Current Understanding of Polonium Evaporation from Irradiated Lead-Bismuth Eutectic (LBE)

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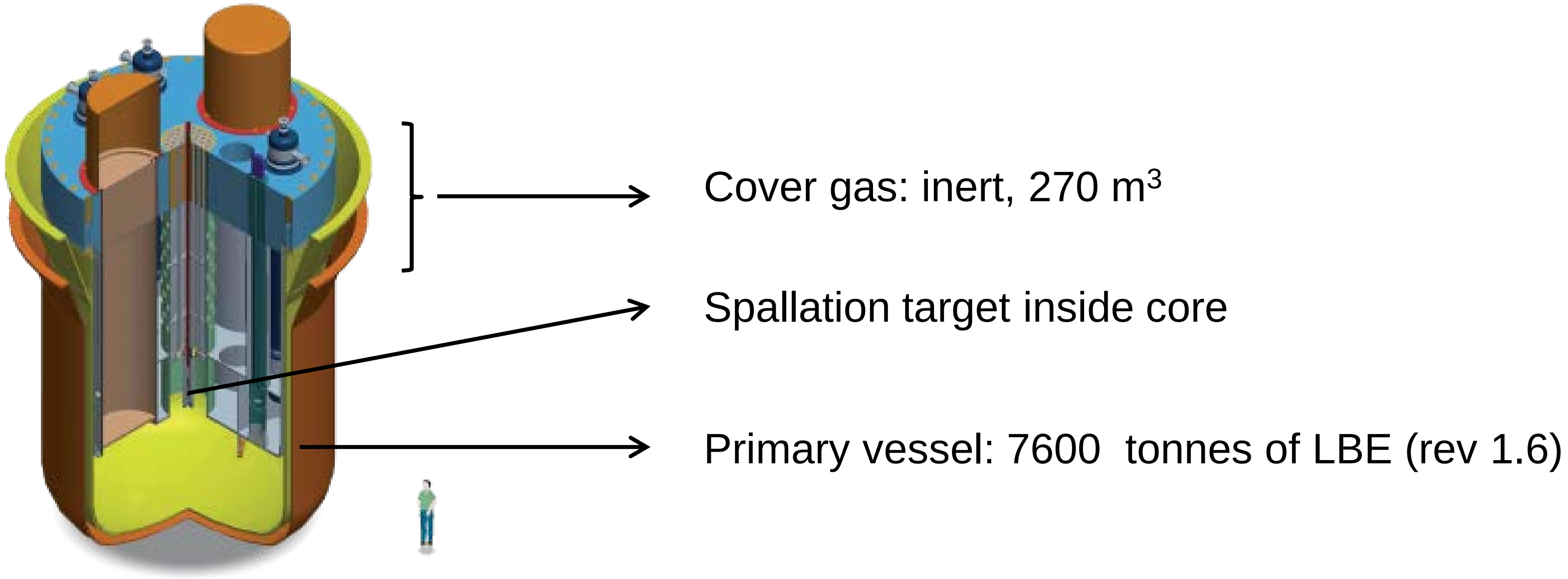
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

- MYRRHA
  - Accellerator driven system: subcritical 100 MW reactor coupled to 600 MeV, max. 4 mA proton accelerator
  - Lead bismuth eutectic: coolant and spallation target (45% Pb, 55%Bi, T_m=125°C)



LBE coolant chemistry R&D at SCK-CEN

- Chemistry and conditioning programme (2010-):
  R&D for licensing and engineering MYRRHA

Activities:

- Control and measurement of dissolved oxygen in LBE
- Impurity (cold) trapping and precipitates filtering → Alessandro Marino's talk
- Evaporation and capture of volatile hazardous radionuclides
  - Activation products: **polonium**
  - Spallation products: mercury, osmium, thallium, polonium …
  - Fission products: iodine, ruthenium, tellurium, ….

Infrastructure: large LBE loops CRAFT & MEXICO, HELIOS3 gas conditioning system, Lilliputter loop, HLM lab, Po lab

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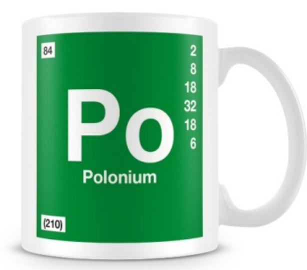
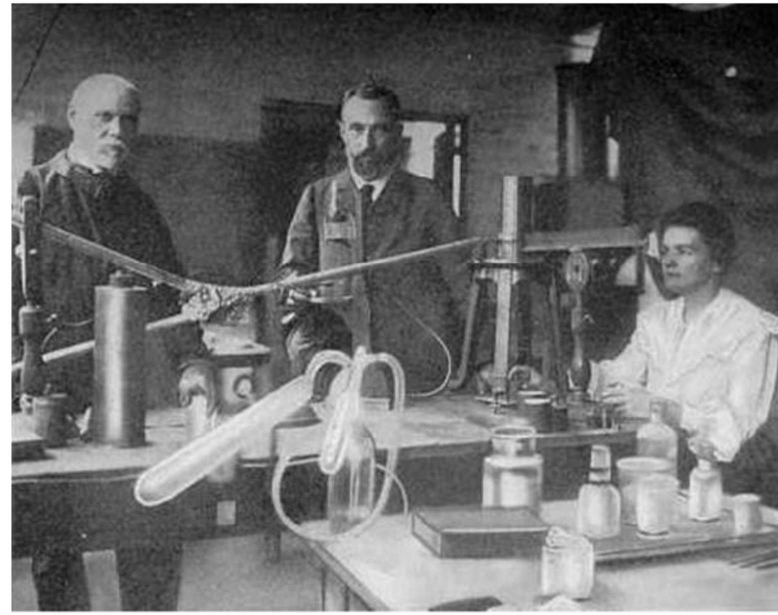
Radiochemical properties of polonium-210

