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**Ivan I. Danilov :: Liquid Metal Chemistry :: Paul Scherrer Institut**

# Volatilisation of $^{134}$Cs, $^{131}$I and $^{210}$Po from lead bismuth liquid metal solutions studied by the transpiration method

**HLMC-2018** **IPPE, Obninsk,**

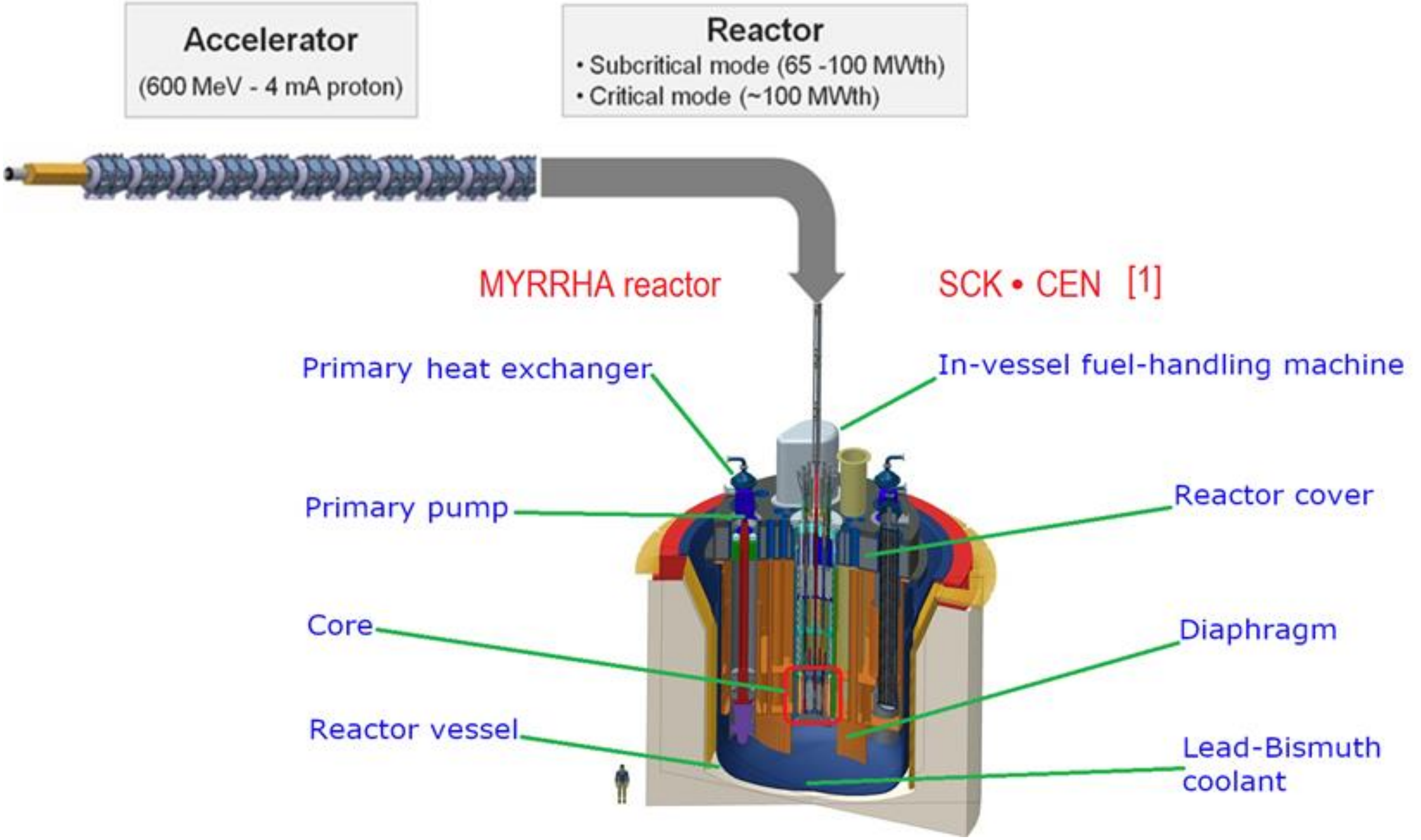
**Wednesday 10th Oktober 2018**

# Overview

- Background
- Objective
- Transpiration method
- Sample preparation
- Data analysis and some practical considerations
- Results
- Summary and Outlook

# Background

**MYRTE – Project** part of the EU-Program for Research and Innovation “Horizon 2020” [1]



**Accelerator**
(600 MeV - 4 mA proton)

**Reactor**
- Subcritical mode (65 -100 MWth)
- Critical mode (~100 MWth)

**Coolant:** liquid lead-bismuth eutectic (LBE).

**Goal:** licencing.

**Previous studies:** volatilization of Po-radionuclides mainly.

**Tasks of this work:** Study the release of radionuclides from lead bismuth eutectic (LBE) results on $^{134}$Cs, and $^{131}$I evaporation.

# Objective

**Radiochemical investigations required for licensing of reactors:**

Which species of volatile elements form under different chemical conditions
to what extent are they released?

Where do they deposit/how can they be caught on filters?

➢Normal operation conditions:

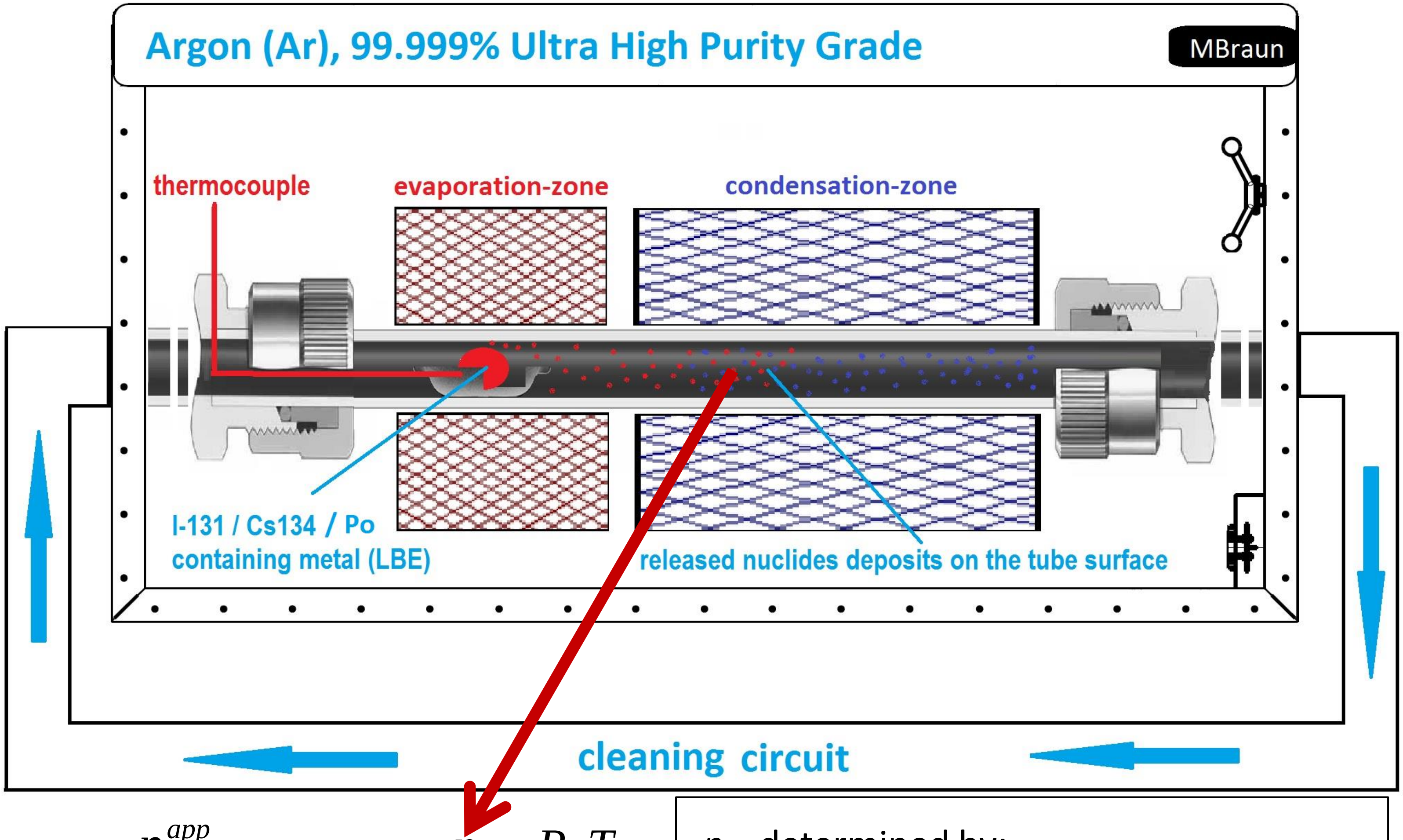
- Cover gas: inert ($N_2$), can contain hydrogen (reducing component) resulting from spallation process and small amounts of moisture formed by reactions of hydrogen with oxides or oxygen dissolved in liquid metal
- Temperature range for LBE coolant 200 to 400°C

➢Accident scenarios:

Steam generator tube rupture (SGTR):

- Large amounts of moisture
- Ingress of oxygen in case of leaks
- Much higher temperatures

