation of the LBE target will come from the production of the Hg-194, a volatile metal, which decays by electron capture. Its half-life of 260 years enounced in the report does not match though with the commonly accepted value of 444"77 years [15]. Nevertheless, the highest toxicity risk will be associated with Po-210 generated predominantly by core neutrons. This radiotoxicity is reduced by 6 orders of magnitude after about 8 years of cooling but a given level of radiotoxicity will be maintained over one million year as a result of the decay of the metastable species of Bi-210, an -emitter with a half life period of 3.10^6 years.

POLONIUM EXTRACTION TECHNIQUES FROM LBE

Historically, the first published Polonium extraction methods were linked to the commercial production of this element, for military or spatial applications, from the irradiation of Bismuth. Most, if not all, of these methods recommend the use of a chemical carrier.

The first separation method of Polonium that has ever been reported concerned the use of fused LiCl-KCl eutectic as chemical extraction agent [16]. When put in contact for 3 hours with fused Bismuth containing trace amount of Po under Argon atmosphere and at operational temperatures comprised between 350 and 530°C, 97% of the Po were removed from the Bi. When the temperature was higher than 500°C, approximately 100% of the Po evaporated, probably under the form of $PoCl_4$. This vapour could be deposited on several metals as elementary Po or polonide.

Later, Moore patented a Po recovery process from neutron-irradiated Bismuth consisting in adding Cerium metal to the melted Bi [17]. Polonium is carried by the Cerium bismuthide precipitate or co-precipitated therewith, probably in the form of Cerium polonide. The Po-containing Cerium bismuthide is lighter than the Bismuth and floats on its top. It can then be separated from the Bismuth by skimming or

by cropping it off after solidification of the entire mass. The quantity of Cerium to be added would amount 0.7 to 2 wt. %.

In the late sixties, Baltisberger [18] invented an electrochemical separation method to separate Polonium from irradiated Bismuth, and to recover a high-purity Bismuth. The principle of the invention was to electrodeposit Bismuth on a Bismuth cathode and to use an electrolyte made of Bismuth cations, recovering a resultant Polonium-carrier constituent precipitate at the anode.

A few years later, Siemens and Wheelwright [19] patented a pyrochemical extraction process. The irradiated Bismuth material is melted and enters an extraction chamber containing molten caustic (e.g. anhydrous Sodium hydroxide), where Po-210 is extracted from molten Bismuth. Since molten caustic and molten Bismuth are known to have highly corrosive effects, the inventors recommend the use of nickel based alloys, like e.g. Inconel 600.

During the next twenty years no publication covering polonium extraction techniques were released. Russians from the Institute of Physics and Power Engineering suggested the use of an alkaline extraction method [6] to remove the Polonium from the coolant. The Idaho National Engineering and Environmental Laboratory (INEEL) and the Massachusetts Institute of Technology (MIT) collaborated on research concerning Polonium extraction systems for LBE-cooled nuclear reactors. They isolated five promising Lead polonide removal mechanisms from LBE [20], that do not require a complicated process, as the early ones. The are summarized in the following paragraphs.

Polonium extraction from LBE by distillation

The vapour pressure of Lead polonide is several orders of magnitude larger than that of LBE across a wide range of temperatures. Under a temperature higher than 600°C, the Lead polonide is dissociated [6], as has been confirmed by Miura *et al.* [21] who reported a complete decomposition to elemental Po at 630°C. This would allow a selective distillation of Polonium from a LBE stream. The vapours could be condensed on a cold surface. Several types of configurations might be proposed: countercurrent mass exchangers, multy-tray distillation columns and evaporation trays. The primary goal is to maximize the LBE surface being exposed. Processing a 50 to 600 kg.hr^{-1} flow rate of Po contaminated LBE (initial Po activity: about 0.1 TBq.kg^{-1}, for a total of 10 tons LBE coolant) at 700°C was found to require a mass transfer surface area of 150 m^2, which can be achieved by bubbling an inert gas through the liquid LBE [6]. The removal efficiency of this process would rate up to 99%. Polonium distillation was found suitable for small scale military applications in Russia. However, in the case of a large reactor, this technique might be impractical and costly because of the large transfer area requirements and the need to operate the system at high temperatures. Indeed, such systems must operate at 900°C-1100°C to be effective. At this temperature, special structural materials would need to be used, since stainless steels are not compatible with these temperatures.

