PAUL SCHERRER INSTITUT

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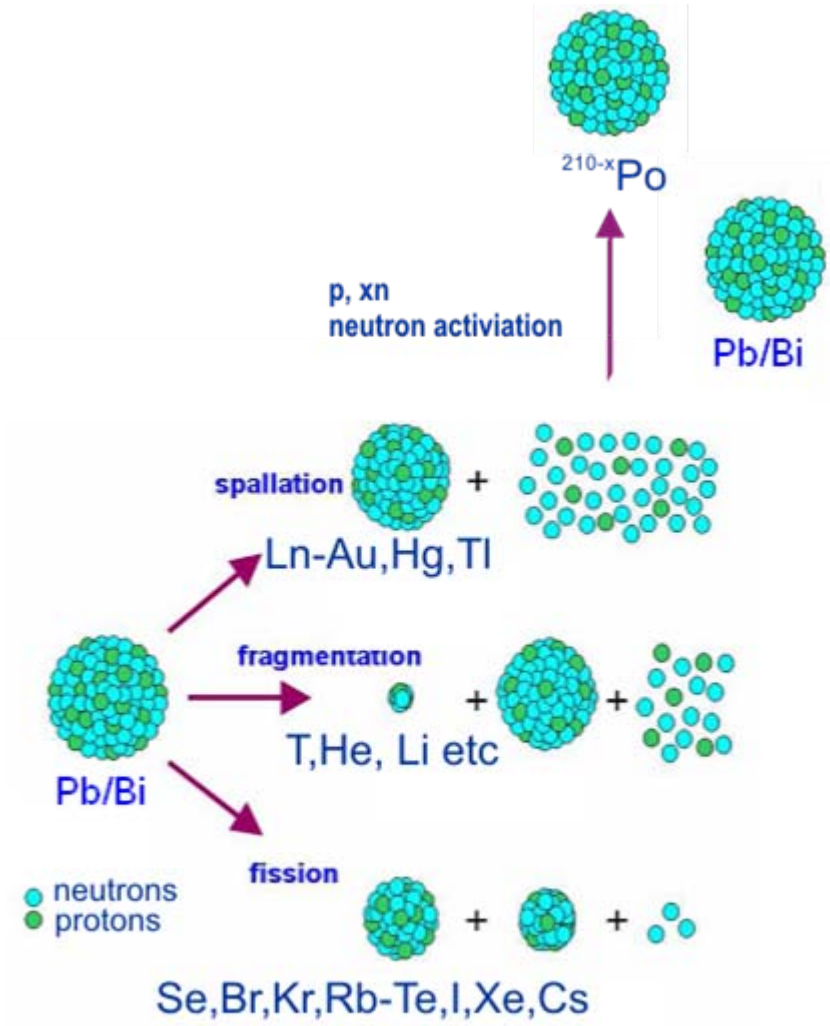
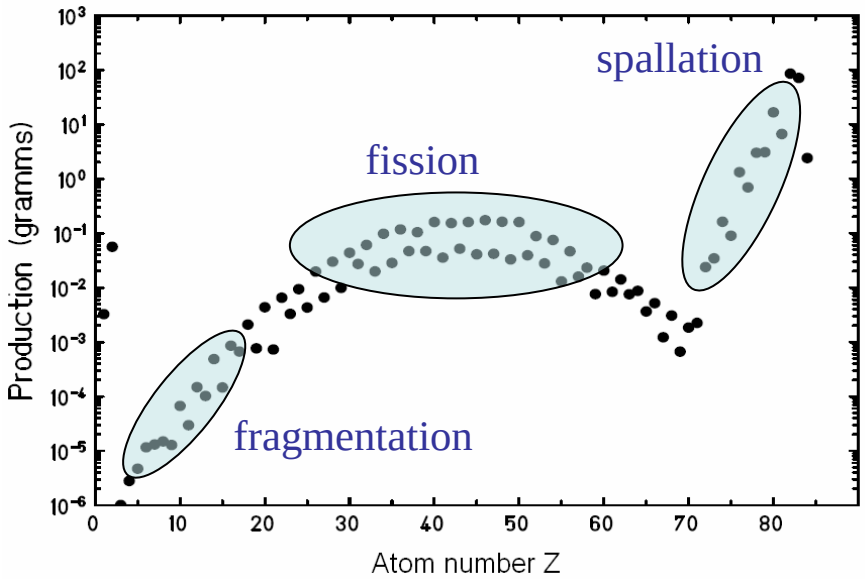
Paul Scherrer Institut

Jörg Neuhausen

Radiochemical Aspects of Liquid Metal Spallation Targets

Production of impurities by nuclear reactions





Calculations for MEGAPIE: L. Zanini

Changes of chemical composition:

All elements of periodic table with $Z \leq Z_{target} + 1$

Mobile in the liquid metal

Kg amounts, mole fractions up to 10^{-4}, 10^{16} Bq

Consequences for the behavior of the system

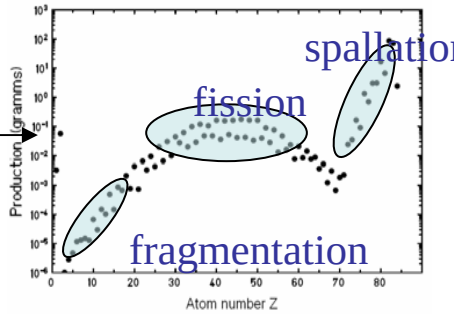
- Normal operation conditions
- Accident scenarios

Graphics courtesy U.Köster (ILL)

Chemical Studies of Impurities in Liquid Metal

Volatilization:
Gaseous elements
Noble gases, (hydrogen)
Elements that are volatile or form volatile compounds
Hg, Po, Br, I, Rb, Cs, Tl
Most important for safety

Chemical Analyses:
Benchmark for codes
Determine radiological hazard
Operational safety + Disposal



Impurities in LM:
Nuclear reaction products:
Mass: up to kg
Mole fraction: up to 10^{-4}
Activity: up to 10^{16} Bq
Corrosion Products:
Macroscopic amounts activated

Distribution of impurities:
Important to know for reliable Analyses
Deposition of material can have Radiological and operational consequences

Removal of radionuclides:
Mitigate radiological issues
Production of valuable nuclides for medical or scientific applications

Effects of impurities on corrosion:
Presence of highly excited atoms
Attack on protecting layers
Catalysis of corrosion reactions
Not much studied yet

Distribution of Radionuclides

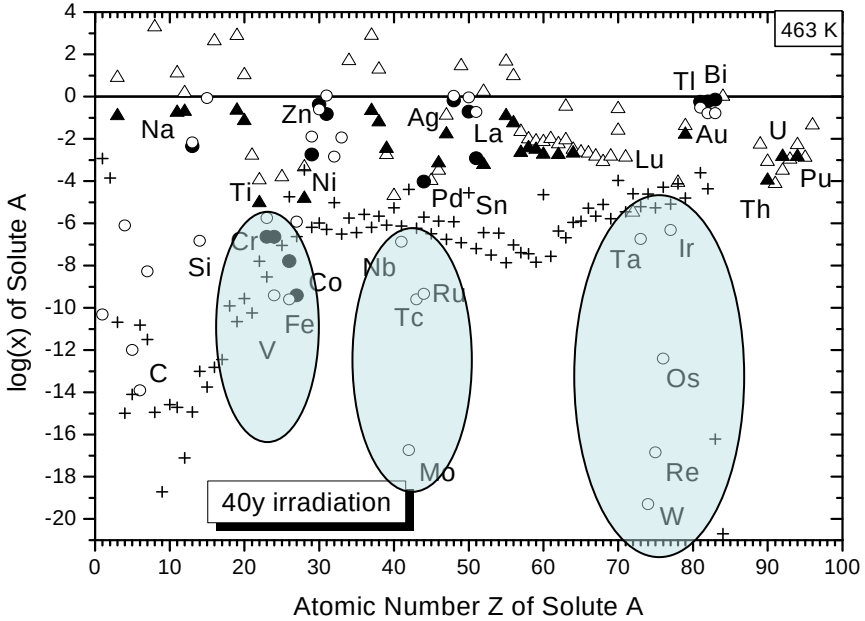
What is expected from chemical reasoning?