# Transpiration method



$$K_H^{Po,app} = \frac{p_{Po}^{app}}{x_{Po}}$$

$$p_{Po}^{app} = \frac{n_{Po}\cdot R\cdot T}{\dot{V}\cdot t}$$

$n_{Po}$ determined by:
liquid scintillation counting ($^{210}$Po)
or $\gamma$-spectrometry ($^{206}$Po, $^{131}$I, $^{134}$Cs)

Henry-constant $K_H$: **equilibrium vapor pressure** over ideal dilute solution
A fundamental parameter for characterizing evaporation

# Sample preparation

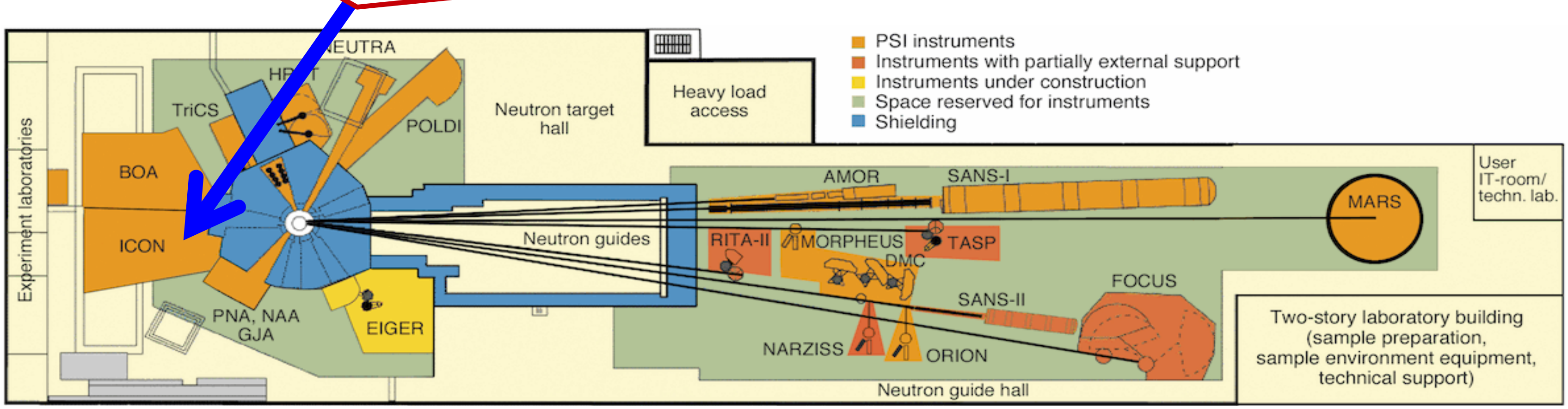
Mixing of LBE with:

- elemental Te
- metallic Cs

in evacuated ampoules

subsequent neutron activation by the SINQ:

$^{130}\mathrm{Te}\ (n,\gamma)\ ^{131}\mathrm{Te}\ (\beta^-)\ ^{131}\mathrm{I}\ (t_{1/2}= 8\ \mathrm{d})$ / $^{133}\mathrm{Cs}\ (n,\gamma)\ ^{134}\mathrm{Cs}\ (t_{1/2}= 2\mathrm{y})$



# Sample preparation for I-131

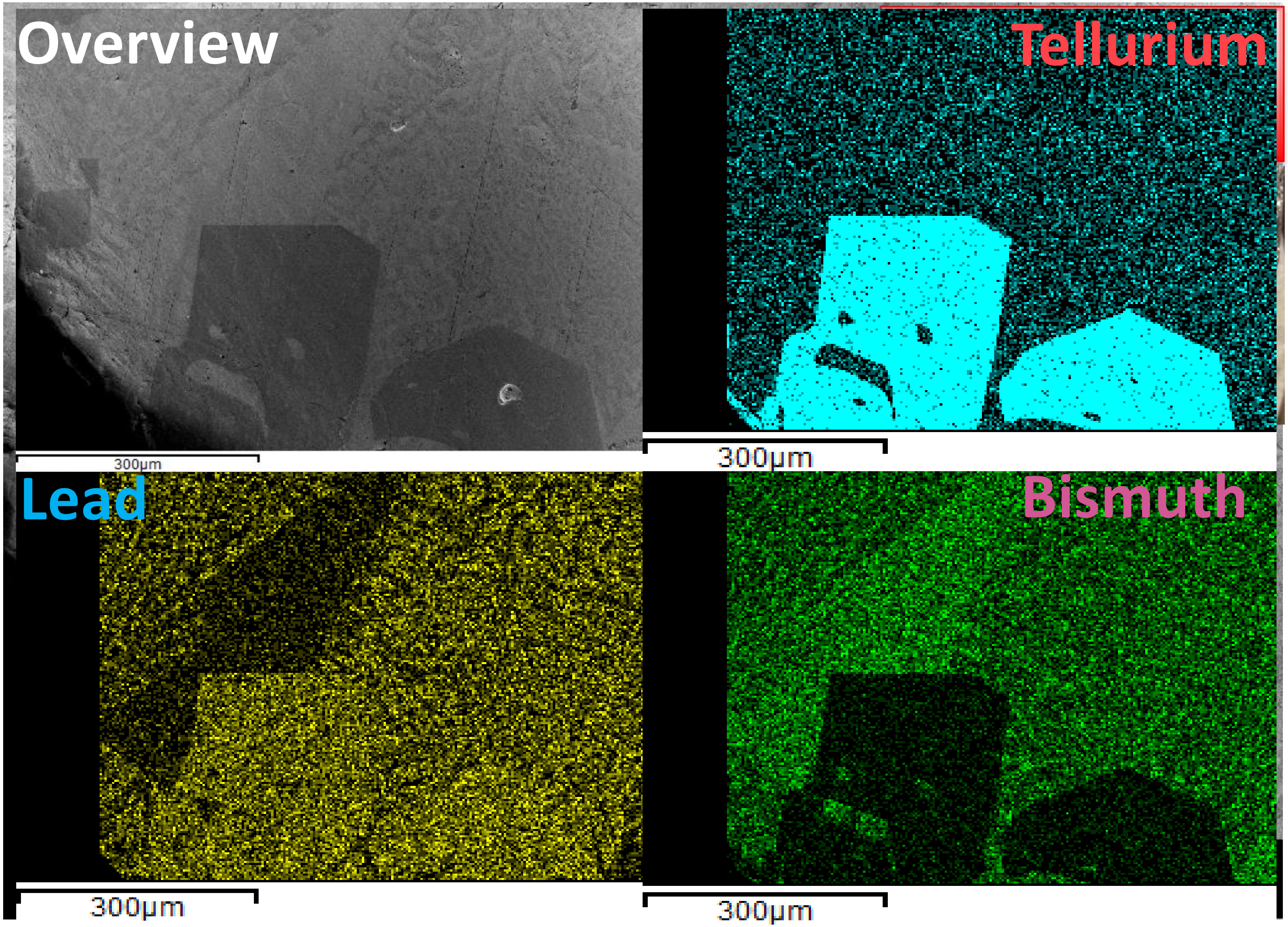


**Fig. 1:** Polished surface of the sample processed at 1100 K and slowly cooled to room temperature. SEM-Mag.: 149X, Size of green bar: **100 µm**.

