

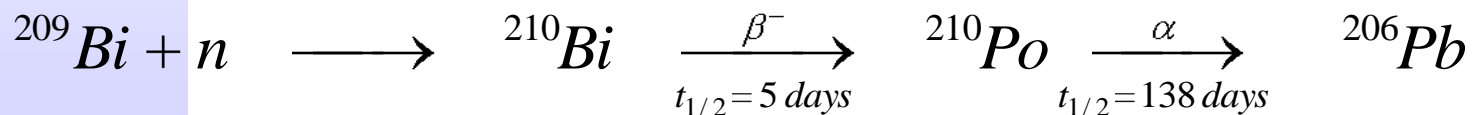
# Literature Review of Polonium Removal Techniques from LBE

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## Description of the Problem (1)

- Use of Pb-55.5Bi eutectic (LBE) as reactor coolant
- Neutron activation of  $^{209}\text{Bi}$  leads to the production of  $^{210}\text{Po}$ , a highly radiotoxic species:



## Description of the Problem (2)

- Po is retained in the LBE coolant during normal operating conditions
- Some Po migrates to the cover gas in the reactor plenum: problem in case of maintenance or refuelling
- Batch or on-line extraction of Po might be required to minimize the radiological risk

# Presentation Structure

- Properties of Po and chemical analogues
- Description of reported Po extraction techniques and evaluation
- Current worldwide related research
- Conclusions

# Properties of Po and Chemical Analogues: Radiological Properties

- Polonium is the heaviest of the Chalcogens group which also contains: O, S, Se and Te
- It has only radioactive isotopes
- Se and Te are generally considered as chemical analogues of Po
- $^{210}\text{Po}$  is a pure alpha-emitter (5.305 MeV), 138.38 days half-life, 166TBq/g of specific activity
- Represents the highest radiotoxicity risk on a short term basis (reduction of 5 orders of magnitude after 8 years of cooling)
- Highly volatile component forming  $\alpha$ -radioactive aerosols
- Absorption of Po causes irreversible damage if ingested to kidneys, spleen and liver. The maximum permissible body burden is 1.11 kBq (equivalent to  $6.8 \cdot 10^{-12}\text{g}$  particle)
- Maximum legal (Belgium) permissible concentration in air: 0.2 Bq/m<sup>3</sup>, in water: 0.83 Bq/l

# Properties of Po and Chemical Analogues: Physical Properties

Property	Se	Te	Po
<b>Atomic number</b>	<b>34</b>	<b>52</b>	<b>84</b>
<b>Number of stable isotopes</b>	<b>6</b>	<b>8</b>	<b>0</b>
<b>Atomic weight</b>	<b>78.96</b>	<b>127.6</b>	<b>(210)</b>
<b>Ionic radius (r)</b> (M <sup>2+</sup> )	<b>1.98</b>	<b>2.21</b>	<b>2.3</b>
(M <sup>4+</sup> )	<b>0.5</b>	<b>0.97</b>	<b>0.94</b>
(M <sup>6+</sup> )	<b>0.42</b>	<b>0.56</b>	<b>0.67</b>
<b>Ionization energy (kJ.mol<sup>-1</sup>)</b>	<b>940.7</b>	<b>869.0</b>	<b>813.0</b>
<b>Pauling electronegativity</b>	<b>2.4</b>	<b>2.1</b>	<b>2.0</b>
<b>Density at 25 C (g.cm<sup>-3</sup>)</b>	<b>4.189-4.389</b>	<b>6.25</b>	<b>9.142 (α) 9.352 (β)</b>
<b>Melting point ( C)</b>	<b>217</b>	<b>452</b>	<b>246-254</b>
<b>Boiling point ( C)</b>	<b>685</b>	<b>990</b>	<b>962</b>
<b>Electrical resistivity at 25 C (ohm.cm)</b>	<b>10<sup>10</sup></b>	<b>1</b>	<b>4.2 10<sup>-5</sup> (α) 4.4 10<sup>-5</sup> (β)</b>