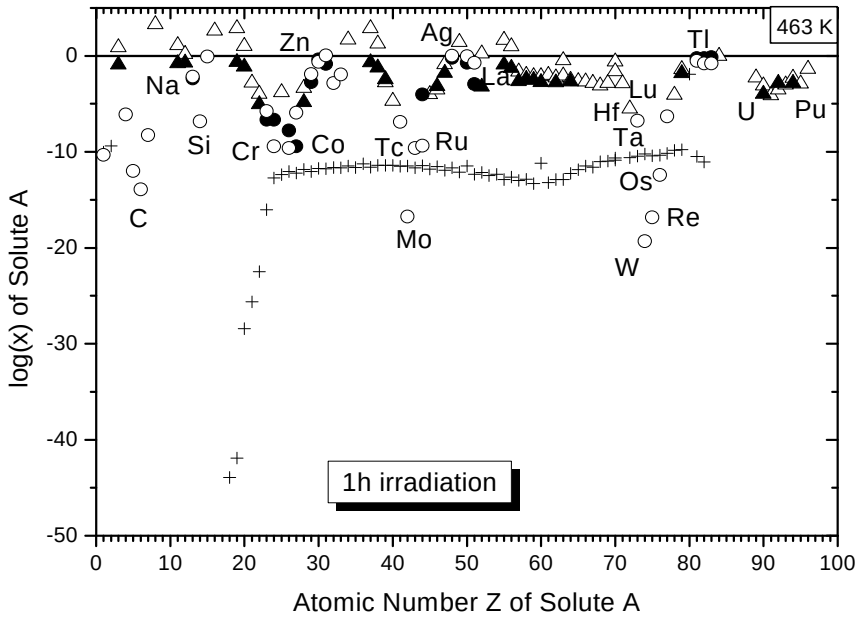
Nuclear reaction products will separate from the liquid metal when the solubility limit is exceeded or in case they form insoluble compounds, e.g. oxides

Thermodynamic calculations and Literature data analysis for EURISOL Hg target system

Solubility limit for refractory metals and various elements contained in steel may be reached already after short irradiation

Many spallation products are electropositive metals that form oxides which are nor reducible by hydrogen

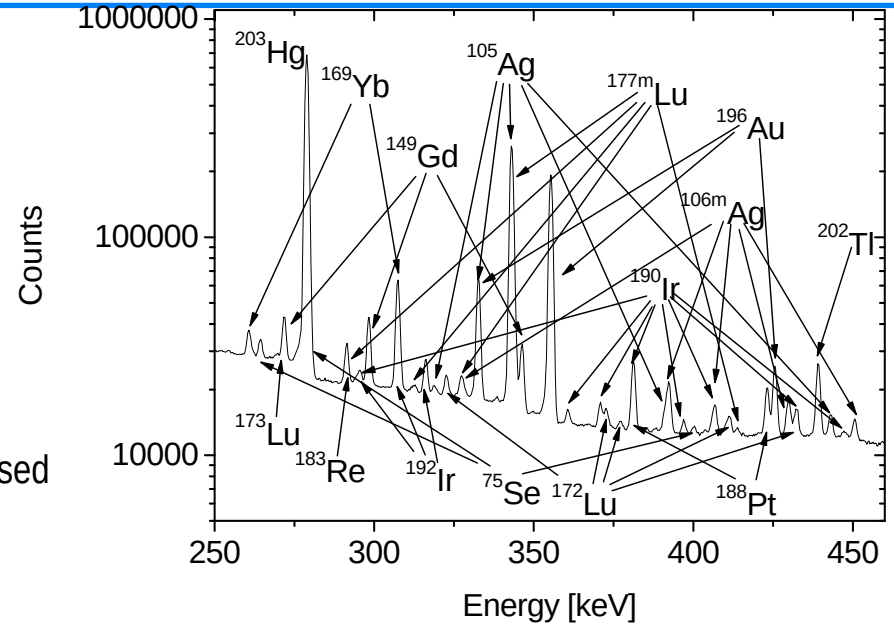


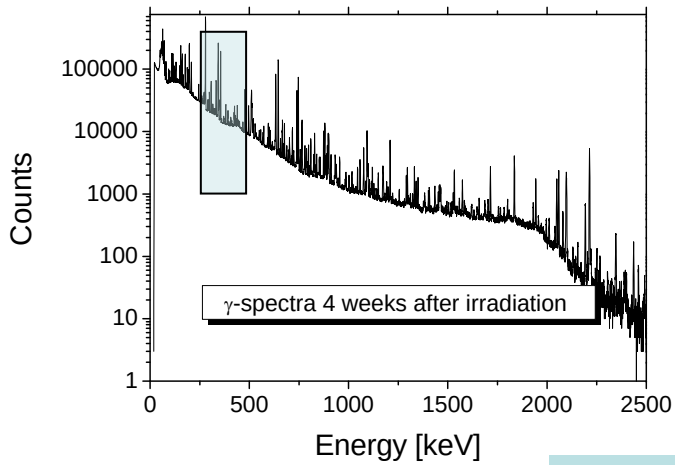


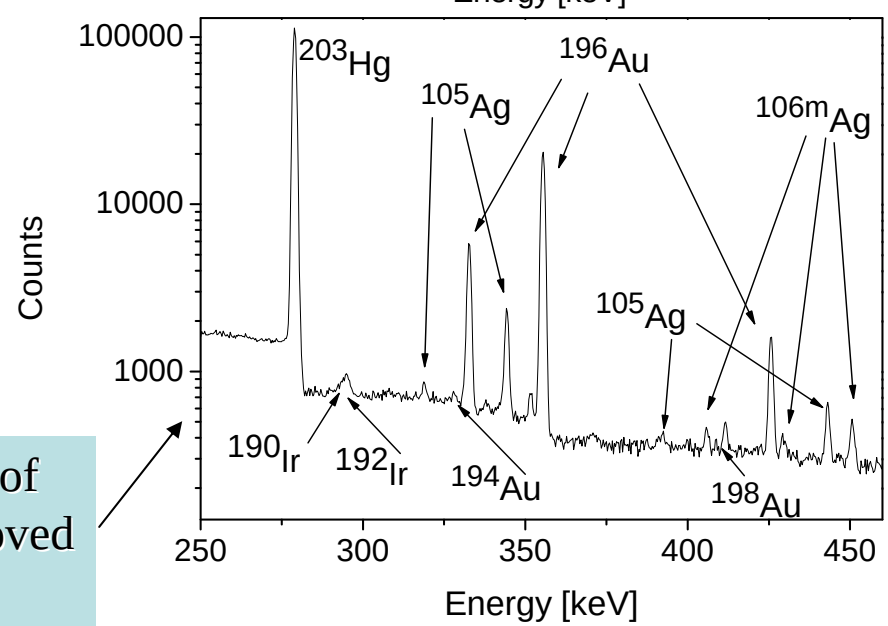
Nuclear reaction product distribution: Experimental results