- Po-210 is “pure” alpha emitter
- $t_{1/2}$=138 days,

  high specific activity: 166 TBq/g
- Hazard: inhalation or ingestion
- LD ~ GBq or μg





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Polonium formation in MYRRHA

- Main formation mechanism: neutron capture on stable Bi in LBE

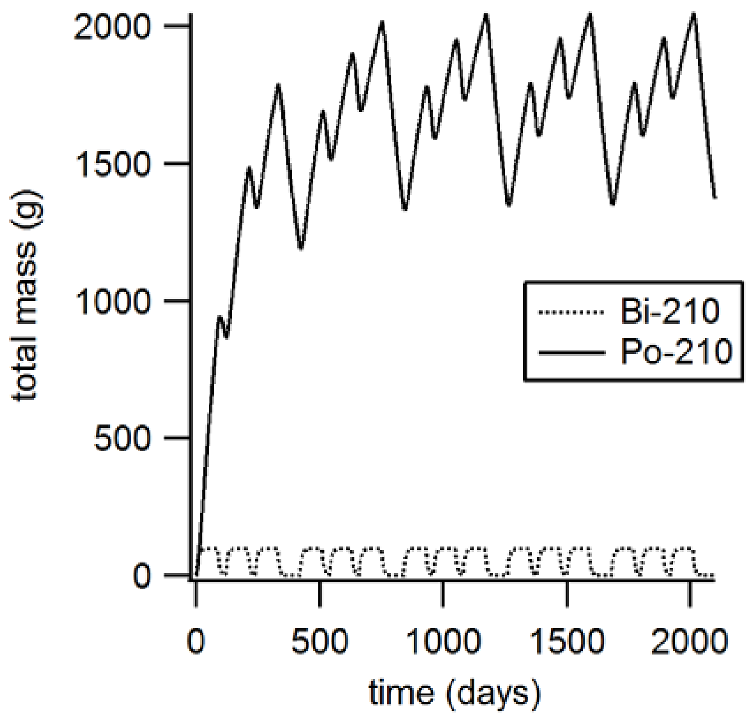
$$^{209}\mathrm{Bi} \xrightarrow{(n,\gamma)} {}^{210}\mathrm{Bi} \underset{t_{1/2=5.01\mathrm{d}}}{\xrightarrow{\beta-}} {}^{210}\mathrm{Po} \underset{t_{1/2=138\mathrm{d}}}{\xrightarrow{\alpha}} {}^{206}\mathrm{Pb}$$

At steady-state:

- Mass of Po-210:

  2000 g Po-210 in 7600 ton
- Concentration of Po-210:

  $x_{Po(LBE)} \approx 10^{-7}$
- + small amount of Po < 210 due to spallation



Not much is known about the volatility of Po

- Po poses no direct hazard when dissolved in LBE
- But when Po evaporates, it is easily transported: contamination, potentially large radiological impact of accidents

=> Good understanding of release mechanisms required

- 2010: limited available data at high temperature suggested good retention of Po in LBE

=> choice was made to leave Po in LBE in MYRRHA (no extraction technology development)

- There exist many "indications" of very volatile Po molecules, but almost no systematic studies relevant for MYRRHA conditions

=> Po evaporation programme at SCK•CEN in collaboration with PSI (experiments) and Ugent (quantum mechanical calculations)

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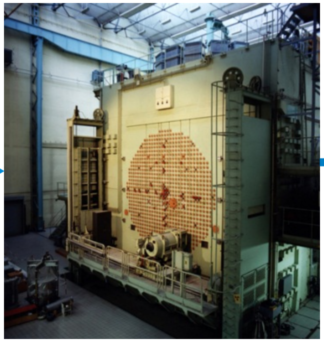
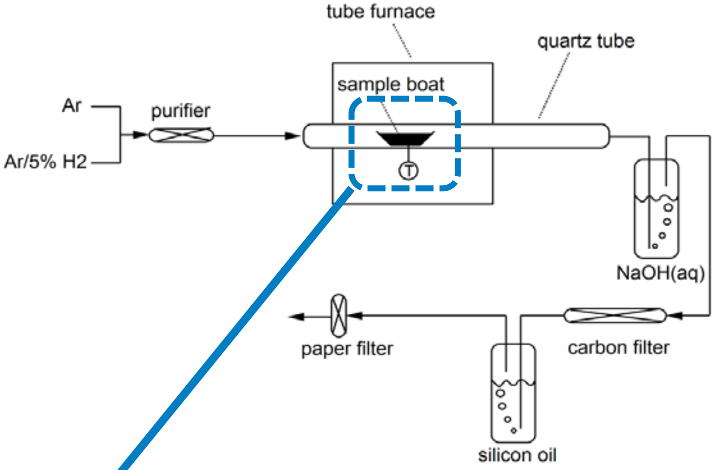
Measurement of Po evaporation from LBE