# Properties of Po and Chemical Analogues: Chemical Properties

- Much similarity between Po and Te concerning chemical properties
- Se, Te and Po combine directly with most elements to form binary chalcogenides
- Most stable compounds for redox=-2 formed with the strongly positive elements of group I and II, and especially with the lanthanides
- Decreasing stability of H<sub>2</sub>X hydrides according to Se>Te>Po
- Po forms PbPo when in contact with LBE

# Properties of Po and Chemical Analogues in Molten LBE

- LBE preferred to Pb because of its lower MP (125°C vs. 327°C) (vapour pressure measured by Ohno *et al.*, 2005)
- Po evaporates under the form of PbPo in molten LBE (vapour pressure measured by Abakumov and Ershova, 1974)
- PbPo melts at 600°C and boils at 1520°C (Witteaman *et al.*, 1960) **THOUGH:**
  - PbPo was reported to decompose to elemental Po at 630°C (Miura *et al.*, 2007)
- PbPo: 3 orders of magnitude lower evaporation rates compared to pure Po at operating conditions
- Te confirmed as analogue of Po
- Measurable amounts of Po release above 700°C (slow evaporation begins at 600°C)

# Polonium Extraction Techniques: R&D Chronology

- Starts about 45 years ago for the extraction of Po (to be used as thermal source, mainly for spatial applications) from the neutron irradiated Bi matrix (use of carriers: LiCl-KCl, Ce, Te, NaOH): complicated purification processes
- In the early 70's, USSR started to use LBE-cooled fast reactors in submarines: they suggest the use of an alkaline extraction method or distillation (no experimental results published)
- No specific publication on extraction techniques during more than 20 years up to late 90's
- MIT and INEEL collaborated with scientists from IPPE to isolate five promising removal mechanisms (1999-2004)
- Collaboration between INEEL and JNC to develop alkaline extraction method, reaction kinetics study (2002-2004)
- Recent research of Tokyo Institute of Technology on surface and gas plenum decontamination (till 2008)
- Accident scenarios development from LANL
- Current development of alkaline extraction technology by PSI
- Development of a filtration-sorption technology by IPPE

## Polonium Extraction Techniques: Five Potential Techniques isolated by MIT

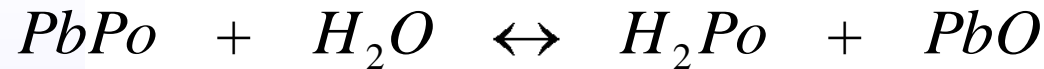
- Distillation
- H<sub>2</sub>Po stripping
- Alkaline extraction
- Rare-earths filtration
- Electrodeposition

# Distillation

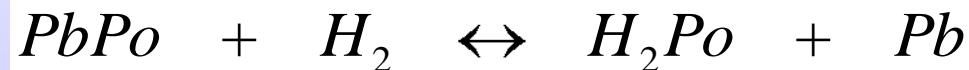
- PbPo vapour pressure several orders of magnitude larger than LBE
- PbPo decomposes to Po at 630°C
- Selective distillation can be performed in a vacuum or inert gas system
- Possible condensation of Po vapours on cold surface
- Necessary maximization of the exchange surface (inert gas bubbling?): a processing of 50 to 600 kg/hr at 700°C requires a mass transfer area of 150m<sup>2</sup>
- Removal efficiency to be expected: 99%
- Suitable for small scale applications, doubtful in the case of large quantities to be treated
- High temperatures required (700°C minimum, nominal range: 900-1100°C): choice of the material?
- For the development of this method: it is necessary to work with Po: license required. Safety burden for an up-scaling to a pilot installation

# H<sub>2</sub>Po Stripping (1)

- Theoretical reaction between PbPo and water



- Unstable gas which readily decomposes to H<sub>2</sub> and Po
- MIT experimented a separation method based on a reaction between PbPo and H<sub>2</sub>