EURISOL-DS
p-irradiation of Hg samples at CERN

Hg filled under Ar in stainless steel capsules (2 samples)
Irradiated with 1.5×10^{15} protons of 1.4GeV
Opened in "inert gas" Glove-Box
No visible solid contamination on Hg surface
γ-Spectrometry: very complex spectrum
Measured at various times to aid nuclide identification based on half-lives







Spectrum of part of the mercury removed using a syringe

Distribution of nuclear reaction products: Experimental results

Analysis of a p-irradiated LBE target from ISOLDE

LBE target irradiated with 1 GeV and 1.4 GeV protons for ~ 2 weeks (~ 1μA)

Ta container, heated under vacuum to various temperatures between 250 and 600°C in order to study the release of volatiles.

Dismantled in several step to give samples that can be handled in a C-Laboratory.

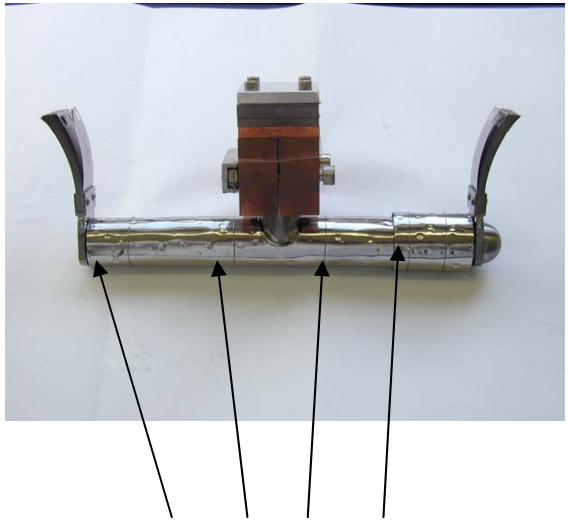
Samples from such a bar have been cut at different positions, using a scalpel:

a) The interface between LBE and the vacuum
b) Directly below the LBE-gas interphase
c) From the bulk LBE
d) From the contact surface between LBE and Ta container

The samples were measured on a γ-spectrometer. Polonium isotopes were determined by α-spectrometry after disolution and plating on a silver plate.

LBE free surface, contaminated with insoluble material

Cutting



Four Disks

Bar-shaped samples were cut from the ISOLDE target:

Bars of ~1-2g in weight, that include the interface between LBE and the gas phase as well as a part of the contact area of LBE and the Ta container.

Both these interfaces are visibly distinguishable from the bulk LBE. They show a thin yellowish cover.

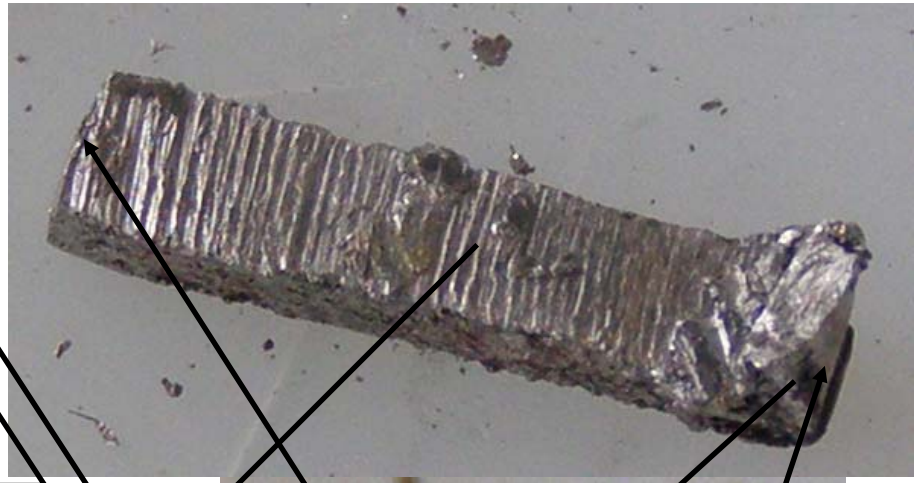
ISOLDE Target sampling and γ+α-spectrometry

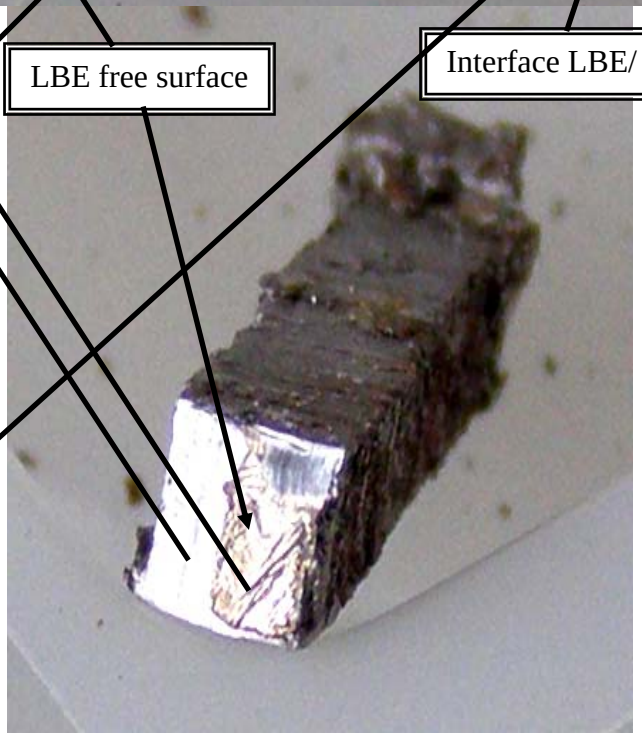
2 samples from surface
Bi-207: 26.8 kBq/g; Lu-172: 200 kBq/g
Bi-207: 27.5 kBq/g; Lu-172: 230 kBq/g
Po-208: 8.3 kBq/g

2 Samples directly beneath the surface
Bi-207: 3!! kBq/g; Lu-172: 9 kBq/g
Bi-207: 28.2 kBq/g; Lu-172: 11 kBq/g
Po-208: 8.1 kBq/g

Several Samples from the bulk
Bi-207: 30,7 kBq/g; Lu-172: 27 kBq/g
Bi-207: 31.8 kBq/g; Lu-172: 28 kBq/g
Bi-207: 30,7 kBq/g; Lu-172: 27 kBq/g
Bi-207: 29,7 kBq/g; Lu-172: 28 kBq/g
Bi-207: 29.3 kBq/g; Lu-172: 104 kBq/g
No Ta-182 (from container)
Some samples show depletion of all main nuclides by a factor 5
Po-208: 6.9 kBq/g