LBE rod
< 10 g

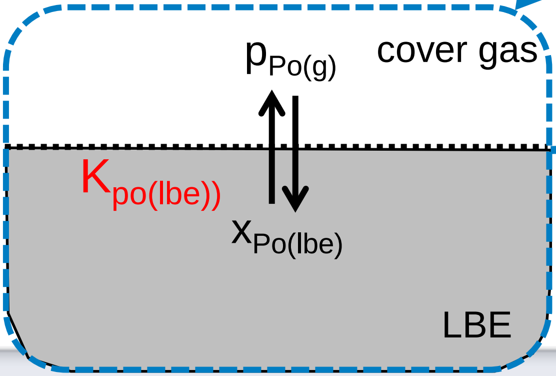
Irradiation in BR1 reactor



Evaporation experiments in “transpiration” setup

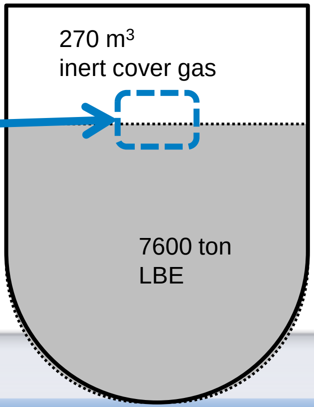


Measurement of release



Henry constant

Release predictions for MYRRHA



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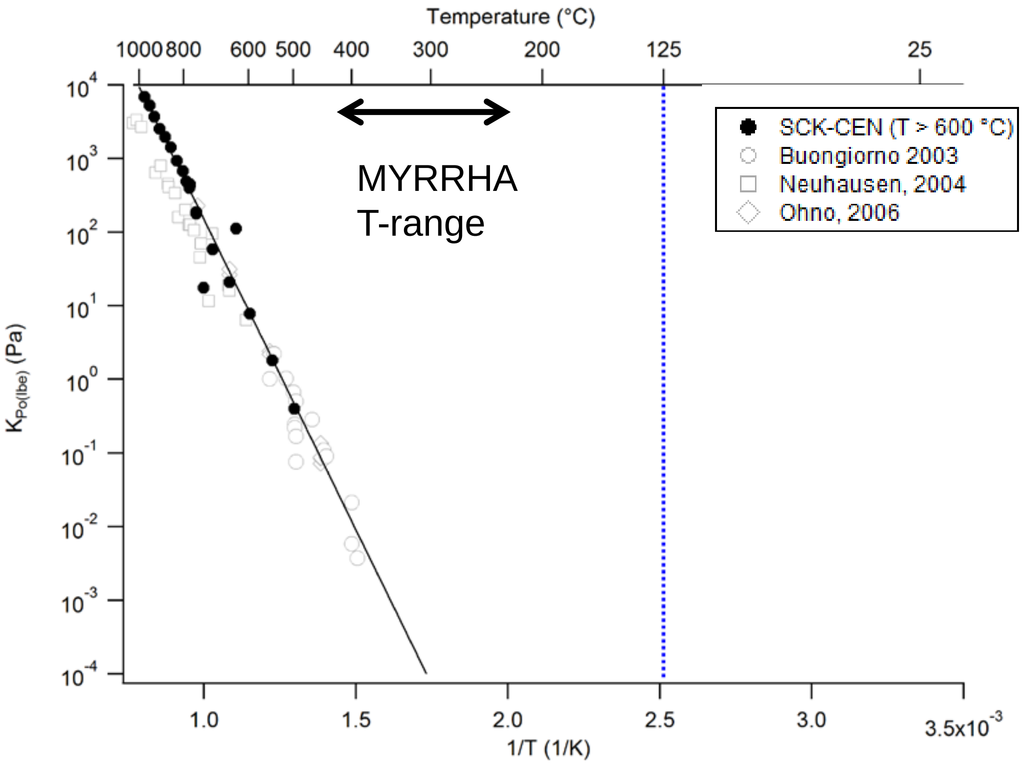
Polonium evaporation from LBE at **T > 600 °C**

- First experimental campaign: Equilibrium (Henry) constants for evaporation at different T >600°C



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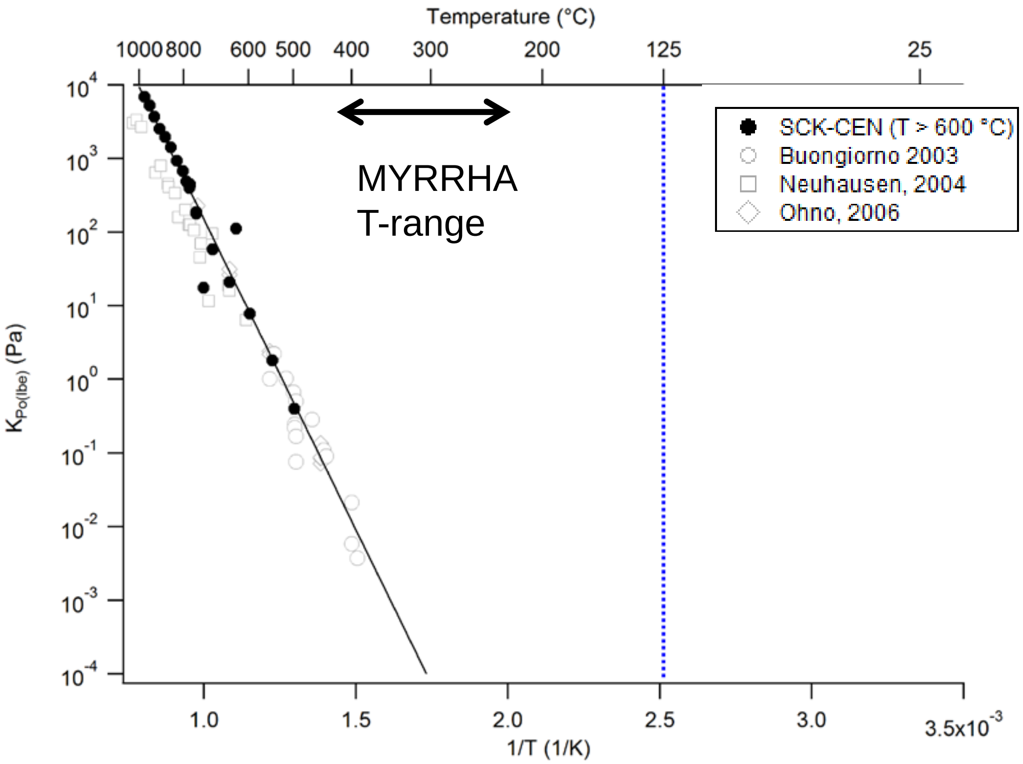

⇒ Single correlation for the *T* dependence of the Henry constant

⇒ Good agreement with literature data

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- Equilibrium (Henry) constants for evaporation

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Additional experiments revealed:

- Evaporation in Ar/%H_2 ≈ Ar ≈ Ar/2%H_2O

⇒ No large influence cover gas composition on Po release

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- Evaporation at different cover gas flow rates

⇒ Confirmed equilibrium conditions + measured maximal evaporation rate

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- Time dependent Po evaporation experiments

⇒ Consistent with model predictions

⇒ Simulations indicate diffusion of polonium in LBE is not limiting evaporation rate

Gonzalez et al. JNM 2013, 450, 299.
Gonzalez et al. RCA 2014, in press.