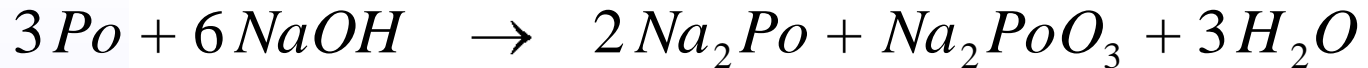


# H<sub>2</sub>Po Stripping (2)

- Release rate of <sup>210</sup>Po and kinetics equilibrium constant investigated for T: 425-500°C and [H<sub>2</sub>] in Ar/H<sub>2</sub> from 0 to 40000 ppm
- [Po]<sub>g</sub> increase with [H<sub>2</sub>] and low temperatures are favourable
- The technique requires an atomization of the LBE in a mass exchanger to optimize the contact with H<sub>2</sub>
- Proposed operating conditions of 150°C and 4 MPa
- Use of an alkaline aqueous solution to trap H<sub>2</sub>Po (radiolysis?)
- Inherent danger of this technique (high pressure H<sub>2</sub>, heavy Po contamination of H<sub>2</sub> line coming from the mass exchanger)
- Periodic regeneration of the alkaline solution needed
- Requires further experimental research, since several recent other sources tend to show that the Po release does not significantly increase when LBE comes in contact with water, H<sub>2</sub>Po formation doubtful
- Necessity to work with Po: no use chemical homologues possible to refine the technique

# Alkaline Extraction (1)

- Based on the following chemical reaction:



- Proposed originally by IPPE (no experimental data published by them)
- Worked with NaOH-KOH eutectic mixture (MP: 185°C) in temperature range 250-500°C. Neither KOH nor LBE seemed to participate to the reaction
- Presence of Oxygen or Pb oxide detrimental to the reaction efficiency
- Necessity to purify the coolant from alkaline residues

## Alkaline Extraction (2)

- INEEL carried out further experimental studies using NaOH melt (MP: 318°C)
- The following reaction was taking place:



- Used Te as Po surrogate
- Te extraction performances measured by ICP in NaOH matrix.
- Experimental results (T: 400-550°C) showed a decreasing Te level in LBE in function of time
- Higher operational temperatures favour the reaction
- Calculated the reaction rate constants: equilibrium reaction

# Alkaline Extraction (3)

- Remaining issues to be solved:
  - Material choice: high corrosivity of LBE-alkali mixtures, especially at high T (Zr and Ni alloys do not offer sufficient performance, other tested materials (graphite, silica,...) are even less efficient)
  - Validation of previous work with Po
  - Effect of alkaline extraction on LBE quality (oxygen and oxides activity, residual impurity concentration,...)
  - Efficient way to remove Po from exhausted NaOH for safe disposal
  - Up-scaling of the process to at least a pilot level

# Rare –earth Filtration (1)

- Large affinity of Po with lanthanides: most stable Po compounds
- LnPo are very stable even at high temperatures and need very high temperatures ( $>1000^{\circ}\text{C}$ ) to vaporize: would remain in LBE phase
- Can be formed by direct contact with Po (requires a threshold temperature to occur: e.g.  $400^{\circ}\text{C}$  for Pr)
- Could be used to decontaminate the gas plenum by the adequate use of a filtration technology (to be developed)
- Some rare-earths (e.g. Eu) have very large neutron cross section, which would limit the neutron dose rate around the reactor
- Tests carried out at MIT with Pr foils exposed to PbPo gas at  $500^{\circ}\text{C}$ , and addition of Pr chips or powder to LBE showed promising results

## Rare –earth Filtration (2)

- Represent the cleanest technology BUT
- Problems to be solved:
  - Development of a support for the Ln (according to a development of a coating technique) with a high specific surface (cassette filter, exchange surface), or of a filtration technology to remove LnPo from LBE: will require large efforts
  - Ln have very high affinity for O<sub>2</sub> and their efficiency decrease dramatically with its least presence. Moreover, it could attack the oxide protective layer of the reactor if dispersed in LBE