Samples from Ta/LBE interface (container wall)
Bi-207: 34.9 kBq/g; Lu-172: 78 kBq/g
Bi-207: 32,4 kBq/g; Lu-172: 66 kBq/g
Po-208: 7.8 kBq/g



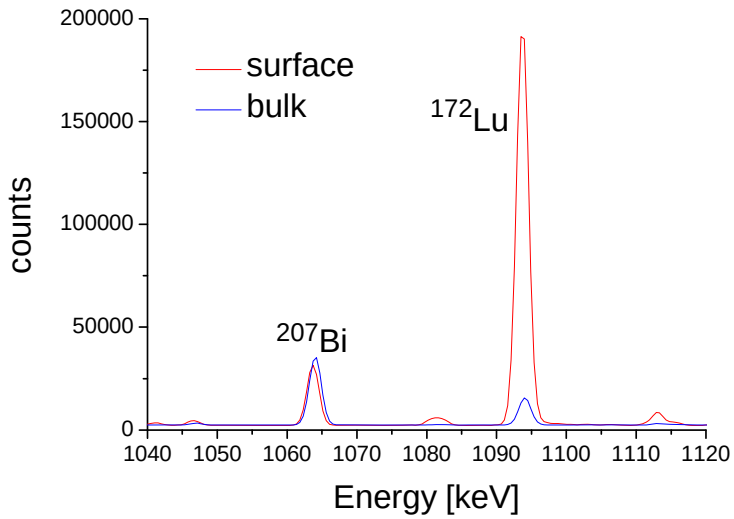


ISOLDE Target: Results

Electropositive elements such as Lutetium or Hafnium are enriched both on the LBE/Gas interface as well as on the walls of the Ta container, indicating that they are bound to oxide phases.

In the bulk, there seem to be both grains that bind dissolved radionuclides and grains that carry less activity than the average

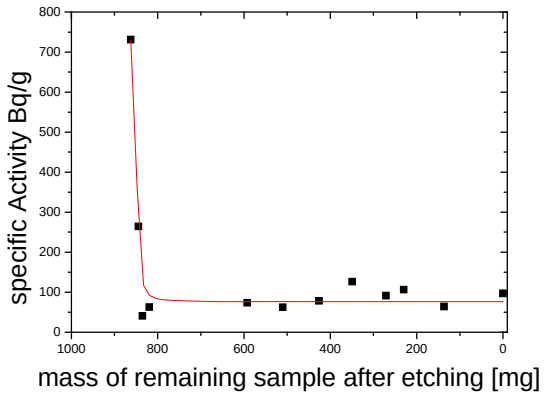
Comparison of bulk and surface:

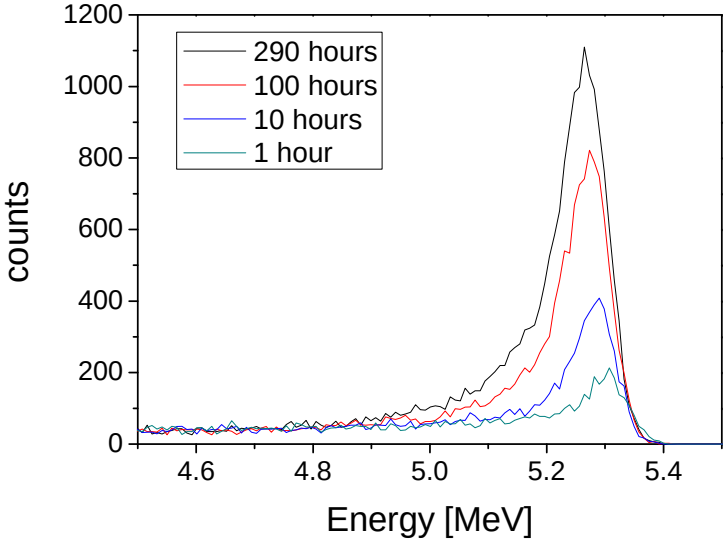


Bulk sample (2 mg) cut in two halves :

Nuclide	A_{spez} [Bq/g] measured	A_{spez} [Bq/g] calculated
^{60}Co	565/1520	1670
^{65}Zn	500/1430	333
^{102}Rh	2310/3920	833
^{110m}Ag	1310/1080	
^{133}Ba	745/2780	1670
$^{172}Hf/Lu$	27900/103000	33000
^{173}Lu	25400/122000	33000
^{207}Bi	29700/29500	33000

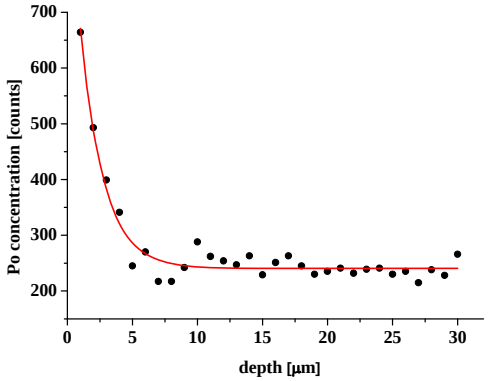
Polonium migration and segregation in solidified LBE



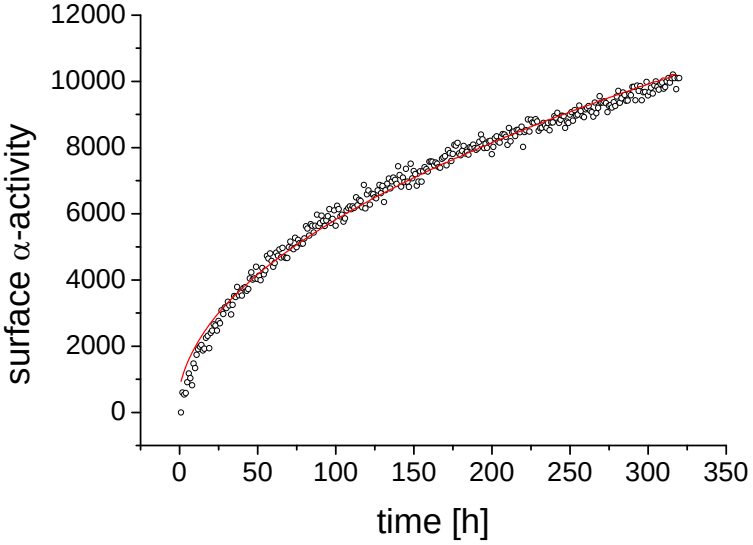


LBE-samples containing ^{210}Po were etched and the etching solutions analyzed by liquid scintillation counting. As shown in the figure, polonium is highly enriched in the surface.