# Sample preparation for I-131

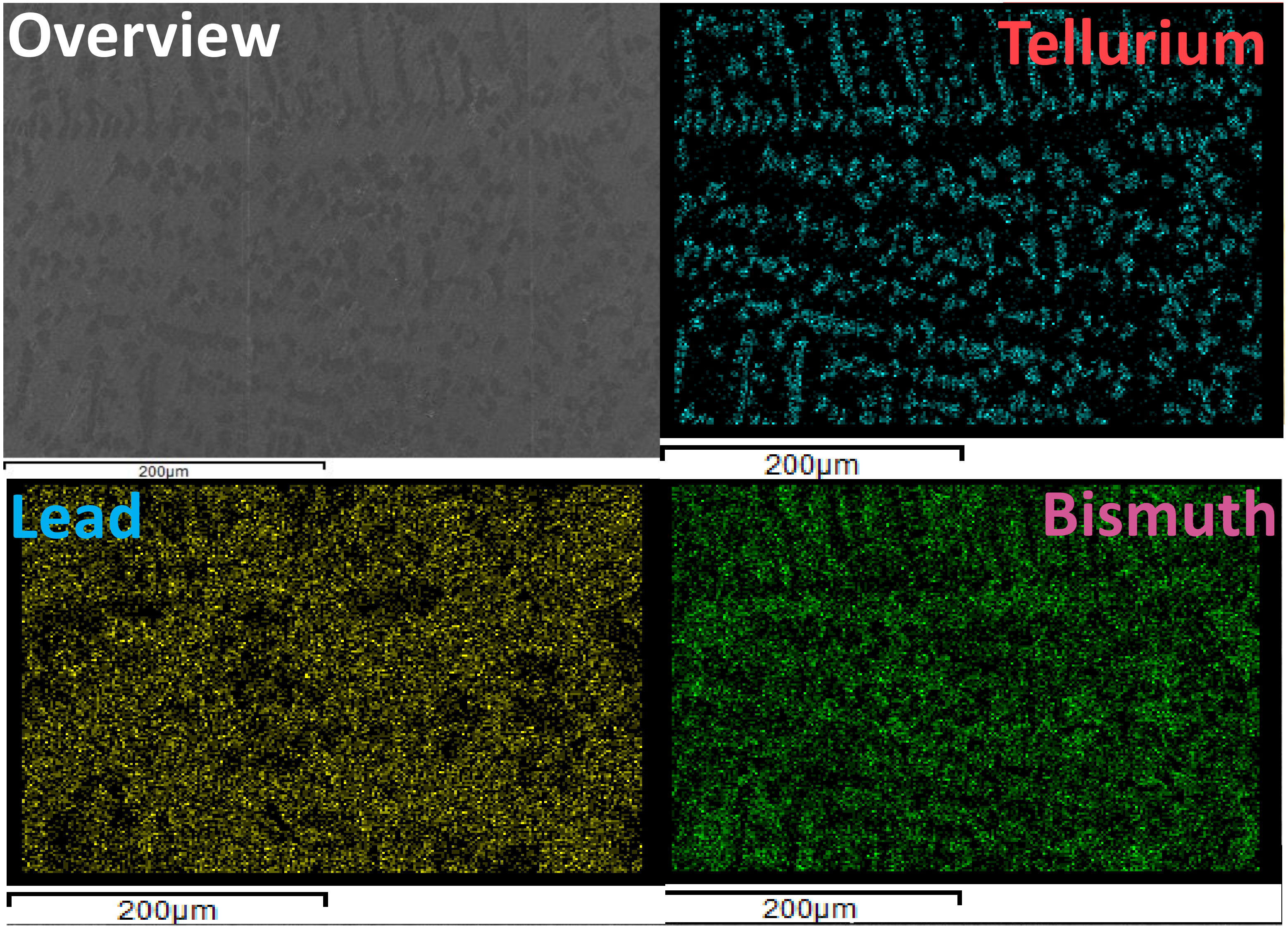


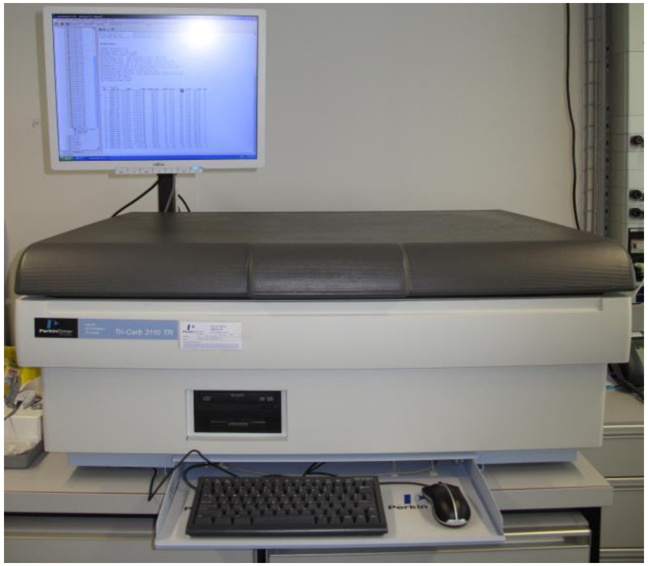
**Fig. 2:** Polished surface of the sample processed at 1100 K and rapid solidified.
SEM-Mag.: 157X, Size of green bar: **100 µm**.

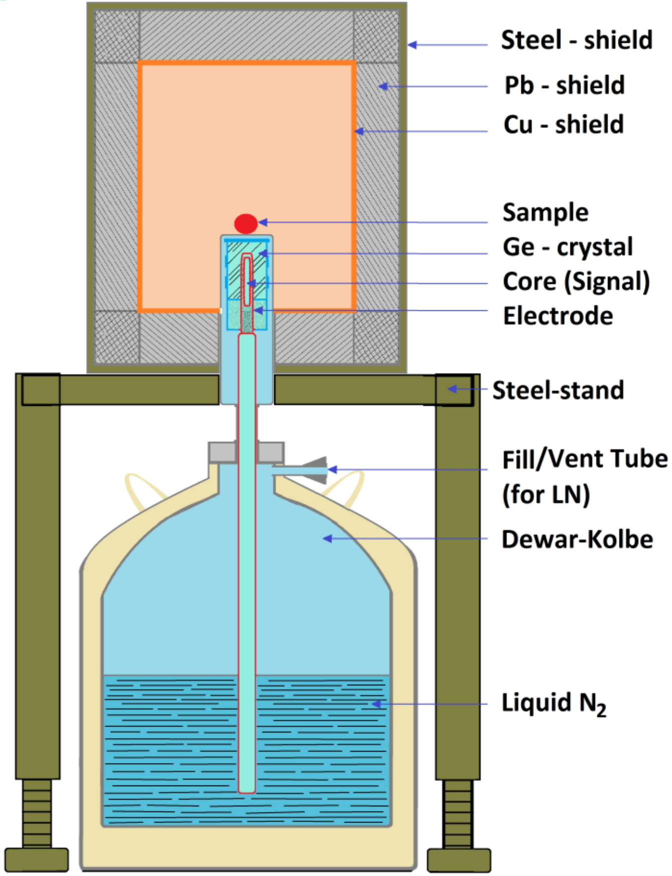
# Liquid scintillation counting (LSC) & γ-measurements uncertainty

## γ-measurements uncertainty (Case: $^{134}$Cs/$^{131}$I):

- Sample positioning uncertainty
- Uncertainty of efficiency
  - uncertainty of calibaration source activity
  - uncertainty of positioning of calibration source
- Counting statistics

Assumed: **10%**





## LSC-uncertainty (Case: $^{210}$Po):

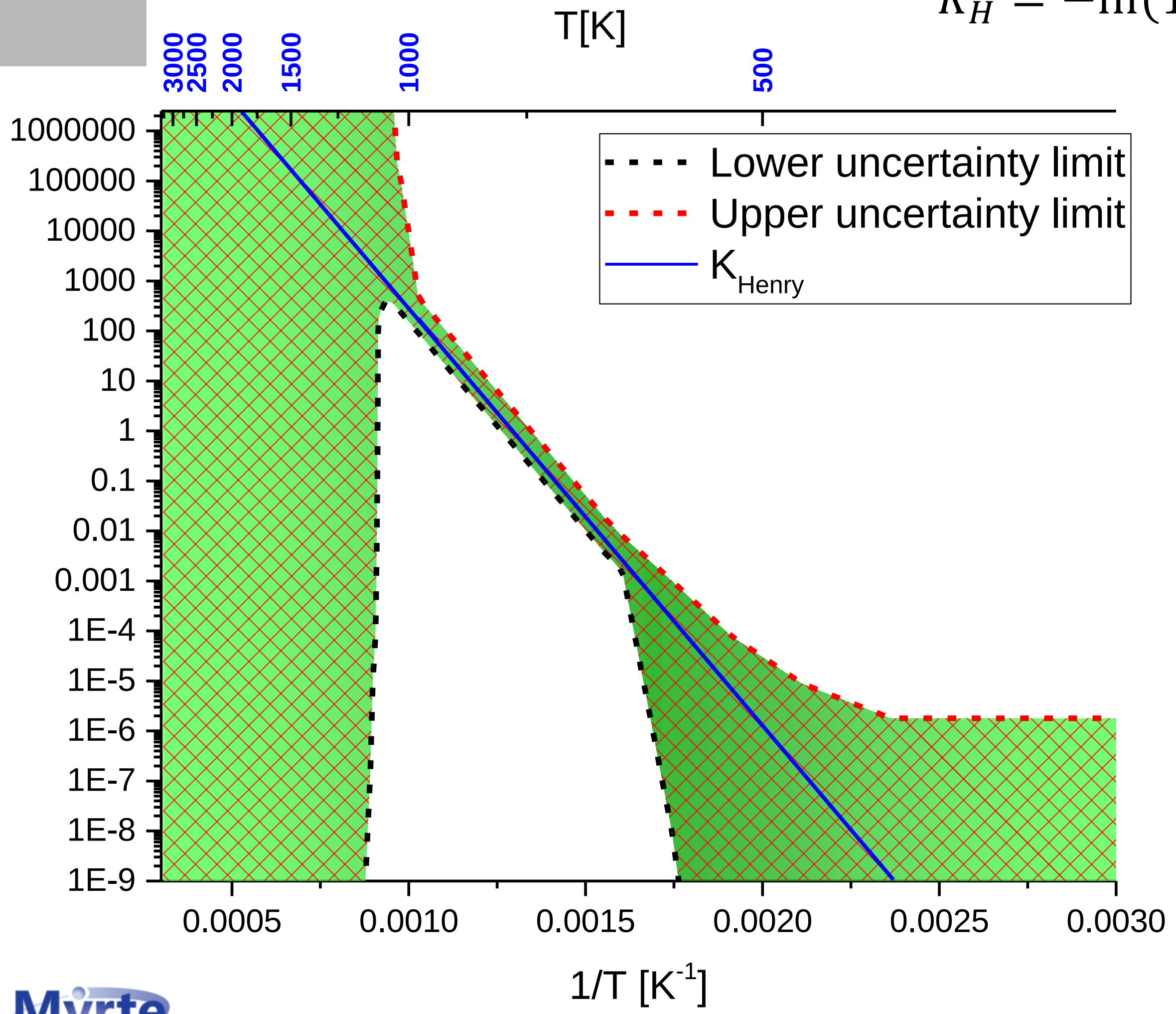
- No sample positioning uncertainty
- Efficiency (for α): **ca. 100%**