Polonium evaporation from LBE at T > 600 °C

- Equilibrium (Henry) constants for evaporation in $Ar/5\%H_2$

⇒ Single correlation for the *T* dependence of the Henry constant

- Evaporation in $Ar/5\%H_2 \approx Ar \approx Ar/2\%H_2O$

⇒ No large influence cover gas composition

- Evaporation at different cover gas flow rates

=> Identified evaporation equilibrium conditions + maximal evaporation rate

- Time dependent Po evaporation experiments

⇒ Predicted by model

⇒ Simulations show diffusion of polonium in LBE is not limiting evaporation rate

At high temperature, polonium evaporation from LBE seems to be well understood and is predictable

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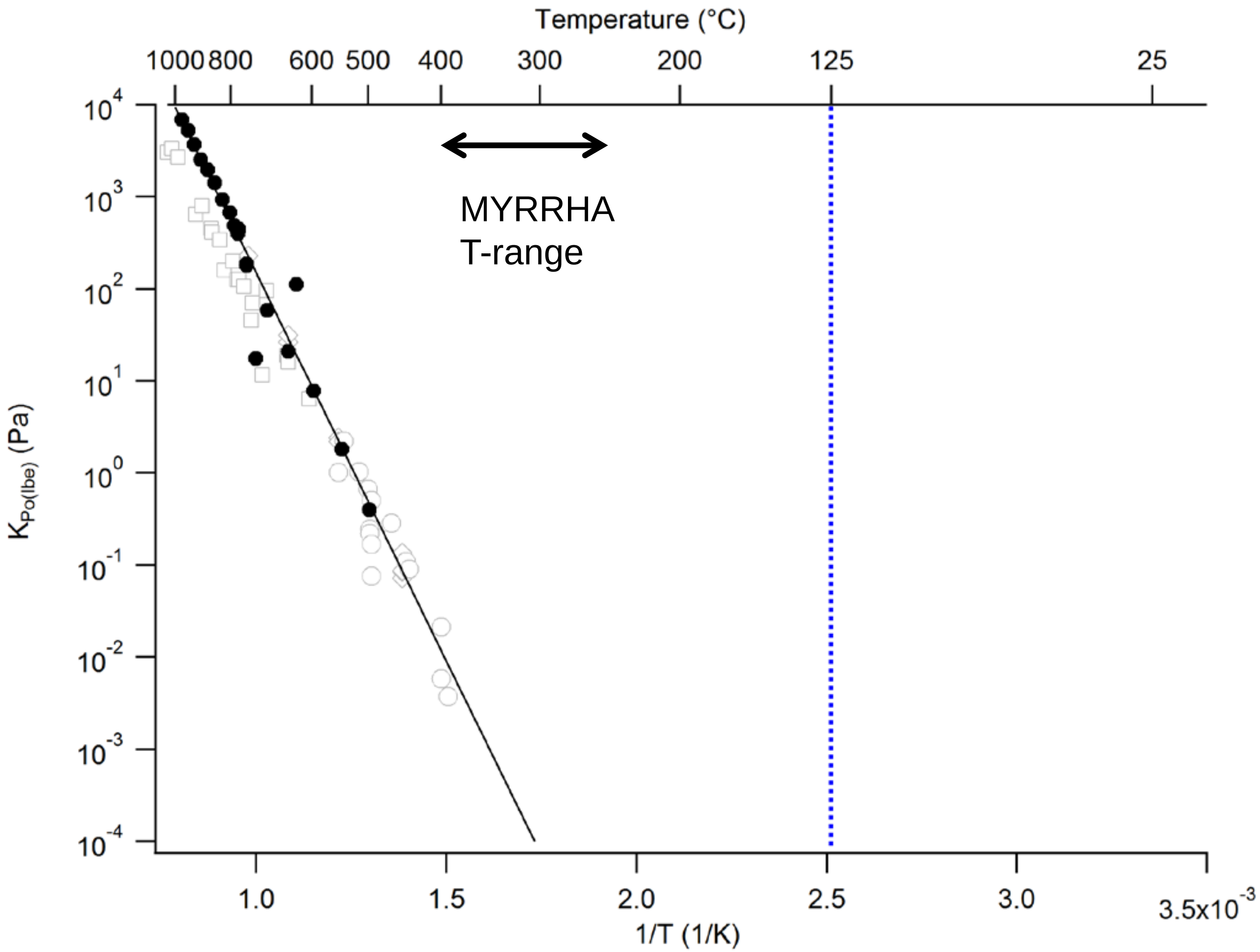
Polonium evaporation from LBE at **T < 600 °C**