Surface layer appr. 5 μm



α-spectra and growth of α-counts as function of time



Driving force for migration?
Oxide phase found in x-ray diffractogram

Conclusions

Observation: In Hg, most of the impurities probably tend to separate from the liquid metal and will float on the liquid metal surface and stick to the walls. Soluble noble metals remain dissolved in Hg

In LBE, a similar but less pronounced accumulation of radionuclides on the liquid metal surface and on the walls of a p-irradiated target have been observed

In LBE, migration and surface enrichment of polonium in the solid eutectic was observed

Probable Reason:
Exceeding of solubilty limit, formation of unsoluble compounds, formation of stable surface layers

Conclusions for chemical Analysis → benchmarking codes + determination of inventory

One sample is not enough for a reliable analysis

Inhomogeneities may be caused by deposition on walls or suspended particles

Concentration gradients may be also caused by crystallization effects

For the analyses of samples from MEGAPIE, samples from all cuts are taken, some of them studying radial distribution. Additionally, samples from the wall and the cover-gas system will be studied to check for depositions

For operation:
Sticking to walls and floatation on free LM surfaces: Larger doses than expected

May be necessity of cleaning of parts for maintance or to increase shielding

Po-enrichment on surface may lead to increased sputtering from spills,

Decay heat accumulation→increased volatilization

Extraction of hazardous nuclides from LBE: Polonium

Alkaline melt extraction, similar to industrial Pb and Bi refining

Harris Process: $3Te+6NaOH \rightarrow 2Na_2Te+Na_2TeO_3+3H_2O$,

$Na_2Te+xTe \rightarrow Na_2Te_{x+1}$

Glassy Carbon Vessel, Quartz tube

Gas supply (H_2, He, N_2, air, O_2)

Resistive heating, magnetic stirring

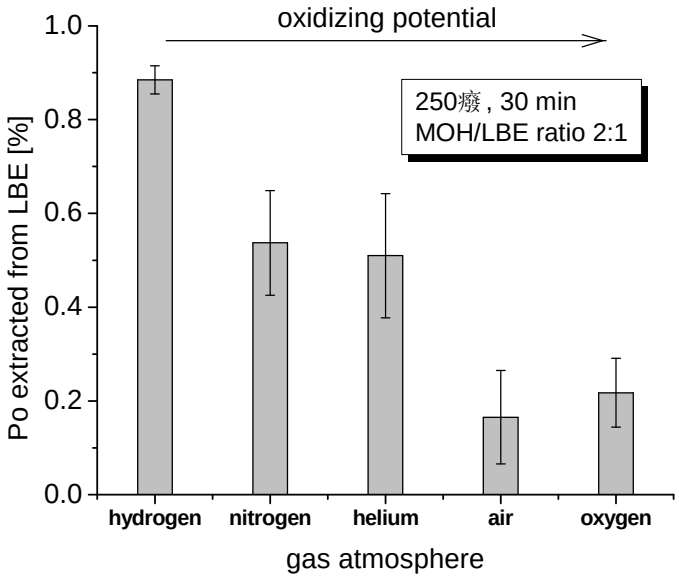
Alkaline melt: NaOH-KOH eutectic (50:50 at %) $T_{eutectic}$ = 170˚C

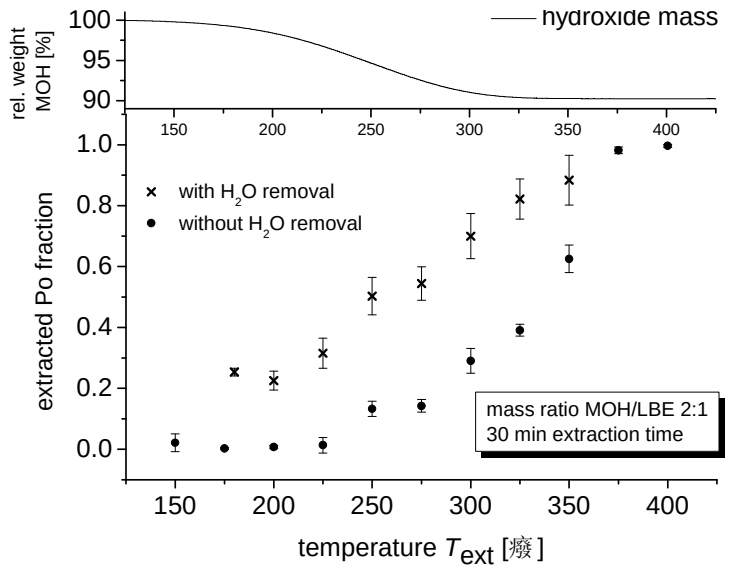
LBE: Pb-Bi (44.5:55.5 at %) $T_{eutectic}$ = 123˚C

typical $A_{spec.}$ = 240Bq/g, $x=1.4\times10^{-12}$

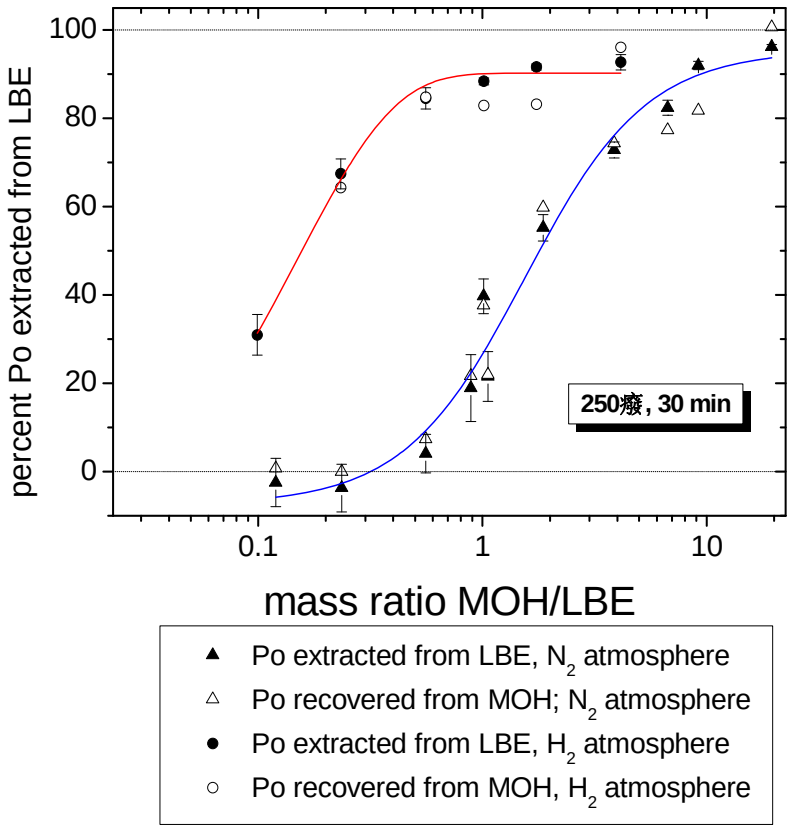
Alkaline/LBE mass ratio range 10:1 – 1:20

Po extraction from LBE: Results





Influence of gas plenum
Temperature curves
Influence of water content of (Na,K)OH
Relative amounts of LBE/MOH

