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# Literature Review of Polonium Removal Techniques from LBE

Lorenzo Ortiz, Johan Braet

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# Description of the Problem (1)

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

$$^{209}Bi + n \longrightarrow {}^{210}Bi \xrightarrow[t_{1/2}=5\,days]{\beta^-} {}^{210}Po \xrightarrow[t_{1/2}=138\,days]{\alpha} {}^{206}Pb$$

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# 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

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# 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
- $^{210}$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 $10^{-12}$g particle)
- Maximum legal (Belgium) permissible concentration in air: 0.2 Bq/m$^3$, in water: 0.83 Bq/l

# Properties of Po and Chemical Analogues: Physical Properties

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

# 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 $H_2X$ 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 (Witteman *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
- $H_2Po$ 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 150m²
- 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

# $H_2Po$ Stripping (1)

- Theoretical reaction between PbPo and water

$$PbPo \quad + \quad H_2O \quad \leftrightarrow \quad H_2Po \quad + \quad PbO$$

- Unstable gas which readily decomposes to $H_2$ and Po
- MIT experimented a separation method based on a reaction between PbPo and $H_2$

$$PbPo \quad + \quad H_2 \quad \leftrightarrow \quad H_2Po \quad + \quad Pb$$

# $H_2Po$ Stripping (2)

- Release rate of $^{210}Po$ and kinetics equilibrium constant investigated for T: 425-500°C and $[H_2]$ in $Ar/H_2$ from 0 to 40000 ppm
- $[Po]_g$ increase with $[H_2]$ and low temperatures are favourable
- The technique requires an atomization of the LBE in a mass exchanger to optimize the contact with $H_2$
- Proposed operating conditions of 150°C and 4 MPa
- Use of an alkaline aqueous solution to trap $H_2Po$ (radiolysis?)
- Inherent danger of this technique (high pressure $H_2$, heavy Po contamination of $H_2$ 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, $H_2Po$ 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:

$$3\,Po + 6\,NaOH \quad \rightarrow \quad 2\,Na_2Po + Na_2PoO_3 + 3\,H_2O$$

- 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:

$$PbPo + 4\,NaOH \quad \rightarrow \quad Na_2Po + Na_2PbO_2 + 2\,H_2O$$

- 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°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°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°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 $O_2$ 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

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# Pros and Cons of each Technique

| Extraction Technique | Advantages | Disadvantages |
|---|---|---|
| Distillation | • Existing data on PbPo, Po and LBE evaporation properties<br>• Simple process principle and easy to build<br>• No further purification of LBE needed | • High temperatures needed implying the use of special materials (no stainless steel)<br>• Inherent danger due to the production of Po in gas phase<br>• Difficult on large scale due to the large required transfer area<br>• Costly |
| Polonium hydride stripping | • Simple process principle and easy to build<br>• No further purification of LBE needed | • Inherent danger due to the work with $H_2$ under high pressures combined with the presence of Po<br>• Instability of $H_2Po$<br>• Regeneration of the trapping solution<br>• Technical difficulty bound to the mixture of LBE with $H_2$ |
| Alkaline extraction | • Process recommended by experimented users of LBE as reactor coolant<br>• Possibility to use a NaOH/KOH eutectic mixture to lower the melting point of the alkali<br>• Possibility to use Te as Po surrogate to develop the process at lab and pilot scale | • Low oxides and $O_2$ concentration necessary<br>• Material compatibility problem with melted alkali (corrosion)<br>• Post-process LBE purification necessary<br>• Validation of the process with Polonium |
| Rare-earth filtration | • Simple process principle<br>• Low vapour tension of resulting polonides<br>• High thermal stability<br>• High melting point<br>• High expected yield<br>• Flexibility: possibility to filter LBE and/or the gas plenum | • Presence of oxides and $O_2$ (even in low quantity) detrimental to the process<br>• Possibility of attacking the protective oxide layer in the reactor if dispersed in LBE<br>• High R&D costs |
| Electrodeposition | • Simple process principle and easy to build<br>• Low development costs<br>• Work at low T (<254 C) | • No relevant data available<br>• Low conversion yield expected due to LBE conductivity and low unbound Po concentration<br>• High process cost |

# 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.

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# 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)