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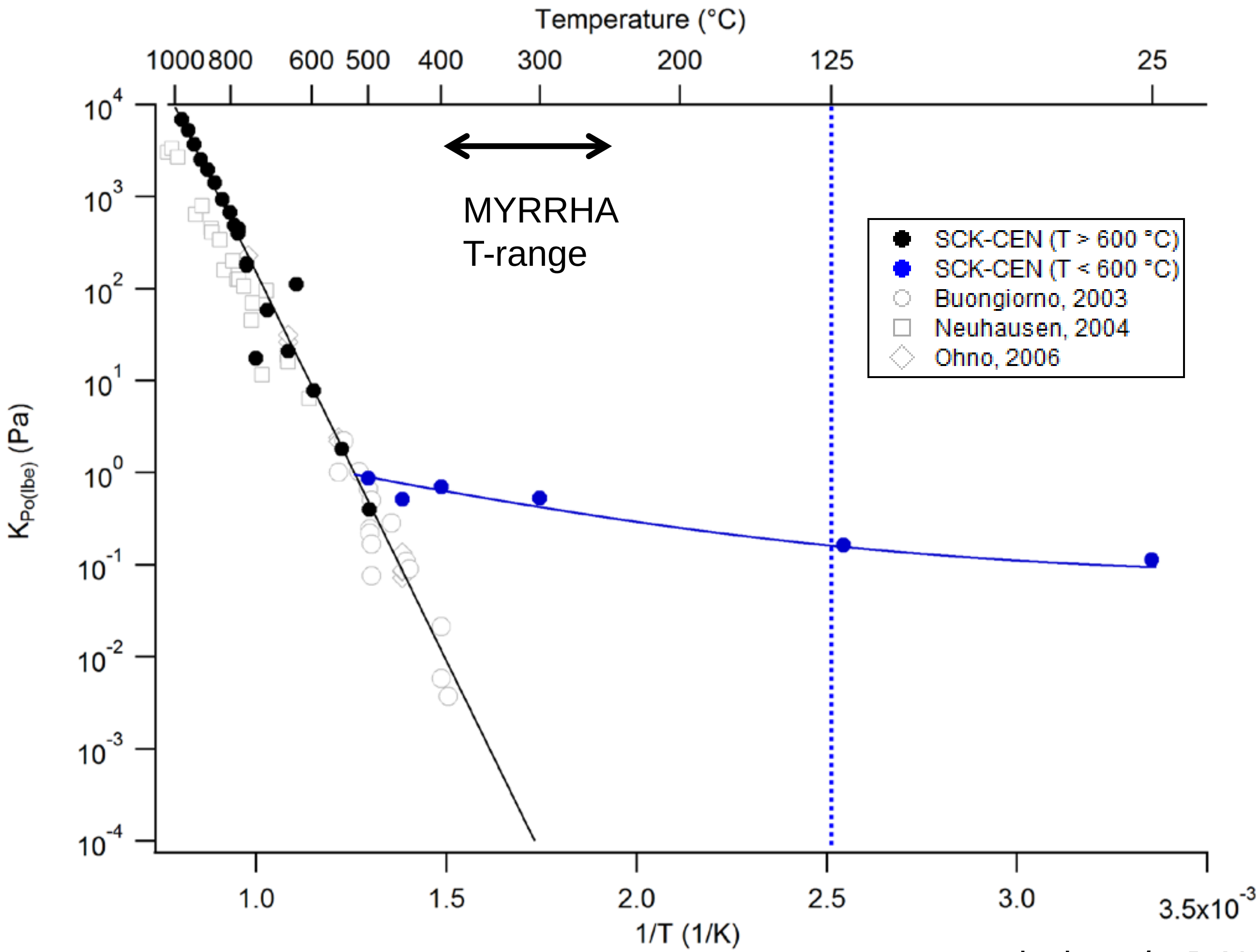
Polonium evaporation from LBE at **T < 600 °C**

- Much more Po evaporation than expected from high-T behavior



Rizzi *et al.*, *J. Nucl. Mater*, 2013.
Gonzalez *et al.*, *J. Radioanal. Nucl. Chem*, 2014

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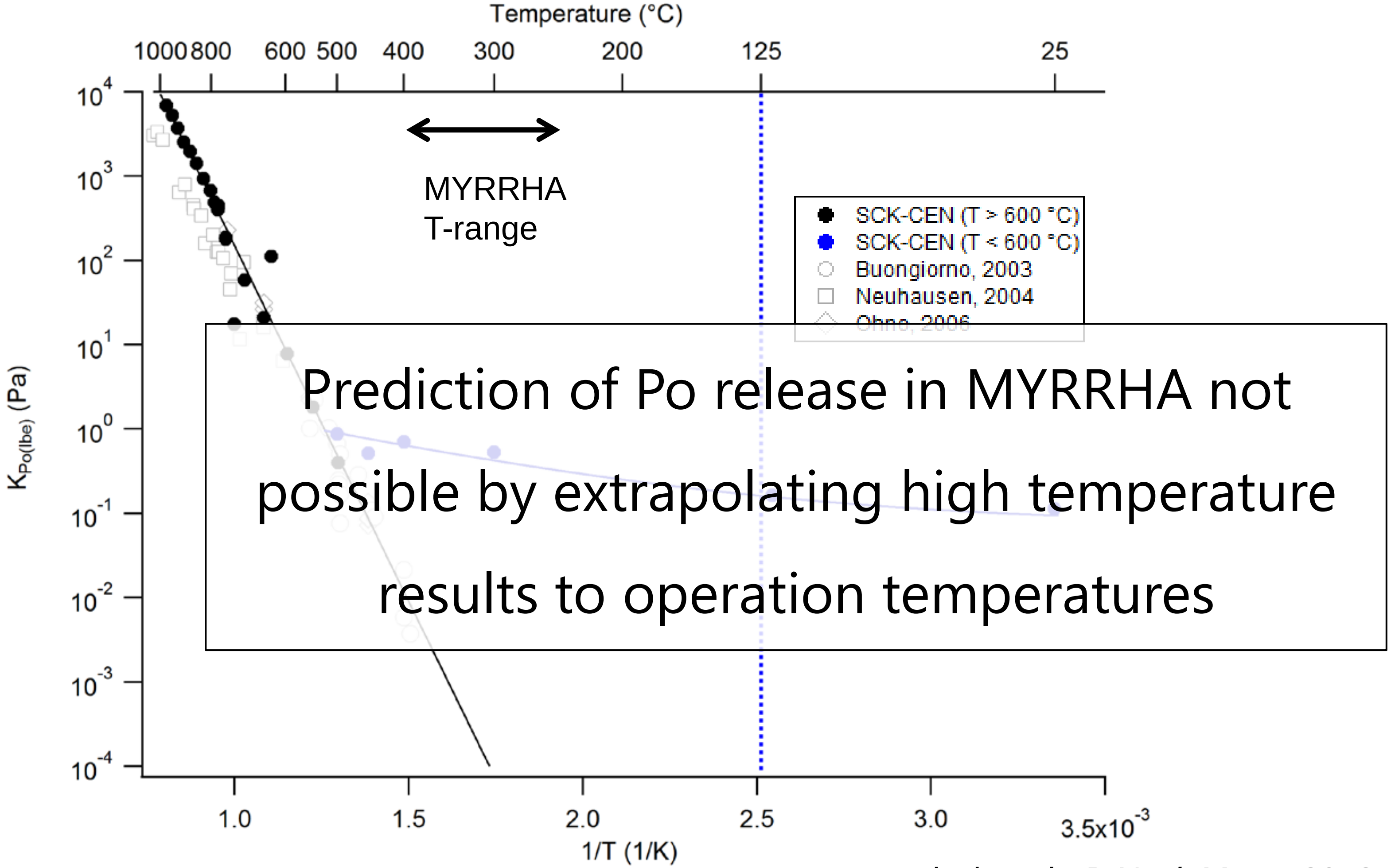