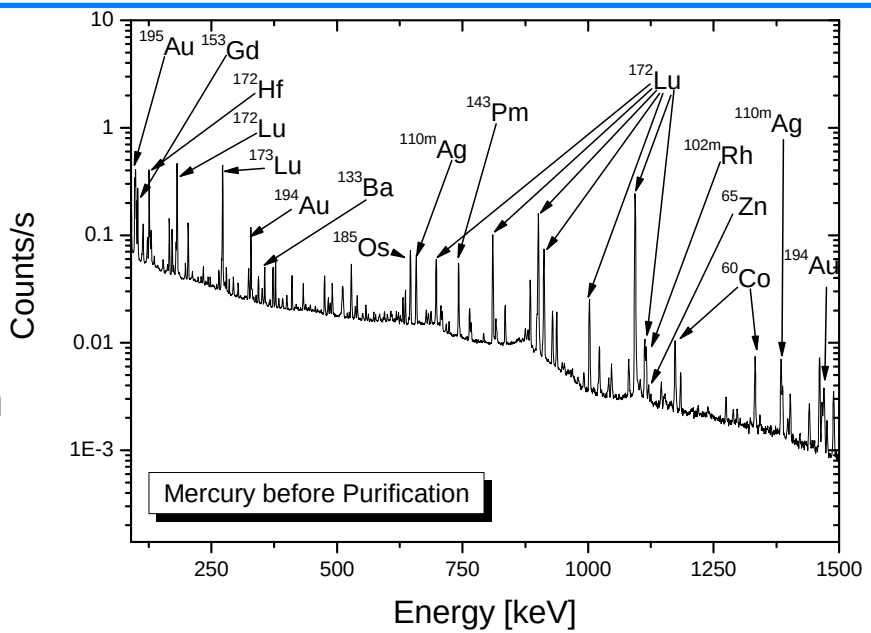


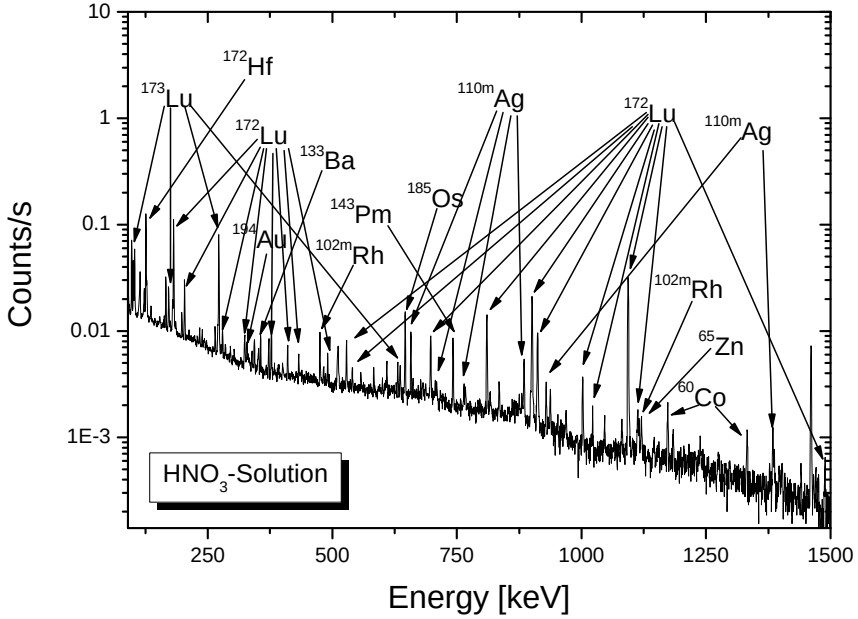
Purification of proton-irradiated Mercury: EURISOL-DS

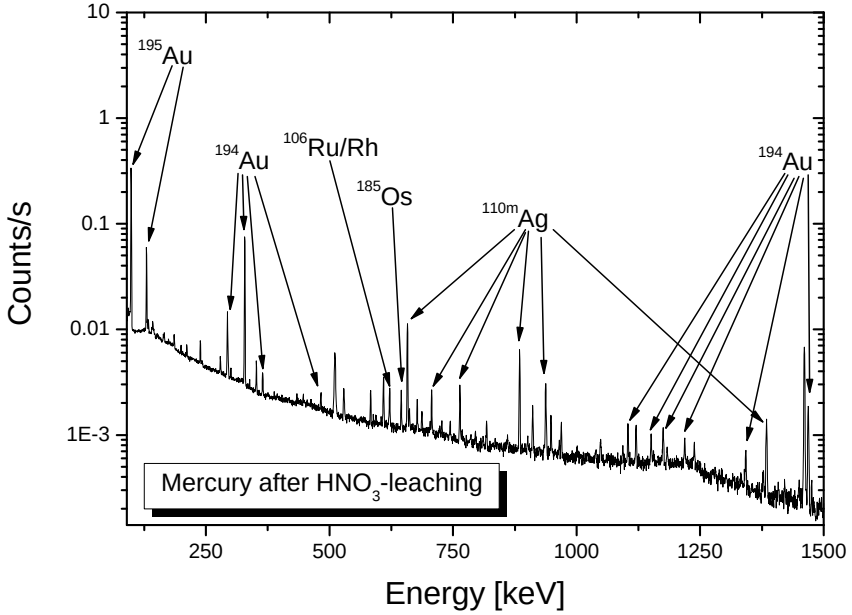
Purification by leaching and distillation

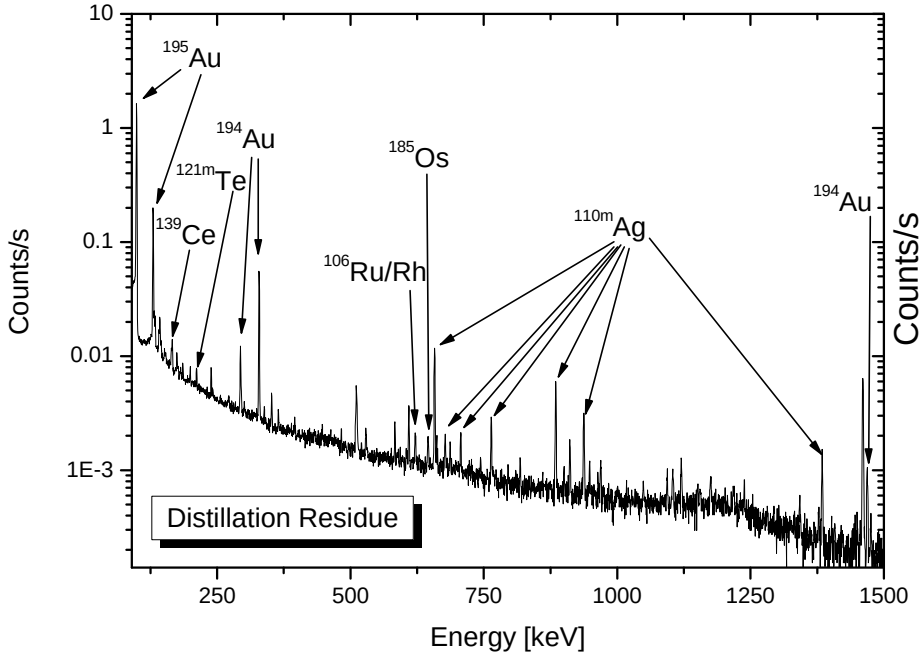
Mercury sample of 9 g washed with 2M HNO_3 (3h, weight loss 14% caused by dissolution of Hg)
Subsequently, distillation at 200 °C and ≅ 20 mbar