# Electrodeposition

- One patent found in literature in aqueous media (Te used as carrier): no experimental data available
- INEEL tried to develop a technique based on the electrolysis of LBE. Metallic Po would migrate to the anode (temperatures lower than 254°C (Po MP) are required). Used Te as Po surrogate. Operation temperatures: 300-400°C.
- Most electric current in LBE expected to come from electronic conduction rather than from ion migration
- Sampling of LBE to measure [Te] produced inconclusive results

# Pros and Cons of each Technique

Extraction Technique	Advantages	Disadvantages
Distillation	<ul style="list-style-type: none"> <li>Existing data on PbPo, Po and LBE evaporation properties</li> <li>Simple process principle and easy to build</li> <li>No further purification of LBE needed</li> </ul>	<ul style="list-style-type: none"> <li>High temperatures needed implying the use of special materials (no stainless steel)</li> <li>Inherent danger due to the production of Po in gas phase</li> <li>Difficult on large scale due to the large required transfer area</li> <li>Costly</li> </ul>
Polonium hydride stripping	<ul style="list-style-type: none"> <li>Simple process principle and easy to build</li> <li>No further purification of LBE needed</li> </ul>	<ul style="list-style-type: none"> <li>Inherent danger due to the work with H<sub>2</sub> under high pressures combined with the presence of Po</li> <li>Instability of H<sub>2</sub>Po</li> <li>Regeneration of the trapping solution</li> <li>Technical difficulty bound to the mixture of LBE with H<sub>2</sub></li> </ul>
Alkaline extraction	<ul style="list-style-type: none"> <li>Process recommended by experimented users of LBE as reactor coolant</li> <li>Possibility to use a NaOH/KOH eutectic mixture to lower the melting point of the alkali</li> <li>Possibility to use Te as Po surrogate to develop the process at lab and pilot scale</li> </ul>	<ul style="list-style-type: none"> <li>Low oxides and O<sub>2</sub> concentration necessary</li> <li>Material compatibility problem with melted alkali (corrosion)</li> <li>Post-process LBE purification necessary</li> <li>Validation of the process with Polonium</li> </ul>
Rare-earth filtration	<ul style="list-style-type: none"> <li>Simple process principle</li> <li>Low vapour tension of resulting polonides</li> <li>High thermal stability</li> <li>High melting point</li> <li>High expected yield</li> <li>Flexibility: possibility to filter LBE and/or the gas plenum</li> </ul>	<ul style="list-style-type: none"> <li>Presence of oxides and O<sub>2</sub> (even in low quantity) detrimental to the process</li> <li>Possibility of attacking the protective oxide layer in the reactor if dispersed in LBE</li> <li>High R&amp;D costs</li> </ul>
Electrodeposition	<ul style="list-style-type: none"> <li>Simple process principle and easy to build</li> <li>Low development costs</li> <li>Work at low T (&lt;254 C)</li> </ul>	<ul style="list-style-type: none"> <li>No relevant data available</li> <li>Low conversion yield expected due to LBE conductivity and low unbound Po concentration</li> <li>High process cost</li> </ul>

# Current Research

- PSI is developing the alkaline extraction process with a NaOH-KOH eutectic mixture (thesis published late 2008)
- LANL is working on scenarios of Po release (Performance Assessment studies)
- The Research Laboratory for Nuclear Reactors (Tokyo Institute of Technology) has recently investigated Po evaporation and adhesion behaviour for the development of Po filters
- IPPE is developing a joint filtration-sorption technology using Te as a chemical analogue.

# Conclusions

- No ideal solution to the Polonium extraction problem, no technique tested beyond lab-scale to date.
- Alkaline extraction (material choice, purification process, waste conditioning) and filtration-sorption techniques are worth further development **if**
- Calculated Po source term commands for removal (based on safety assessment studies)