# Practical considerations & Uncertainties

Two cases[11]:

$$K_H = -\ln\left(\frac{A_{remaining}}{A_{before}}\right) m_{LBE} RT/(M_{LBE}\,\dot{V}t)$$

$$K_H = -\ln\left(1-\frac{A_{evap}}{A_{before}}\right) m_{LBE} RT/(M_{LBE}\,\dot{V}t)$$



High T, experiments with long duration

$A_{remaining}$ → 0

$A_{evap} / A_{before}$ → 1

Low T, experiments with short duration

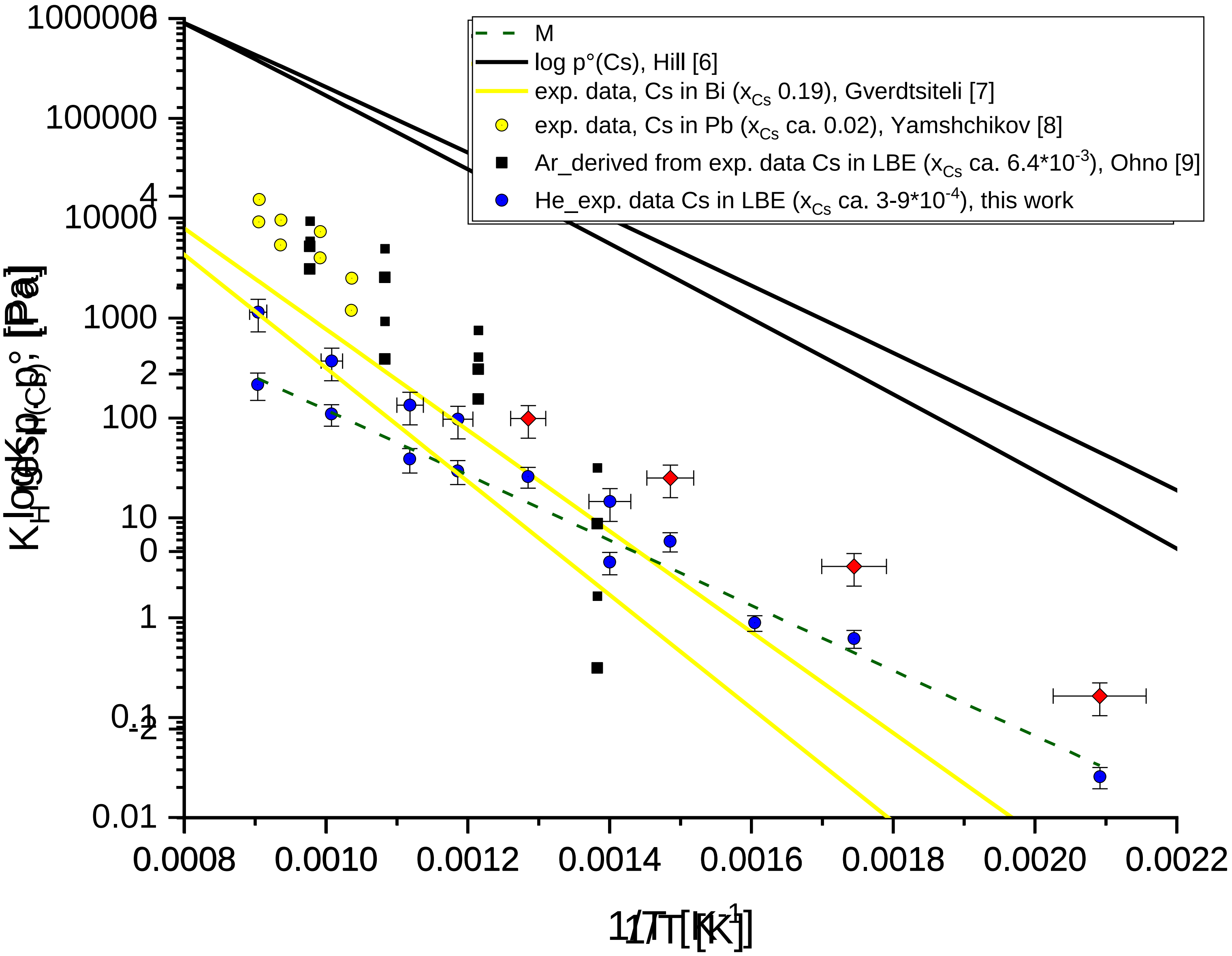
$A_{remaining} / A_{before}$ → 1

$A_{evap}$ → 0

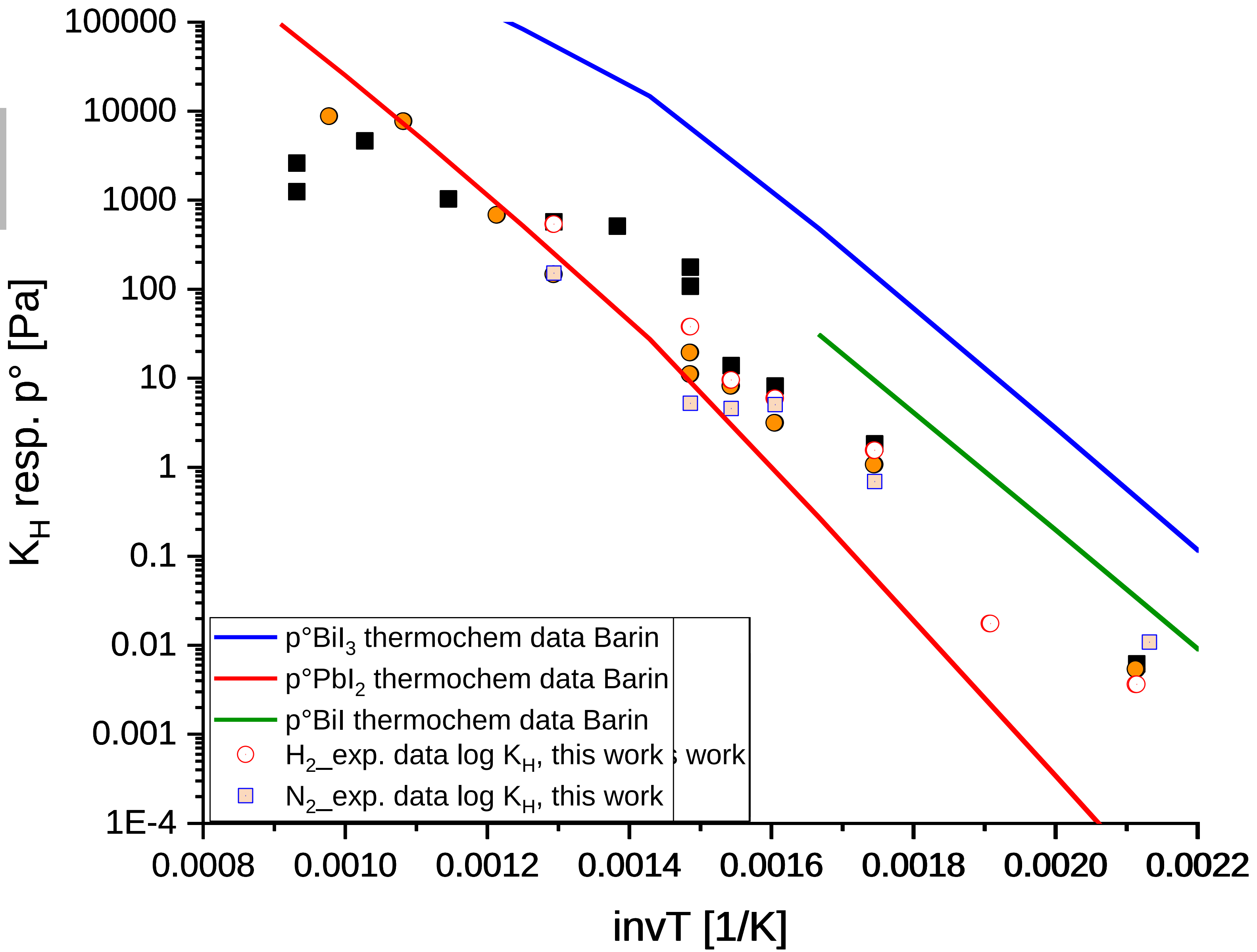
Limits of determination of $K_H$ are caused by limit of quantification (A → 0)

or by the precision the ratios $A_{evap}/A_{before}$ and $A_{remaining}/A_{before}$ can be determined