Polonium extraction from LBE by H$_2$Po stripping

In a LBE system, the Polonium hydride can be produced by reaction of lead polonide with water:

$$PbPo \ + \ H_2O \ \leftrightarrow \ H_2Po \ + \ PbO \qquad\qquad\qquad (Eq. 3)$$

Polonium hydride H$_2$Po is a volatile and chemically unstable gas which readily decomposes into Hydrogen and Polonium. It is hard to produce in sizable amounts. The MIT [22] produced experimental results concerning the H$_2$Po stripping separation method, which consists in provoking a chemical reaction between Lead Polonide and Hydrogen to generate Polonium hydride according to the following reactions:

$$PbPo \ + \ H_2 \ \leftrightarrow \ H_2Po \ + \ Pb \tag{Eq. 4}$$

The rate of release of Po-210 due to PbPo and H_2Po was experimentally investigated in order to determine the kinetics equilibrium constant for various temperatures (425°C and 500°C) and concentrations of H_2 in Ar/H_2 mixtures (from 0 to 4%). The outcome was that the total concentration of gaseous Po (H_2Po + PbPo) increased with increasing amounts of H_2, and that more gaseous Po was formed at lower temperatures.

The authors of the study [8] recommend a removal system that requires the atomization of the LBE in a mass exchanger to maximize the contact area with pure hydrogen stream and promote the formation of H_2Po and its separation from the LBE. A cooler and a pump would bring the LBE to proposed operating conditions of 150°C and 4 MPa. The gas exiting the mass exchanger would be bubbled through a pool of alkaline aqueous solution (operating at the same temperature and pressure conditions) that would trap the Polonium hydride. While in theory this system could reduce the amount of Po in the LBE by a factor of "120, the authors claim its inherent dangers that make its use unlikely: namely the use of H_2 at high pressure and the heavy Po contamination of the Hydrogen line coming from the mass exchanger. Besides, the trapping solution needs a periodic regeneration by removing the accumulated Polonium, and the feasibility of a LBE atomizer with the required performance needs to be demonstrated.

Polonium extraction from LBE by alkaline extraction

This method is based on the following chemical reaction:

$$3\,Po + 6\,NaOH \ \rightarrow \ 2\,Na_2Po + Na_2PoO_3 + 3\,H_2O \tag{Eq. 4}$$
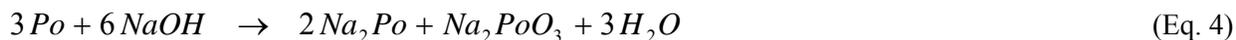
This method was originally proposed by the researchers [5,6] of the IPPE. They claim a high efficiency of this method according to their experimental data, though none of these data has been published. The alkaline extraction studies were carried out in the temperature range of 250-500°C with a eutectic mixture of NaOH and KOH (melting point: 185°C). Neither KOH, nor the molten LBE seemed to participate in the chemical reaction. It appeared that the presence of oxygen or Lead oxide in the system strongly reduced the removal efficiency. They pointed out the necessity of the coolant purification from the alkaline residues and of further experimental studies to better understand the mechanism of alkaline extraction.

The INEEL carried out further experimental studies on alkaline extraction [8,22,23,24] using NaOH melt (melting temperature: 318°C). The choice of using NaOH only instead of a NaOH-KOH eutectic mixture was based on the possibility to isolate the effect of NaOH. The following reaction occurs when a mass of Po-contaminated LBE is placed in contact with NaOH melt:

$$PbPo + 4\,NaOH \ \rightarrow \ Na_2Po + Na_2PbO_2 + 2\,H_2O \tag{Eq. 5}$$
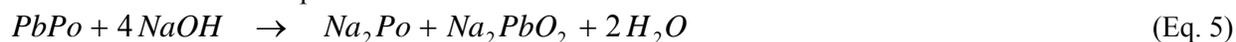
In order to reduce experimental costs and to speed research efforts, they chose to work with Tellurium as a Polonium surrogate because of their common properties, as justified earlier in Section 0. It can thus be assumed that the alkaline extraction reaction for Tellurium is:

$$PbTe + 4\,NaOH \ \rightarrow \ Na_2Te + Na_2PbO_2 + 2\,H_2O \tag{Eq. 6}$$

Details of the experimental set-up are to be found in [22,23]. They first investigated a suitable candidate material for the crucibles containing the LBE and NaOH held at 500°C for 8 hours. SEM analyses showed that Zr crucibles would provide adequate performance, although only for short term experiments (less than 24 hours) given the corrosion rate of 2.8 mm.yr^{-1} at 540°C in NaOH. Nickel-Chromium alloys

had a relatively thick interaction layer. This material issue is crucial and would still need to be solved in the case of the development of a large scale alkaline extraction installation.