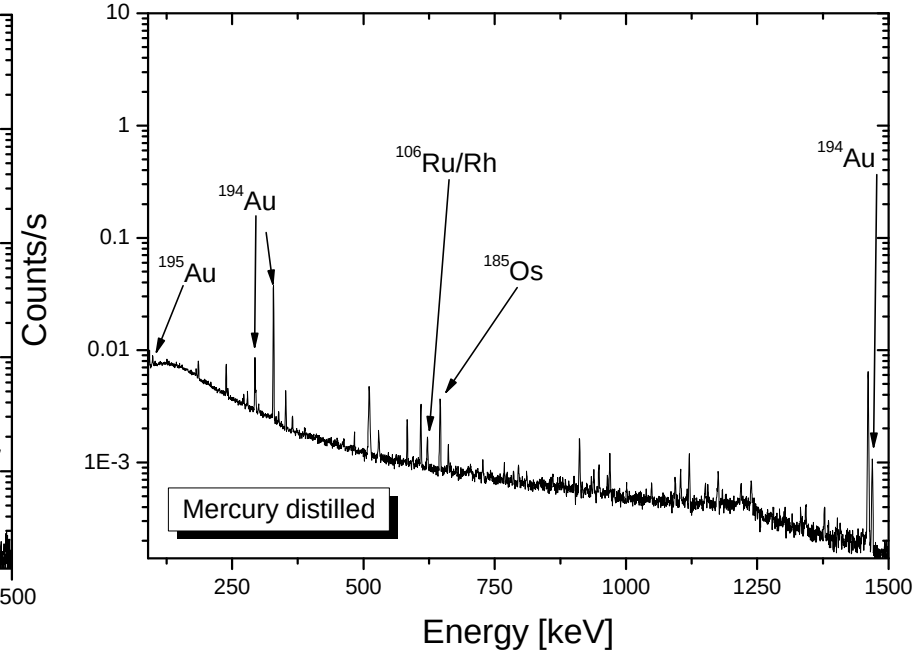
Results leaching:
Base metals are extracted to the acid
Os - and very tiny amounts of Ce and Te not indicated in figure - are to a large part removed, but a small fraction remains in Hg
Ag distribution is roughly 50/50
Au and Ru remain in Hg











Results distillation:

During the distillation, Ru and Os are partly carried over with Hg most probably as MO_4.

The by far largest part of Au remains in the residue. A small fraction of ^{195}Au is carried with the mercury. The ^{194}Au detected in the distilled Hg comes from decay of ^{194}Hg.

Thus, the applicability of the conventional purification techniques is proven for complex spallation-target-like mixtures that contain radionuclides in very small concentrations

($x \cong 10^{-11}$ to 10^{-16} in mercury based on activity measurements, but stable isotopes have also been produced by irradiation and subsequent decay).

Purification of proton-irradiated Mercury

Alternative methods:
Metal-absorbers to remove dissolved Gold from Hg

Avoids production of liquid radioactive waste and volatilization of large amounts of activity

Criteria for Absorbers:

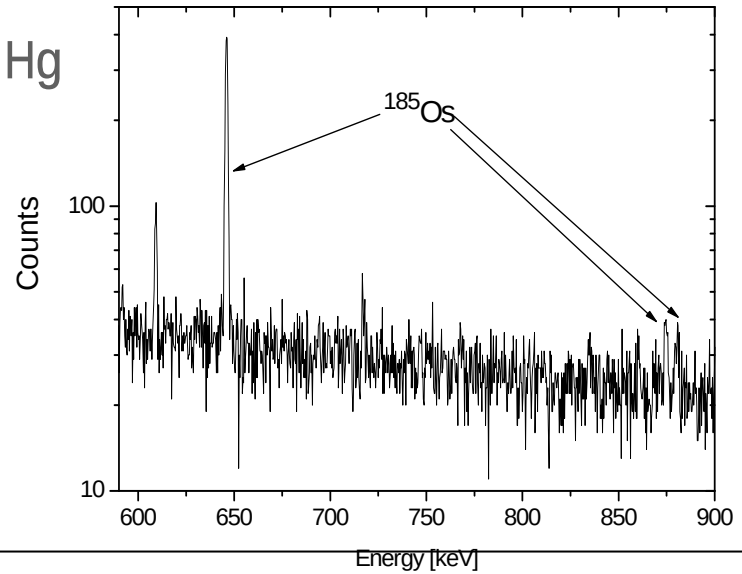
- Stronger chemical interaction of the absorber material with the element to be extracted, compared to Hg
- Must have low solubility in Hg

Miedema Model predicts stronger interaction of group 4 and 5 metals with Au, compared to Hg-Au interaction

Zr and Ta have a very low solubility in Hg

First test using a tantalum foil show that it is not wetted by Hg

To achieve wetting, pretreatment of metal-surface required (ion beam bombardment)



Spectrum of Ta-foil etched in conc. HF and submerged in Hg for 3 weeks:
Visually, no wetting observed, but ^{185}Os was detected on the surface.

No contamination of detector or signal from external source

^{185}Os (half life 94 d) is one of the dominant spallation products

Very weak line at 646 keV indeed was found after careful search in Hg spectrum

Gold, silver and osmium removal: Cu-Absorber

Copper:

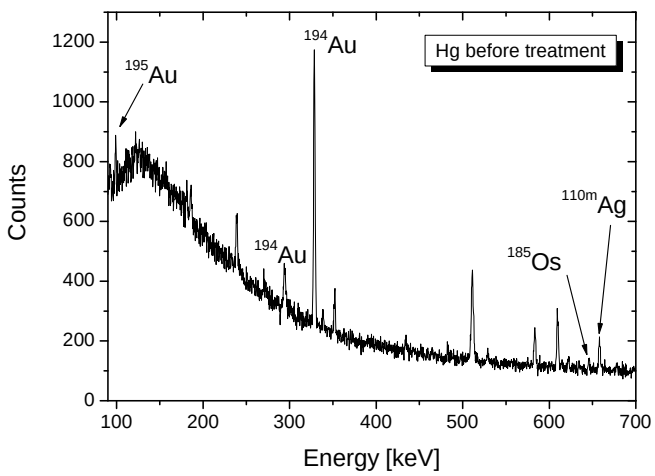
Thermodynamic prerequisites fulfilled

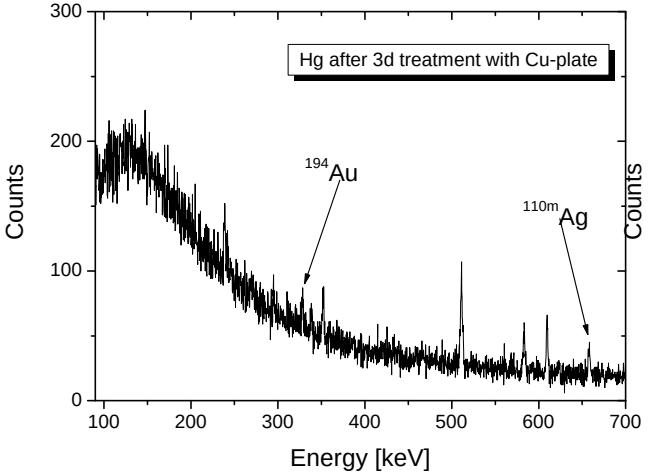
solubility of Cu in Hg fairly low

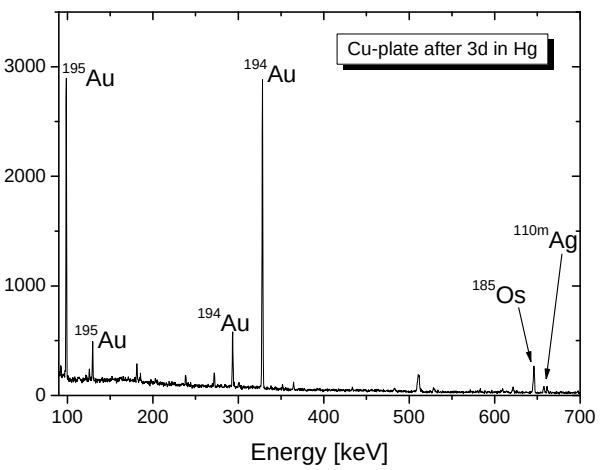
Wetting of Cu by Hg can be achieved by chemical amalgamation