# Compared with another exp. and lit. Results



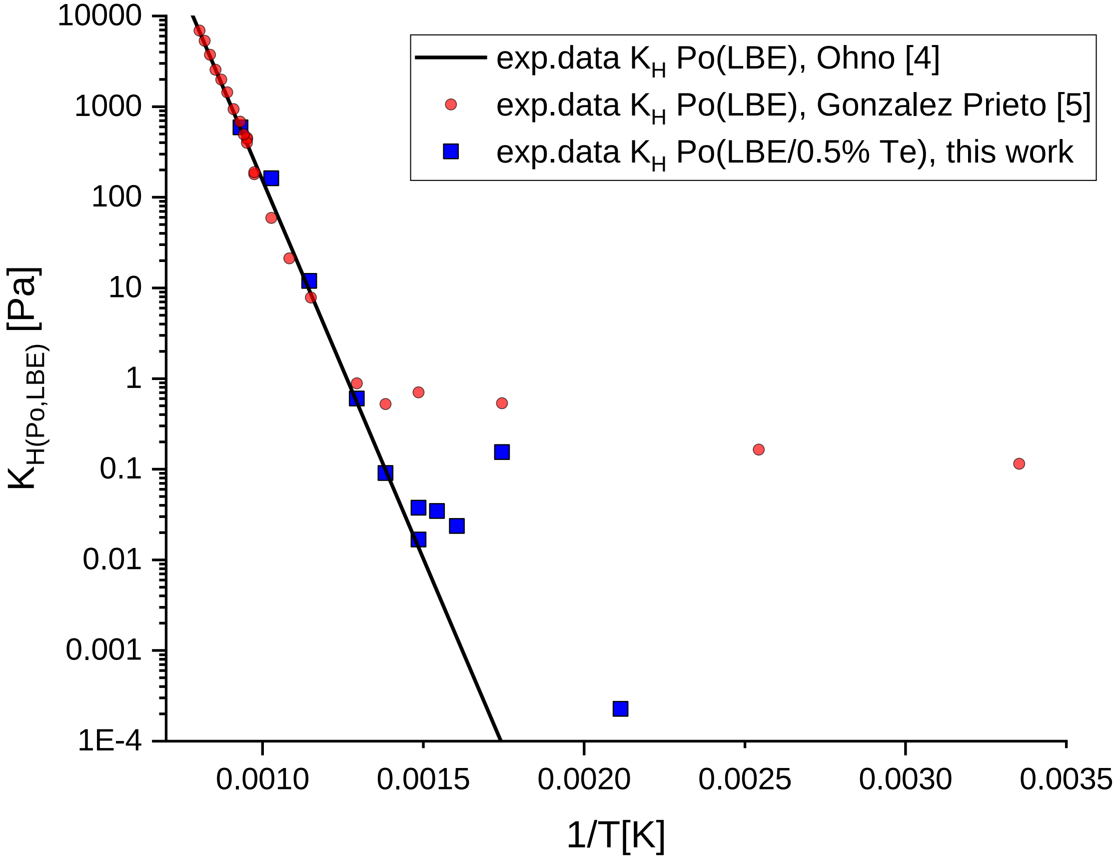
# Results for I-131 compared with lit. data



# Po-transpiration experiments

**Source for the moment:** Po from Te- and Cs-containing LBE

In Cs-containing LBE we don’t find Po anymore after dilution with inactive LBE: Po seems to be bound to Cs and precipitate on the walls of the dilution-vessel.



Results for Po evaporation from LBE(0.5%Te) used for iodine experiments Po-210 measured by LSC

**Possible reasons for differences at low T:**

- LBE was reduced with Ta-metal at 1000°C before doping with Te
- High purity gas
- Lower $O_2$ concentration in LBE and gas
- Less moisture in gas

# Summary

- ✓ Experimental facility
- ✓ Sample preparation is improved
- ✓ Assessment of the limits for reliable measurements and uncertainties.
- ✓ Results are reasonable when compared to existing literature and experimental data.
- ✓ Log $K_H$ of $^{131}$I & $^{134}$Cs much lower that the vapor pressure of the pure elements.
- ✓ Log $K_H$ show linear behavior when plotted vs. the inverse T, as expected.
- ✓ Deviations from linearity for $^{131}$I – beyond the limits of reliable measurements.
- ✓ Using the results of $^{131}$I & $^{134}$Cs the simultaneous release of $^{210}$Po was investigated.

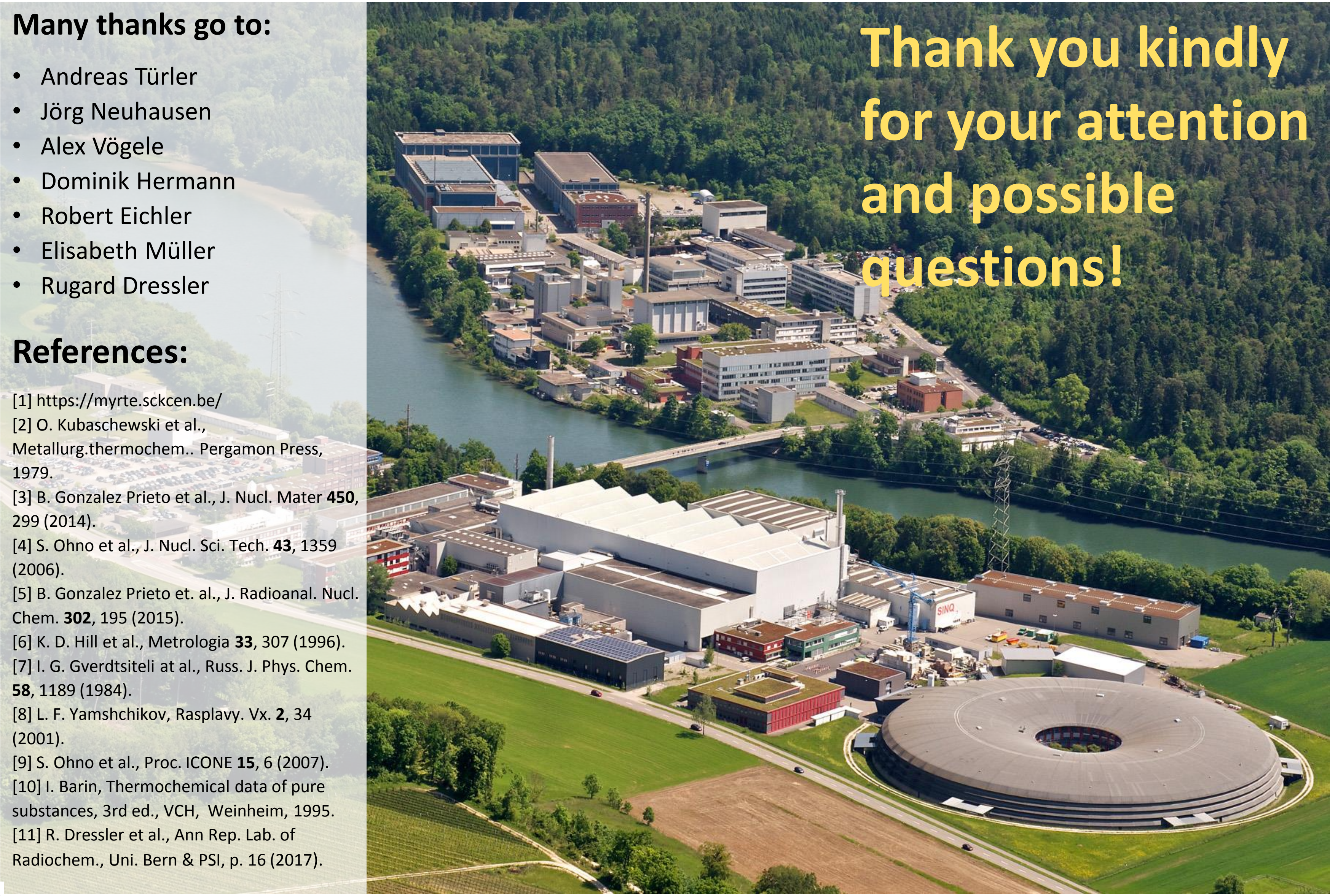
# Outlook

- Verify saturation of gas (flow-dependent experiments, different $m_{sample}$)
- Check concentration dependency of Cs evaporation behaviour
- Study different carrier gases (Cs)
- Dedicated Po-evaporation studies under control of $c(O)_{LBE}$
- Study simultaneous release of Po, Tl, Hg and Te

*We do not inherit* the *Earth* from *our ancestors*,
*we are borrowing* it from *our* children
(*Antoine* de *Saint Exupery*).

**300 000 MTHM**

What is eco-friendly is economical - let's make it nature like back!



## Many thanks go to:

- Andreas Türler
- Jörg Neuhausen
- Alex Vögele
- Dominik Hermann
- Robert Eichler
- Elisabeth Müller
- Rugard Dressler

## References:

[1] https://myrte.sckcen.be/

[2] O. Kubaschewski et al., Metallurg.thermochem.. Pergamon Press, 1979.

[3] B. Gonzalez Prieto et al., J. Nucl. Mater **450**, 299 (2014).