Rizzi *et al.*, *J. Nucl. Mater*, 2013.
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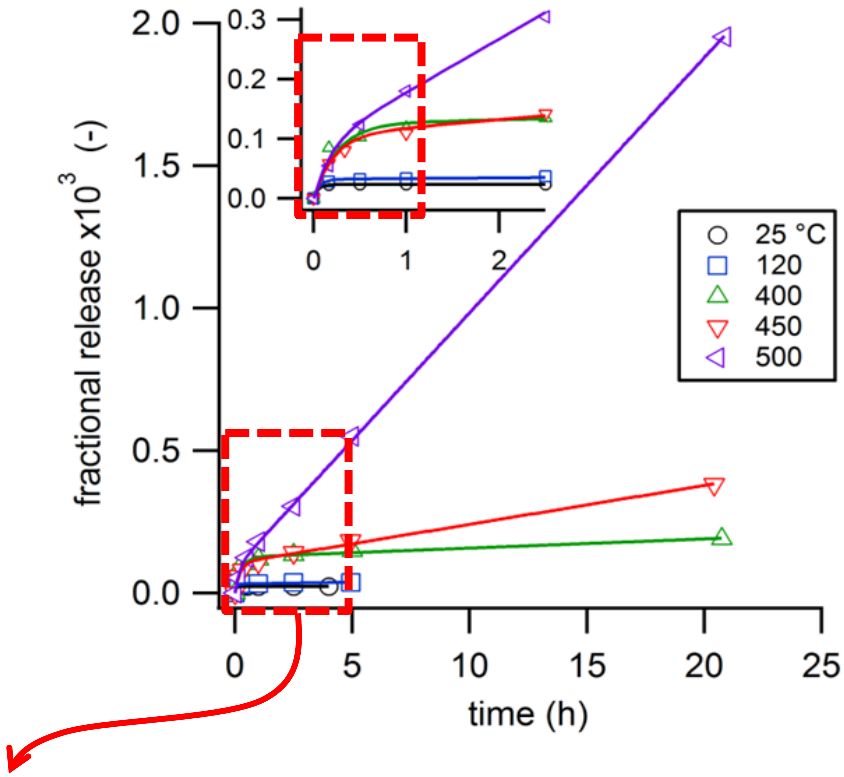
Polonium evaporation at low temperature: Insight from time-dependent evaporation experiments

- Fractional release of Po from LBE versus time at T<500 °C
- From results at high *T*: linear time-dependence expected



- At low T, fraction of Po is released unexpectedly **fast**

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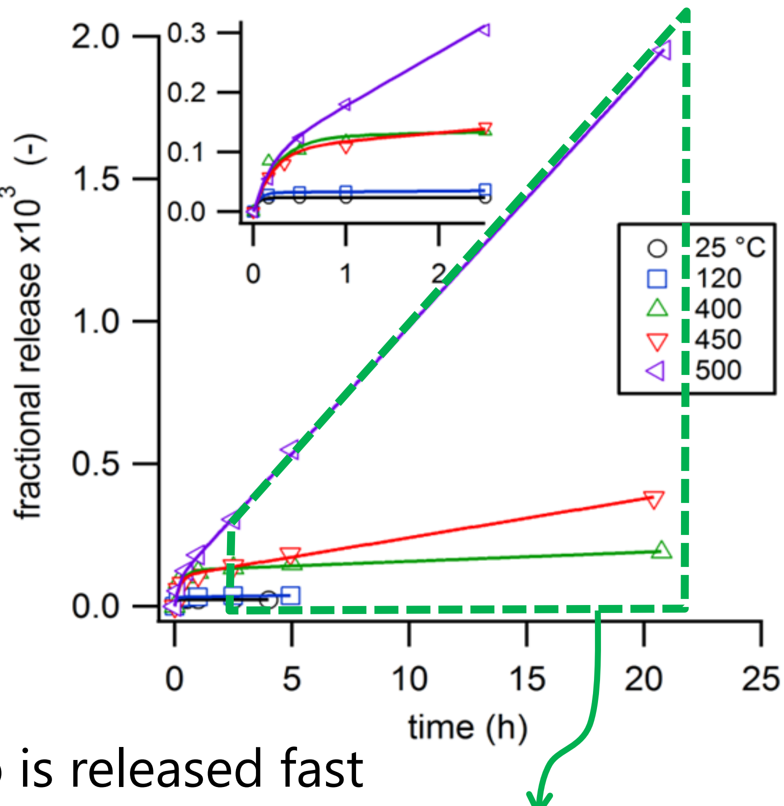
Polonium evaporation at low temperature: Insight from time-dependent evaporation experiments

- Fractional release of Po from LBE versus time at T<400 °C
- From results at high *T*: linear time-dependence expected



- Fraction of Po is released fast
- Other Po fraction evaporates more **slowly** according to high-temperature behavior