Tellurium extraction performances were measured by ICP analyses in a NaOH matrix. A first set of experiments was carried out at temperatures comprised between 400 and 550°C. The analytical results show decreasing Te levels in the LBE in function of the time. Larger quantities of Te are removed by NaOH at higher temperature. A second set of experiments was carried out to investigate alkaline extraction chemical kinetic data [24]. First and second order rate constants for extraction of Te from LBE as Na_2Te were determined based on experimental data for a temperature range comprised between 400 and 550°C. The evaluation of the chemical kinetics of the experiments shows reproducible rate constants, allowing the determination of the activation energy based on the Arrhenius equation.

Nevertheless several issues remain open:
- The validation of previous experimental work with Polonium;
- The choice of a suitable material that would not undergo a corrosion process when brought in contact with alkali melt;
- The effect of alkaline extraction on the LBE quality (i.e. oxygen and oxides activity, residual impurity concentration) has not been quantified;
- Efficient ways to remove Polonium from the exhausted NaOH should be explored for safe disposal;
- It remains to be determined if this technology can be applied on a large scale.

Polonium extraction from LBE by rare-earths filtration

Kershner *et al.* [25] prepared several rare-earth polonides by reaction of Polonium metal with the rare-earth metal or hydride. The syntheses were carried out in compartmented sealed quartz reaction tubes contained in a furnace. They also measured the melting and decomposition point of the reaction products. The dissociation of these polonides did not start at temperatures below 1000°C for most species. The melting points ranged between 1253°C (Praseodymium polonide) and 2212°C (Ytterbium polonide). The thermal stability of some rare-earth polonides was further investigated by Steiger and Miles [26] with a mass spectrometer. They confirmed the stability of the components. The Neodymium polonide had the lowest vaporization temperature of the investigated species: Po^+ and Po_2^+ were detected at 850°C. The vaporization process occurred predominantly in an incongruent way according to:

$$(RE)Po_{(s)} \rightarrow (RE)Po_{1-x(s)} + xPo_{(g)} \tag{Eq. 7}$$

Ershova *et al.* [27] carried out Polonium vapour reaction with some solid chemical elements, amongst with Gadolinium and Praseodymium, to form the corresponding monopolonides. The reaction began at 400°C and was completed at 470°C for Praseodymium (this is 130°C lower than the reaction temperature announced between solids by Kershner *et al.* [25]), and began at 500°C and completed at 600°C for Gadolinium. The thermal stability of these components was tested and confirmed for temperatures up to 1050°C. Abakumov reported the results of similar experiments for the formation of sesquipolonides RE_2Po_3. They are formed at higher temperatures and during a longer period of time compared to the monopolonides. Their thermal stability is equivalent.

Larson was the first in his thesis to emit the idea of dissolving rare-earths in the LBE to reduce the Polonium volatility. Based on the above information, he suspected that Polonium could theoretically be removed from the LBE by forming rare-earth species that are more stable than the Lead polonide. He studied the interaction of Lead polonide and Praseodymium. Three Pr foils were exposed to PbPo gas for varied amounts of time under a pressure of 1.4 MPa at 500°C. The results showed a clear interaction. The surface oxidation of the Pr foil had a negative effect on the total amount of deposited Polonium. Less than fifty minutes were necessary to reach equilibrium.Furthermore, he carried out a second experiment where

he added Pr chips or powder to LBE and measured the composition of cover gases in function of the temperature (between 300 and 500°C). It was demonstrated that the incremental addition of Pr reduces the vapour pressure of Po species by the formation of PrPo.

Finally, he addressed the feasibility of developing a rare-earth filtration technology by identifying the most promising of liquid-metal filtration systems and their respective supplemental processes. Rare-earth incorporation into filters could be designed by suspension in ceramic matrix, by liquefaction, by epitaxial growth, by sputtering or electrodeposition onto a fibre mesh. Fiberglass filters have been used by the Russians for LBE filtration. They could remove impurities with sizes down to 20 μm [8].

Care must be taken though that the addition of a rare-earth element in the LBE will have an effect on the neutronics in the reactor. Most of them have indeed relatively high capture cross section at high energy. Depending on the objective (neutron shielding or neutron economy), different choices of rare-earth can be made. If neutron shielding is an issue, Europium is the best choice, with a capture cross section of 0.36 b at 14 MeV [28]. If the choice is for neutron economy, Lanthanum (with 7 mb at 14 MeV), Cerium (with 15 mb at 14 MeV) or Praseodymium (with 19 mb at 14 MeV) are the best solutions.