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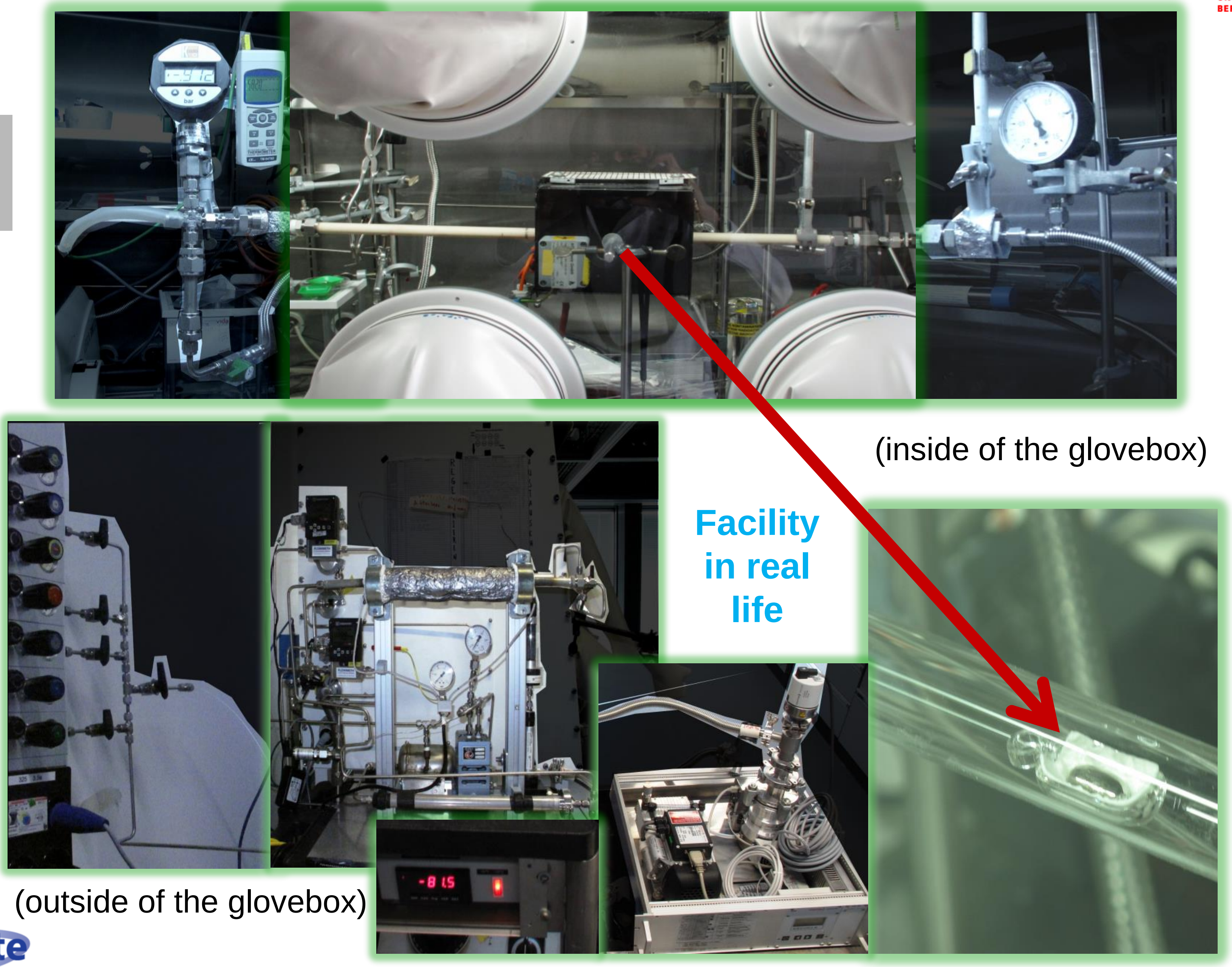
[10] I. Barin, Thermochemical data of pure substances, 3rd ed., VCH, Weinheim, 1995.

[11] R. Dressler et al., Ann Rep. Lab. of Radiochem., Uni. Bern & PSI, p. 16 (2017).

**Thank you kindly for your attention and possible questions!**

# Transpiration setup

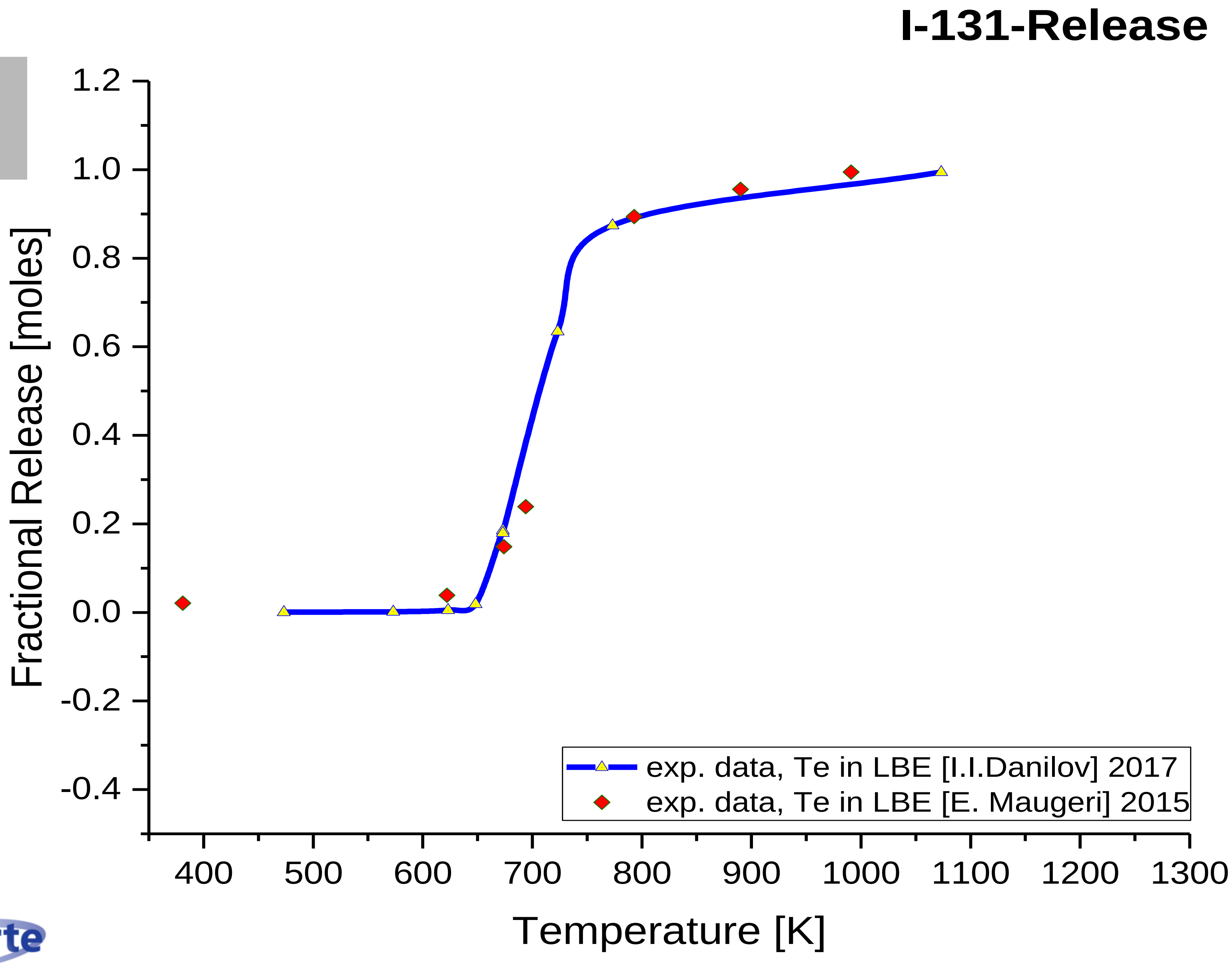


(inside of the glovebox)

**Facility in real life**

(outside of the glovebox)

# Release of I-131 in Temperature profile



# SEM & EDX analysis of the Cs-dopped LBE

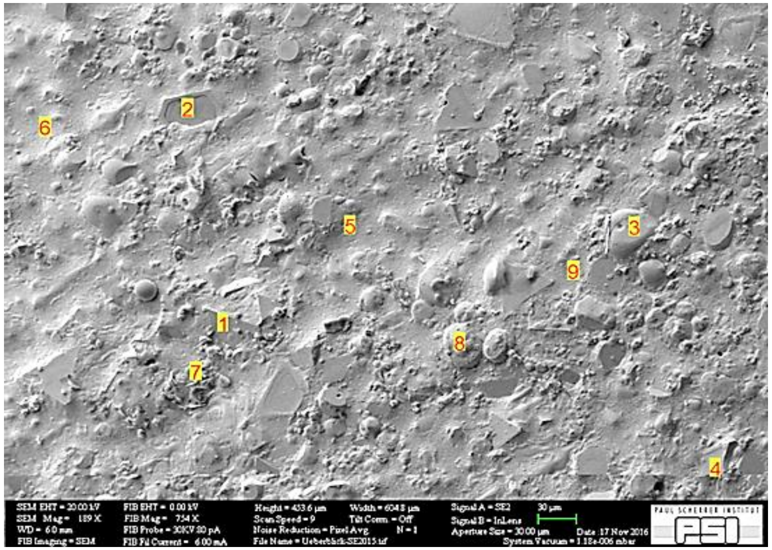


**Fig. 1:** Polished surface of the sample processed at 300°C and slowly cooled to room temperature. SEM-Mag.: 189X, Size of green bar: **30 µm**.