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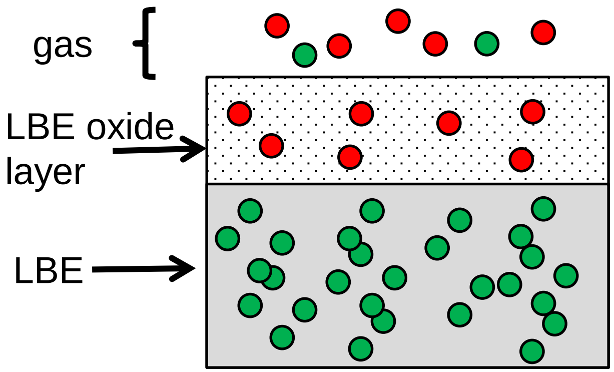
Polonium evaporation at low temperature: Properties of "fast-released" Po

Further experiments indicated that "fast-released" polonium

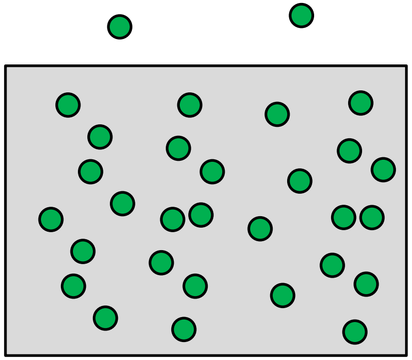
- is enriched at free **surface** of LBE;

  slow-released Po in bulk of LBE
- is incorporated in **oxide layer** on top of LBE

Oxygen saturated LBE
Fast Po release in Ar 5%H_2



Oxygen undersaturated LBE
No fast Po release in Ar/5%H_2



⇒ evaporation strongly dependent on oxygen content LBE

- evaporation and **speciation** strongly dependent on composition cover gas

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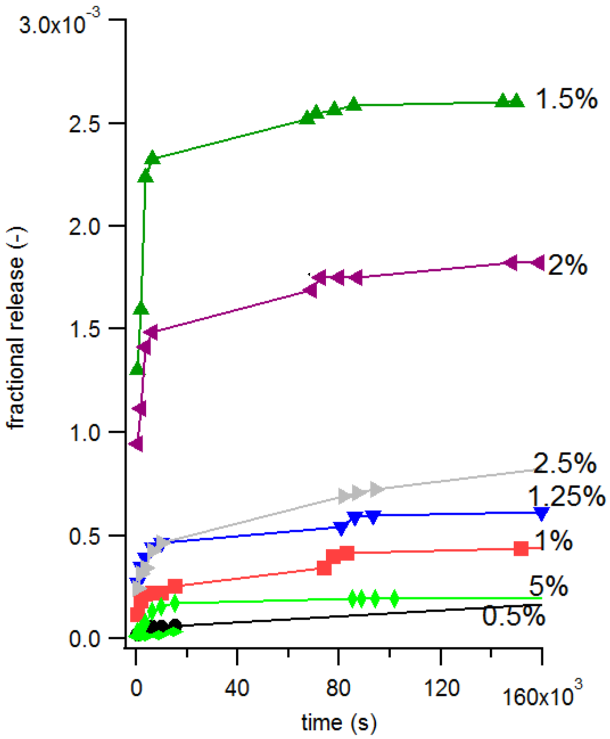
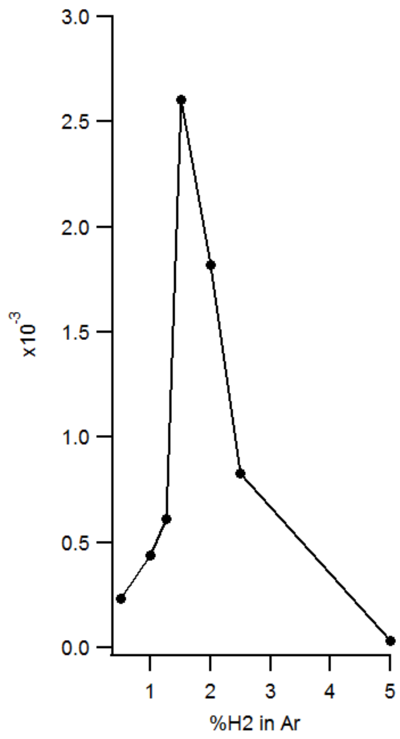
Polonium evaporation at low temperature: Polonium release vs hydrogen content cover gas

- Carrier gas: 0-5%H_2 in Ar, evaporation at 400 °C
- Po/LBE samples without initial (visible) oxide layer: fast-released Po formed *in situ*