This rare-earth filtration technology looks promising, but a lot of R&D work is needed to tackle the following issues:
- To develop a support for the rare-earth and to develop a coating technique to aim at a high specific surface for the LBE and/or the gas plenum filtration;
- To develop a filtration technology if loose rare-earth is dispersed in the LBE;
- To investigate the effect of rare-earth presence in LBE on the oxide protective layer of the reactor material and on its corrosion;
- To determine the rare-earth filtration efficiency in function of the oxygen activity in the LBE.

Polonium extraction from LBE by electrodeposition

To the exception of the patented process of Baltisberger, almost no information concerning electrodeposition technique was found in the literature. Larson mentions the possibility of applying an electric field in the LBE. While Lead would migrate to the cathode to form metallic Lead, Polonium would migrate to the anode and form metallic Po that would attach to the electrode if the system is operated at a temperature below the melting point of Polonium (254°C). However, since most of the electric current in the LBE is expected to come from electronic conduction rather than from ion migration due to the low resistivity of LBE, Polonium yields at the cathode may be minimal.

People from INEEL investigated this technique [23] with Tellurium as a chemical surrogate of Polonium. The system temperature was varied between 300 and 400°C. Because the melting point of Te is 452°C, it is expected that the metallic Te collected at the anode would remain solid and stick to the electrode. LBE was regularly sampled to measure the rate at which Te was collected at the anode in function of time. No conclusive evidence was obtained to substantiate the ability to move Te by applying an electrical potential across molten LBE. Some movement was observed but it was not consistent and the small sample collected limited data quality. Two temperatures were tested, but the temperature does not seem to affect the Te collection. Since no electrodeposition rate could be derived, no model could be determined.

PERFORMANCE ASSESSMENT OF POLONIUM CONTAMINATION SCENARIOS

LANL analyzed Polonium release hazards in reactors using LBE as coolant under normal operating conditions and in case of an accident. Three accident scenarios have been considered:
- Worst case scenario: Po in the gas system releases into the room all at once with no ventilation and no aerosol deposition;

- A complete Po discharge from the gas system occurs in 100 seconds, personnel is evacuated under 10 minutes, there is ventilation and aerosol deposition;
- Massive coolant spill scenario.

The given figures take the US regulation standards into account.

Under normal operating conditions, a small gas system leak of 0.5% volume of gas per day with a ventilation rate of one volume turnover every hour are considered. If the Po aerosol deposits to surfaces quickly, there is little danger of Po inhalation during normal operation. However, the surface accumulation of Po can be problematic. Body showering and clothes washing are strongly suggested after each shift.

A worker exposed to the worst case scenario would accumulate at once 290 hours equivalent dose. This is well below the 50-50 chance lethal dose extrapolated from experiments on mice. In real life, consequences should be less severe as more realistic scenarios (with ventilation and aerosol deposition) are expected. A worker exposed to the second accident scenario would accumulate 47 hours inhalation dose.

In the case of a massive coolant spill, we can not exclude that Po will be released from LBE by volatile Polonium hydride formation through interaction with moisted air in the room. This situation would lead to a Po concentration in air that is a factor 25 higher than the US standards. Nevertheless, this activity level should decrease considerably if sufficient ventilation is provided.

The outcome of this publication seems to question the need of Polonium removal from LBE. However, it is necessary to carry out a similar performance assessment exercise for the MYRRHA conditions and taking the Belgian regulation standards into account.

CURRENT ONGOING RESEARCH

There are currently three known research institutions that are working on the Polonium issue: the Paul Scherrer Institute (PSI, Switzerland), the Los Alamos National Laboratory (LANL, USA), the Tokyo Institute of Technology (Japan) and the Institute of Physics and Power Engineering (IPPE, Russia).

Researchers from PSI are currently working on two distinct aspects of the Po problematic: Po release studies, Po migration in solid LBE and Po extraction from LBE. The latter research is based on the alkaline extraction technique with the use of Te as Po surrogate, and NaOH-KOH eutectic as alkaline melt. A complete extraction is assessed for an extraction temperature equal to at least 400°C [29].