(Cu dipped in saturated aqueous $HgCl_2$-solution)

Amalgamated Cu sheet is easily wetted in Hg







Results: Au and Os are adsorbed on Cu-plate, Ag mainly remains in solution

Works also for Sn and Sb, but not for Zn and Cd

Conclusion: Purification processes

Removal of hazardous radionuclides:

- ❑ LBE/Po system: In principle, effective extraction is possible using alkaline melts.
- ❑ Upscaling to technical scale and safety studies needed
- ❑ Similar liquid-liquid extraction methods may be developed for other nuclides.
- ❑ Selectivity for different nuclides (by variation of extracting agent, additives, gas atmosphere etc.)
- ❑ Hg: most of the impurities probably tend to separate from the liquid metal: therefore, filtering and/or skimming seem most reasonable cleaning procedure, if desired
- ❑ Leaching may be considered for removing material adhering to the walls
- ❑ Alternative methods such as metal absorbers may be used for selective extraction of either hazardous or useful nuclides of certain elements, but a technical application of the technique requires still large R&D efforts

Volatilization

Equilibrium Evaporation:
Elements or volatile compounds

Can be calculated if thermodynamical data of all involved species are known: Evaporation as elements: $P = \gamma \cdot x \cdot p^0$
Required data: γ and p°

Concerning Pb, Bi and LBE, literature data have been reviewed by M Jolkkonen (KTH) and Neuhausen for Po, Hg, Tl, I, Cs, Sr

P^0 known for all elements, except Po: discuss

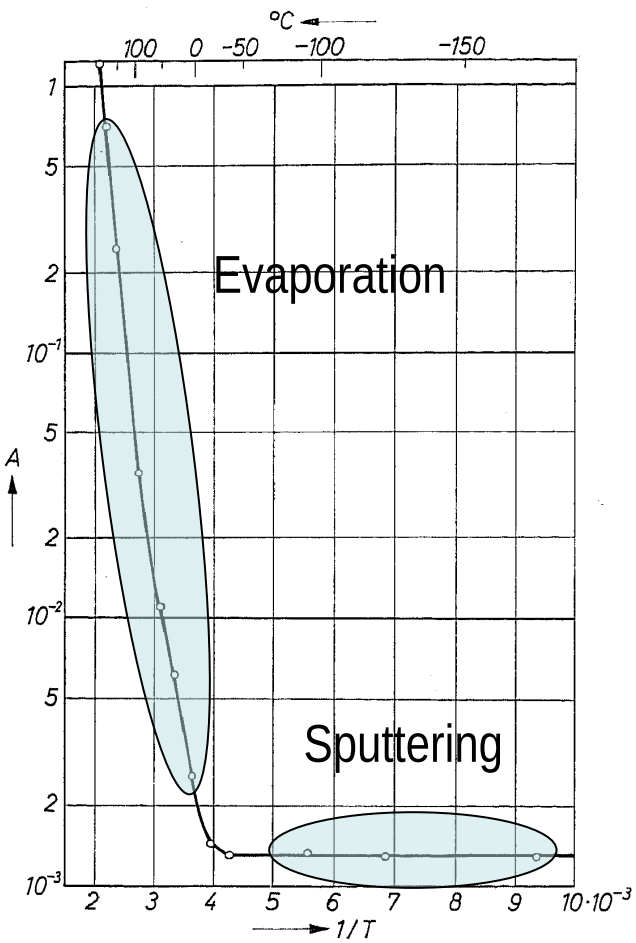
However, γ only known for mixtures of single elements with Pb or Bi, not the eutectic.

For evaporation with chemical reaction, the reaction including involved species and their thermodynamica data have to be identifiec

Problematic systems: e.g. PoH_2, TlOH

Alternatively, an effective p can be determined by dedicated experiments under various conditions

There are only few exp data, mostly on Po



Other processes leading to radioactivity transfer to the gas phase:
Sputtering, Aerosol formation

Not much studied yet

Open systems

No equilibrium → mass transport

Elementary processes: Diffusion and transport in liquid and gas, Evaporation process

Calculations:

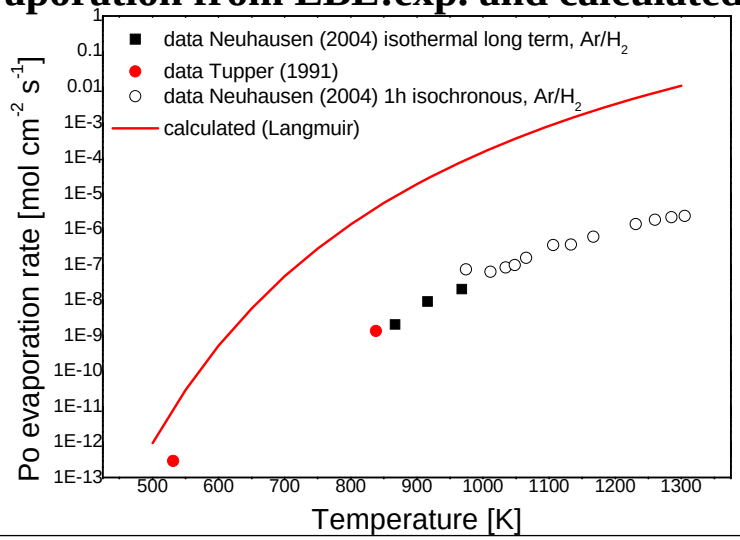
Kinetic gas theory (Langmuir): Max. evaporation rate in vacuum can be calculated from p°

Mass transfer calculations, e.g. film theory: $J=k*\Delta p$

very specific for a certain geometry and flow field, diffusivity, viscosity, all as function of temperature

Analytical solutions only for simple cases (flat plate, tube, sphere)

Po-evaporation from LBE:exp. and calculated data



Conclusion:

- ❑detailed measurements of fundamental parameters (p°, D, γ) for volatile nuclides in LBE and other alloys
- ❑ experimental data that support theoretical evaporation calculations under relevant conditions are essential for licensing of LM-facilities
- ❑ systems with chemical volatilization processes, e.g.interaction with water and compound formation (volatile PoH_2, TlOH, HI….) have to be studied
- ❑Aerosol formation and transport needs to be studied
- ❑Sputtering to needs be studied

Acknowledments:

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