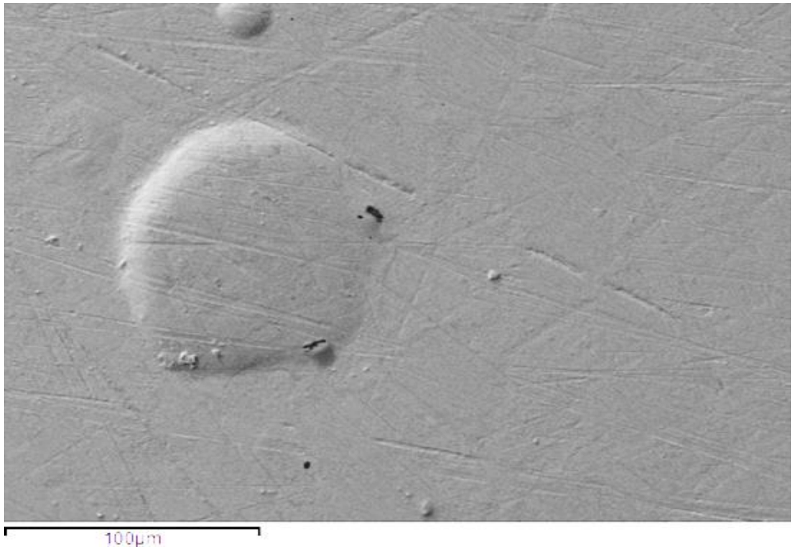


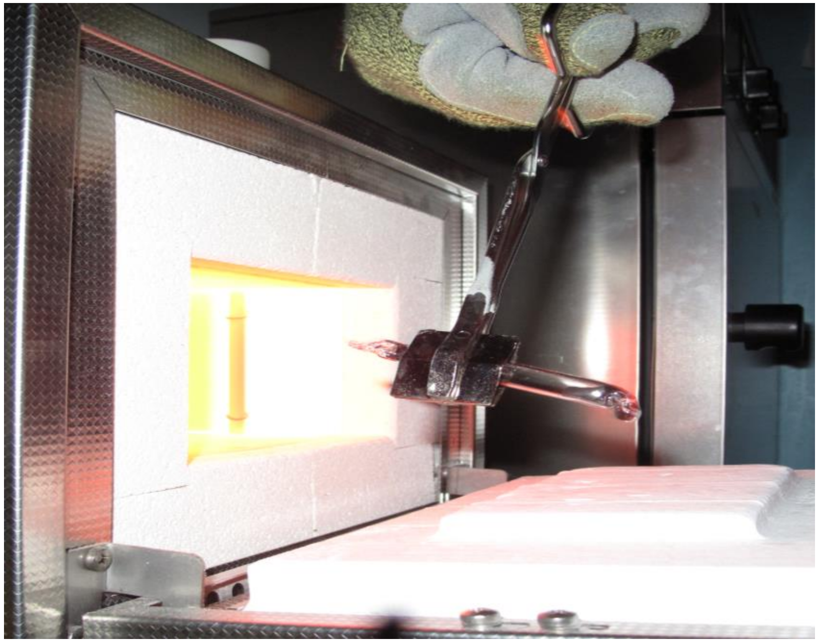
**Fig. 2:** Plateau observed on the surface of a sample processed at 300°C after grinding and polishing. In the region of the plateau increased Cs and Bi concentrations were detected. **100 µm.**

| Position | Cs, Atom% | Pb, Atom% | Bi, Atom% |
|---|---|---|---|
| **1** | 25.75 | 0.21 | 74.04 |
| **2** | 49.14 | -2.51 | 53.37 |
| **3** | 29.27 | -0.08 | 70.81 |
| **4** | 30.04 | 0.28 | 69.68 |
| **5** | 0.28 | 1.47 | 98.26 |
| **6** | 0.16 | 59.36 | 40.47 |
| **7** | 1.34 | 96.64 | 2.02 |
| **8** | 29.64 | 6.06 | 64.30 |
| **9** | 0.55 | 62.15 | 37.31 |

# Dilution and Homogenization for Cs-134

## Homogenization at 573 K without shaking

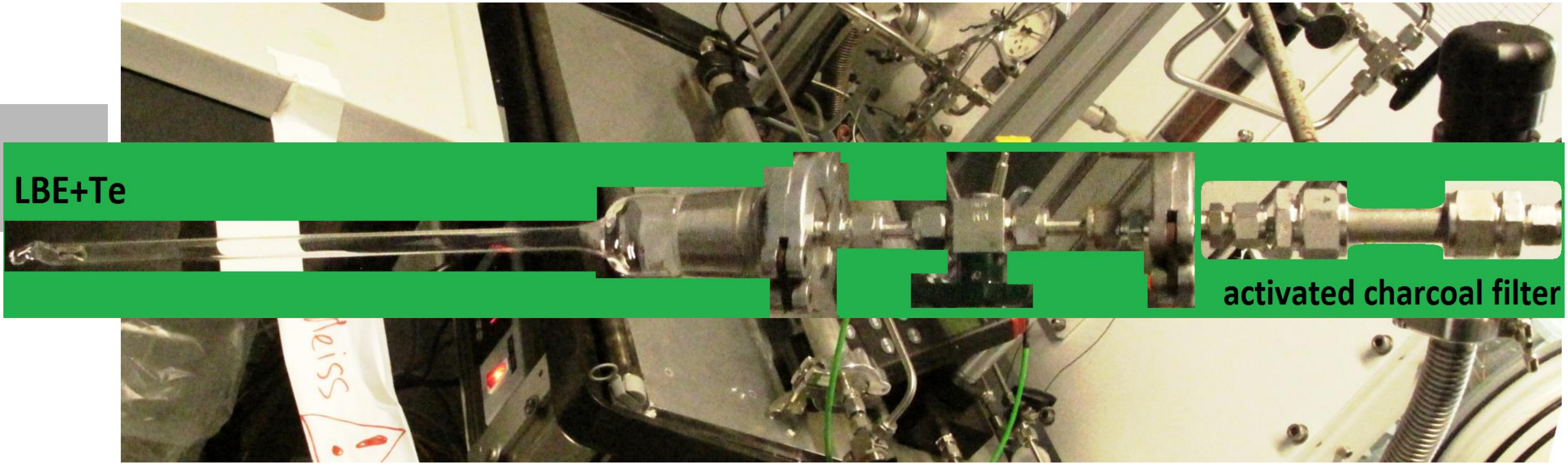
| Part | Weight, g | Activity, Bq/g |
|---|---|---|
| **1** | 0.3975 | 34 |
| **2** | 1.6947 | 16 |
| **3** | 0.291 | 14 |
| **4** | 3.2259 | 4000 |
| **5** | 0.3667 | 22000 |
| **Total** | 5.9758 | |



## Homogenization at 623 K with shaking

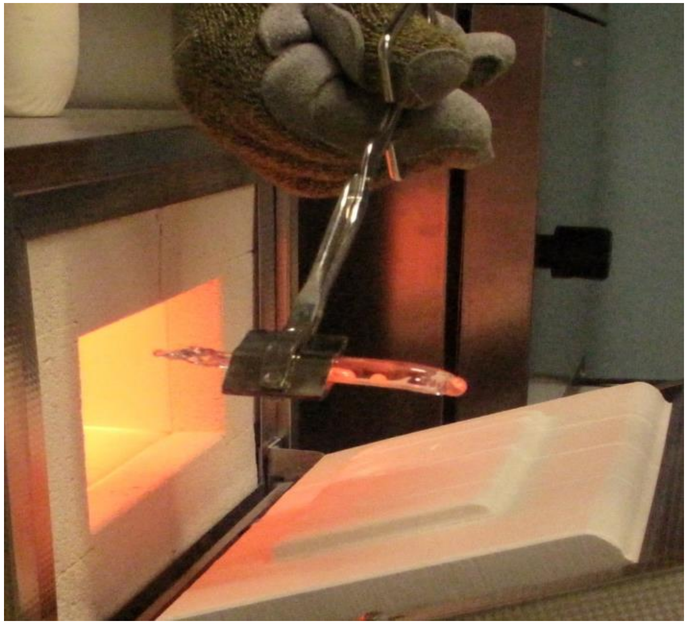
| Part | Weight, g | Activity, Bq/g |
|---|---|---|
| **1** | 0.1576 | 16.8 |
| **2** | 2.1852 | 14.6 |
| **3** | 0.3352 | 14.4 |
| **4** | 1.7689 | 14.3 |
| **5** | 0.175 | 14.6 |
| **6** | 1.2883 | 14.0 |
| **7** | 0.063 | 15.4 |
| **Total** | 5.9732 | |

# Homogenization of irradiated Te with LBE



## Homogenization at 1100 K with shaking

| Part | Weight, g | Activity, KBq/g |
|---|---|---|
| 1 | 0.24945 | 25.2 |
| 2 | 0.56405 | 21.6 |
| 3 | 0.39388 | 21.4 |
| 4 | 0.65622 | 20.3 |
| 5 | 0.60215 | 22.05 |
| 6 | 0.66812 | 18.9 |
| 7 | 0.85131 | 21.5 |
| Total | 3.98518 | |

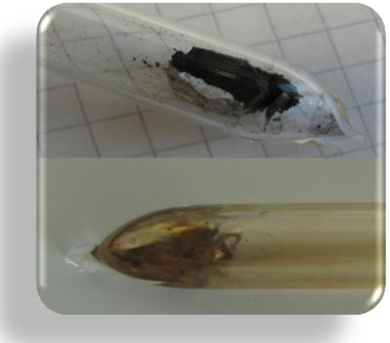


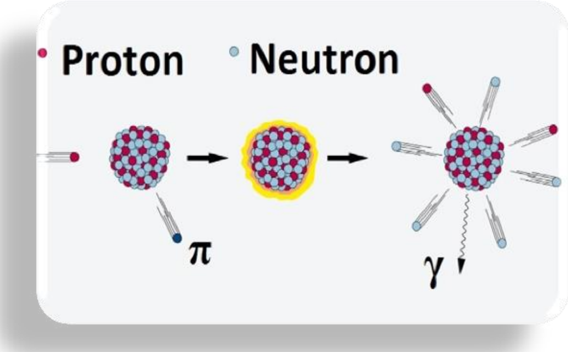
# Yield & Loss behaviour during sample preparation