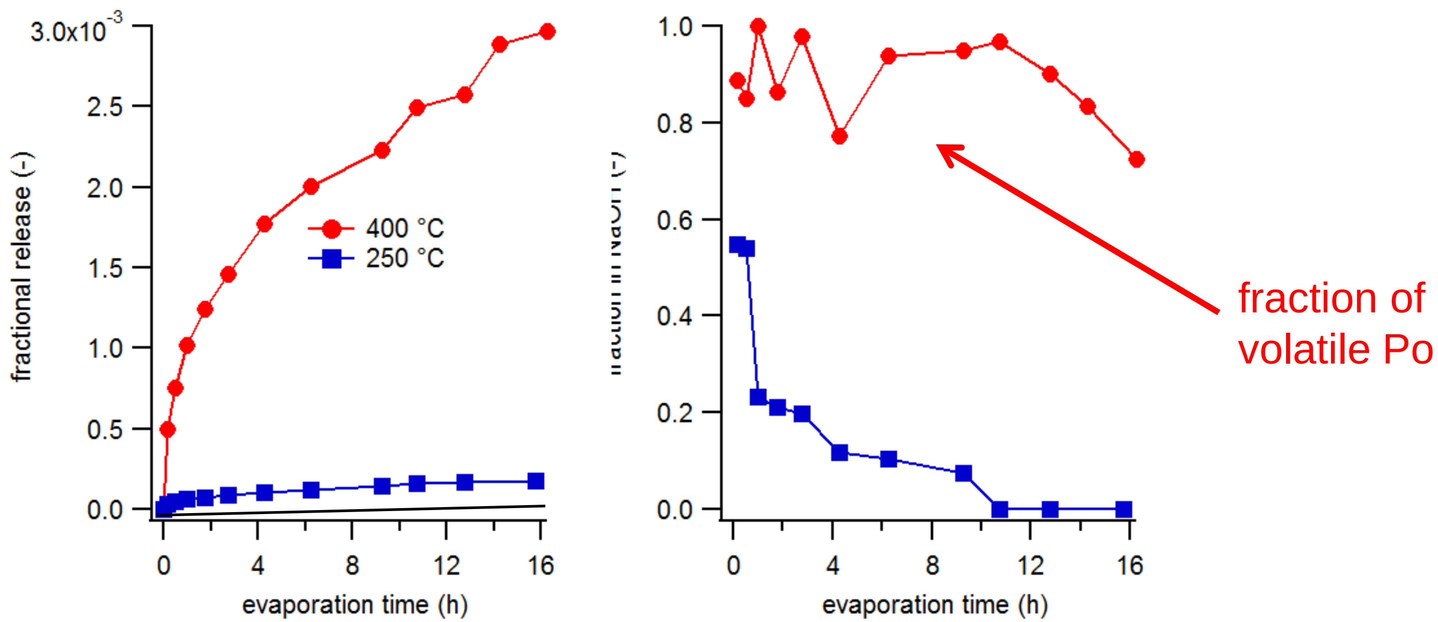




- Complex dependence on H_2 content cover gas
- Up to 1000 times more evaporation than expected from high temp data
- In H_2: evaporated species not very volatile: condense at ~300 °C
  - vapor species possibly (Po(g), BiPo(g) or PbPo(g)
- Important for LBE oxygen reduction system using H_2 gas

Polonium evaporation at low temperature: Po release in presence of water vapor

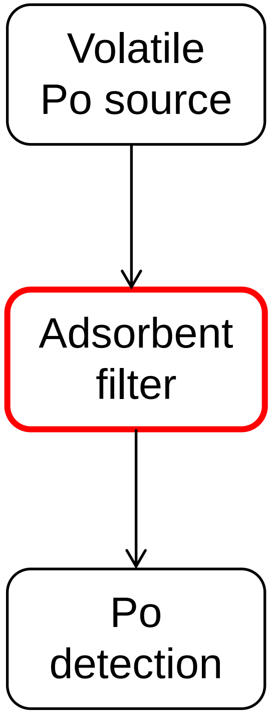
- Water ingress in LBE due to leak/rupture secondary circuit
- Po-release with time:

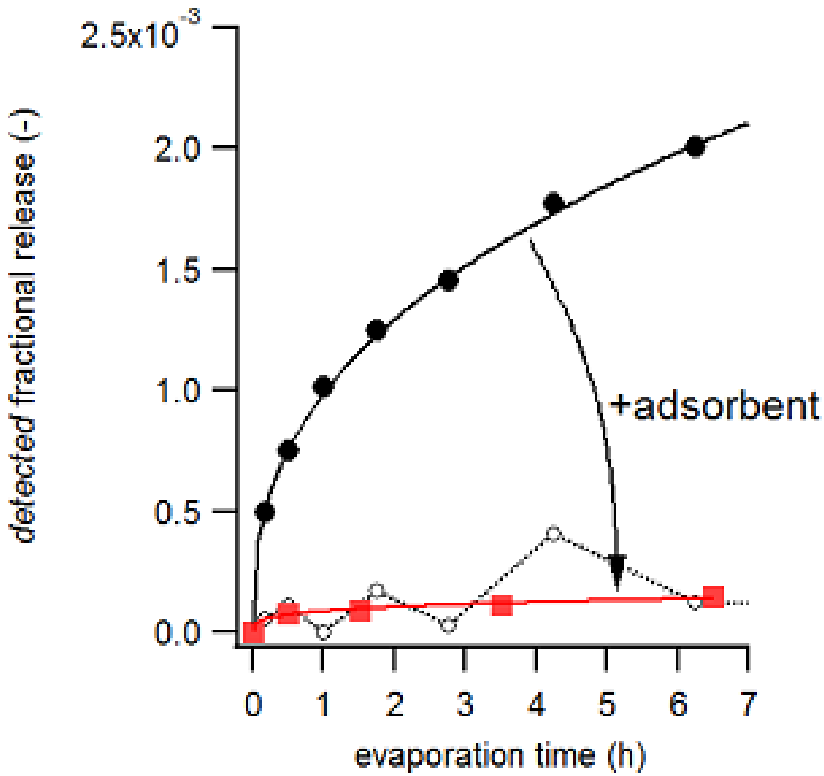


- High Po evaporation at 400 °C
- **Very volatile Po species**, easily transported at room temperature
  PSI results: possibly $Po(OH)_x$, $PoO(OH)_2$
- Potentially large radiological impact: design changes + filter development

First exploratory capture studies of volatile Po

- Experiments without and with activated carbon bed between source and detection





- Activated carbon efficient adsorbent for volatile Po

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Conclusions

- At high T Po evaporation from LBE seems to be well understood and not very sensitive to cover gas composition; based on our experiments we have developed models that allow reasonably accurate predictions of polonium release

- At low T polonium evaporation is much more complex. A fraction of the dissolved polonium is released much faster than expected from high temperature behavior. The magnitude of its release and the volatility of the evaporated Po molecules are controlled in a complex way by
  - dissolved oxygen concentration in LBE or other HLM
  - composition of the cover gas

- When water vapor comes in contact with LBE, large quantities of very volatile polonium molecules may be released

- More R&D needed to understand physical chemistry
- **MYRRHA: conservative design change to double walled HX to significantly reduce water ingress probability**

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