The LANL team is doing Po assessment for a spallation target driven materials test station. They are mainly working on the safety issues, in terms of source terms, speciation, volatility, release mechanisms and consequences.Tokyo Institute of Technology. A recent publication shows that in the Tokyo Institute of Technology they are developing a Polonium filtering technology. Their research is currently suspended because of financial support shortage.

At IPPE a research team is investigating a Polonium filtration technique of the coolant and the gas plenum. They are developing a two-stage filter, which is composed of a tissue fabric that is used to remove aerosols or solid particles, and a subsequent sorbent layer that chemically binds Po present in LBE. They are working with Te as a Po analogue for obvious safety reasons. Up to now, they have been able to remove 75% of the Te content, but they are continueing their research on the technique and have good hope to reach an acceptable solution in a the future. Until now they did not reveal the nature of the sorbent they use and they are not entitled to carry out experiments with Polonium.

RECOMMENDATIONS AND CONCLUSIONS

A summary of the advantages and disadvantages, mainly in the frame of an application for MYRRHA, is given in Table III.

It shows that there is no ideal solution to the problem. The Polonium hydride stripping and electrodeposition methods can already be ruled out, the former for obvious safety reasons, the latter because no convincing results could be provided to date. The distillation process is rather simple and could also be coupled to the subsequent removal of Hg-194 from the gas plenum, but a pilot scale investigation would require to work with Polonium. A possibility would be to work with a less problematic isotope than Po-210. The other main drawbacks of the method are that it necessitates a large transfer area and that high temperatures are required. It also bears an inherent and obvious safety risk

The alkaline extraction method represents the most extensively studied technique because of the possibility to develop it with Tellurium as Polonium surrogate. The main challenge of the technique will be to find a material that could adequately cope with the high temperature and the corrosivity of the alkali melt. There is a multidisciplinary approach to lead, and a close collaboration between chemistry and materials specialists will be necessary. The development costs are expected to be reasonable if shared with other research institutions.

The rare-earth filtration represents the most elegant technology but would still require a lot of research and development efforts since a broad expertise is needed in many fields (surface chemistry and treatment, chemical engineering, materials sciences, reactor physics,…). This could difficultly be carried out alone as internal research at SCK•CEN. If this option is chosen, a collaboration with an academic research unit specialized in surface chemistry and treatment would be a plus.

Table III: Comparison of the advantages and disadvantages of the proposed Polonium extraction techniques

Extraction Technique	Advantages	Disadvantages
Distillation	Existing data on PbPo, Po and LBE evaporation properties Simple process, easy to build No further purification of LBE needed	Use of special material due to high temperature (no stainless steel) Inherent danger: production of Po in gas phase Large equipment Costly
Polonium hydride stripping	Simple process, easy to build No further purification of LBE needed	Inherent danger: H_2 under high pressures combined with Po Instability of H_2Po Regeneration of the trapping solution Technical difficulty: mixture LBE/H_2
Alkaline extraction	Recommended by users of LBE as reactor coolant Possible to use NaOH/KOH eutectic	Low oxides/O_2 concentration required Material compatibility problem with

	to lower melting point of alkali Possible to use Te as Po surrogate to develop process at lab and pilot scale	melted alkali (corrosion) Post-process LBE and NaOH purification necessary Validation of process with Polonium Difficult upscaling to industrial scale
Rare-earth filtration	Simple process Low vapour pressure of resulting polonides High thermal stability High melting point High expected yield Flexibility: possibility to filter LBE and/or the gas plenum	Any presence of oxides and O_2 is detrimental to the process attacking of the protective oxide layer in the reactor if dispersed in LBE High R&D costs
Electrodeposition	Simple process principle and easy to build Low development costs Work at low T (<254°C)	No relevant data available Low conversion yield expected due to LBE conductivity and low unbound Po concentration High process cost

In the case of alkaline extraction, one of the first priorities will be to define a suitable material to work in such harsh conditions. It is recommended to use a NaOH/KOH eutectic mixture as alkali melt and Tellurium as Polonium surrogate. A purification process of the LBE that has been brought in contact with alkali melt should be elaborated, and a waste conditioning process should also be proposed. Eventually, a validation study with Polonium should be carried out.

In the case of rare-earth filtration, the easiest approach would be to consider the gas plenum filtration rather than coolant filtration. This would avoid unexpected reactor corrosion problems, and would favour the filtration selectivity and kinetics. Let us bear in mind though that a minimal temperature is required for the rare-earths to react with Polonium by direct combination. A filter technology development will require a partnership with another research institution specialized in surface chemistry and treatment.

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