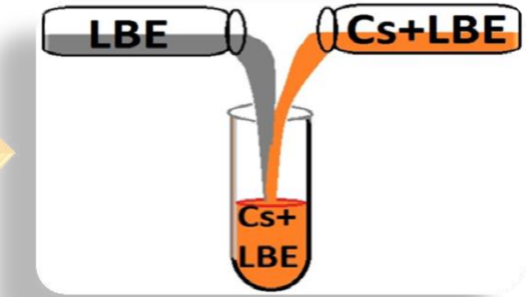
## Smelting

## Irradiation

## Dilution







**Loss: up to 30%**

**CsCl used as standard:**

**75% of expected Activity**
**(neutron flux lower than nominal)**

**Loss: 60 - 75%**

Cs obviously reacts with surface of the $SiO_2$ ampoules (hard to avoid)
There is still enough Cs in the samples to perform experiments

# Activity balance for low&high temperature experiments

## Percentage of starting activity

**Hot Zone**

Sample: 71-99%

Ta-Boat: 3.6-11%

**Condensation zone**

Tube surface:

1-25%

**Filter**

0-0.3%

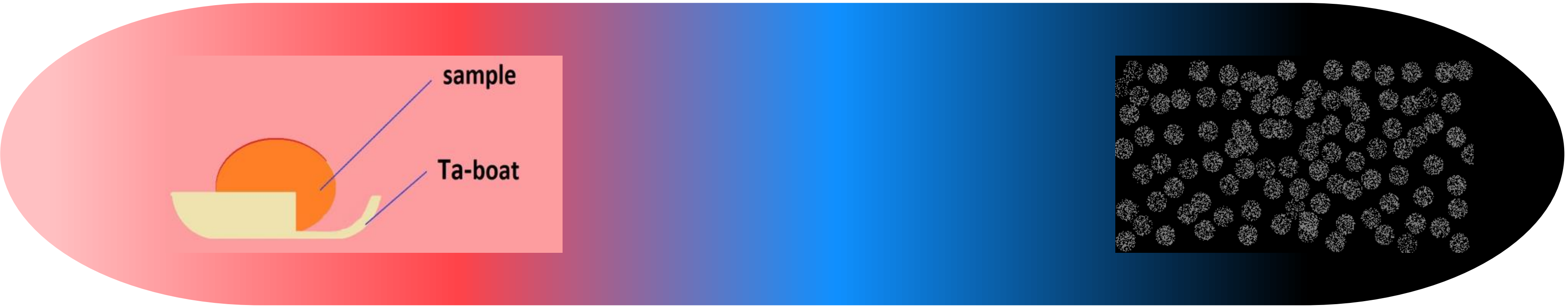
Low Temperatures: 200-400°C

High Temperatures: 500-800°C

We able to find:

∑>95% activity

Evaporation Condensation Filtering



Cs: different boat materials

Ta metal works best in He (low contamination)

# Activity balance for low temperature experiments

## Percentage of starting activity

### Hot Zone

- Sample: 1-10%
- $SiO_2$-microfiber: 0.1%
- Boat: 0.005%

### Condensation zone

- Tube surface: 83-92.5%
- $SiO_2$-wool: 0.5-2%

### Filter / Trapping

- KOH: 3.5 %
- ACF: 1 %

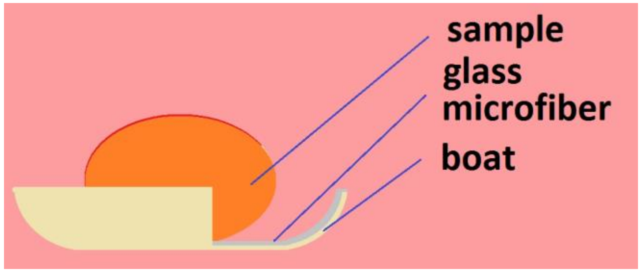
**Low Temperatures: 200-350°C**

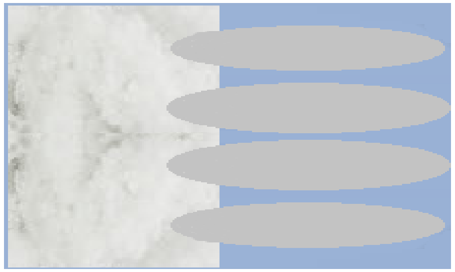
**High Temperatures: 400-800°C**

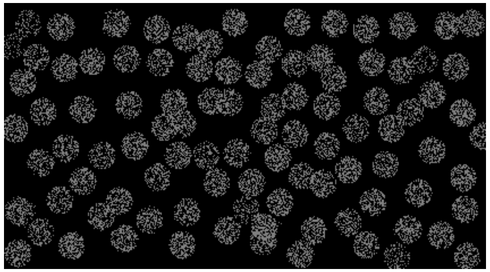
**We able to find:**

**∑>95% activity**

Evaporation Condensation / Trapping Filtering



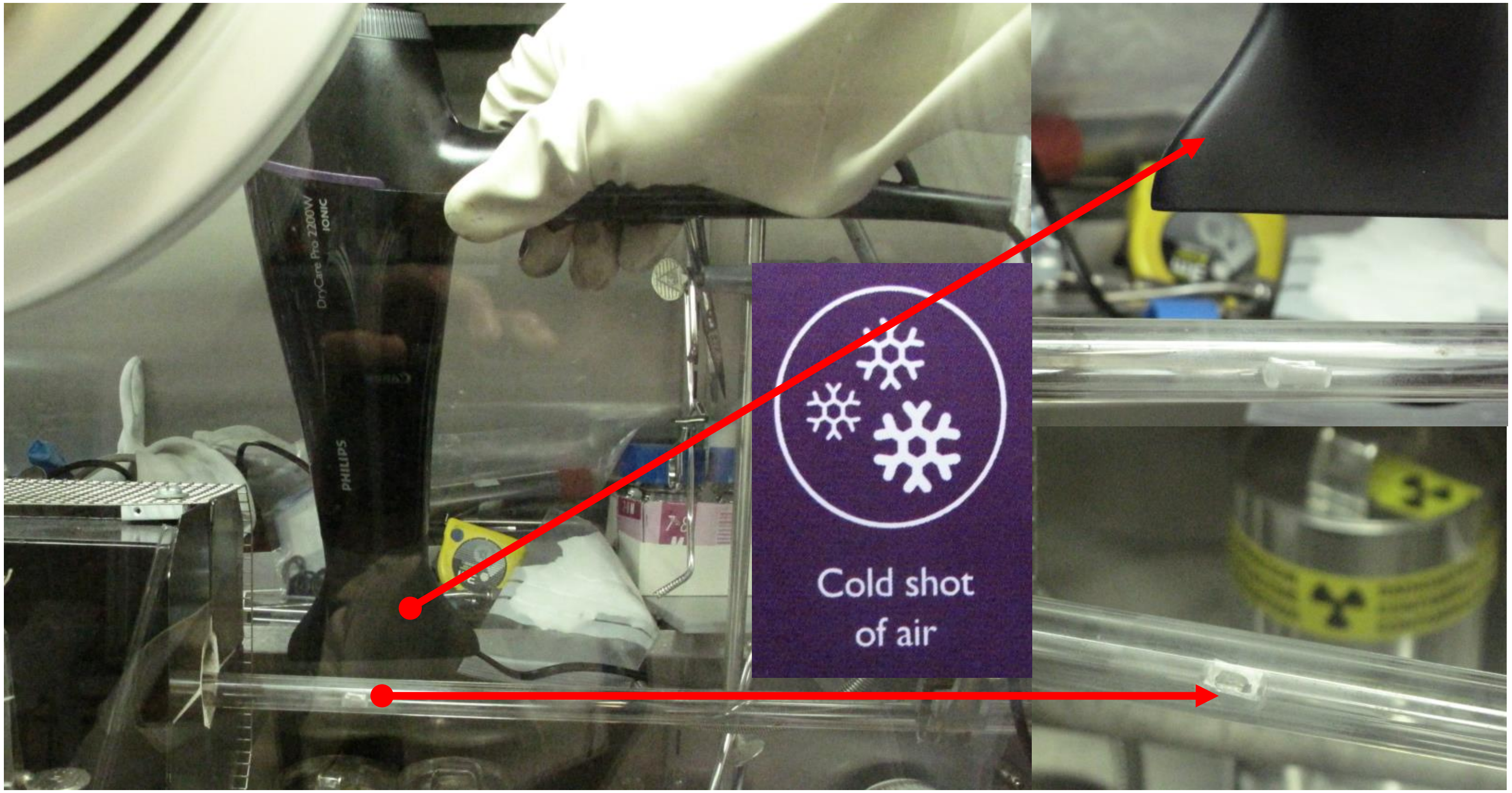




# Cooling phenomena of I-131 samples

At normal cooling:

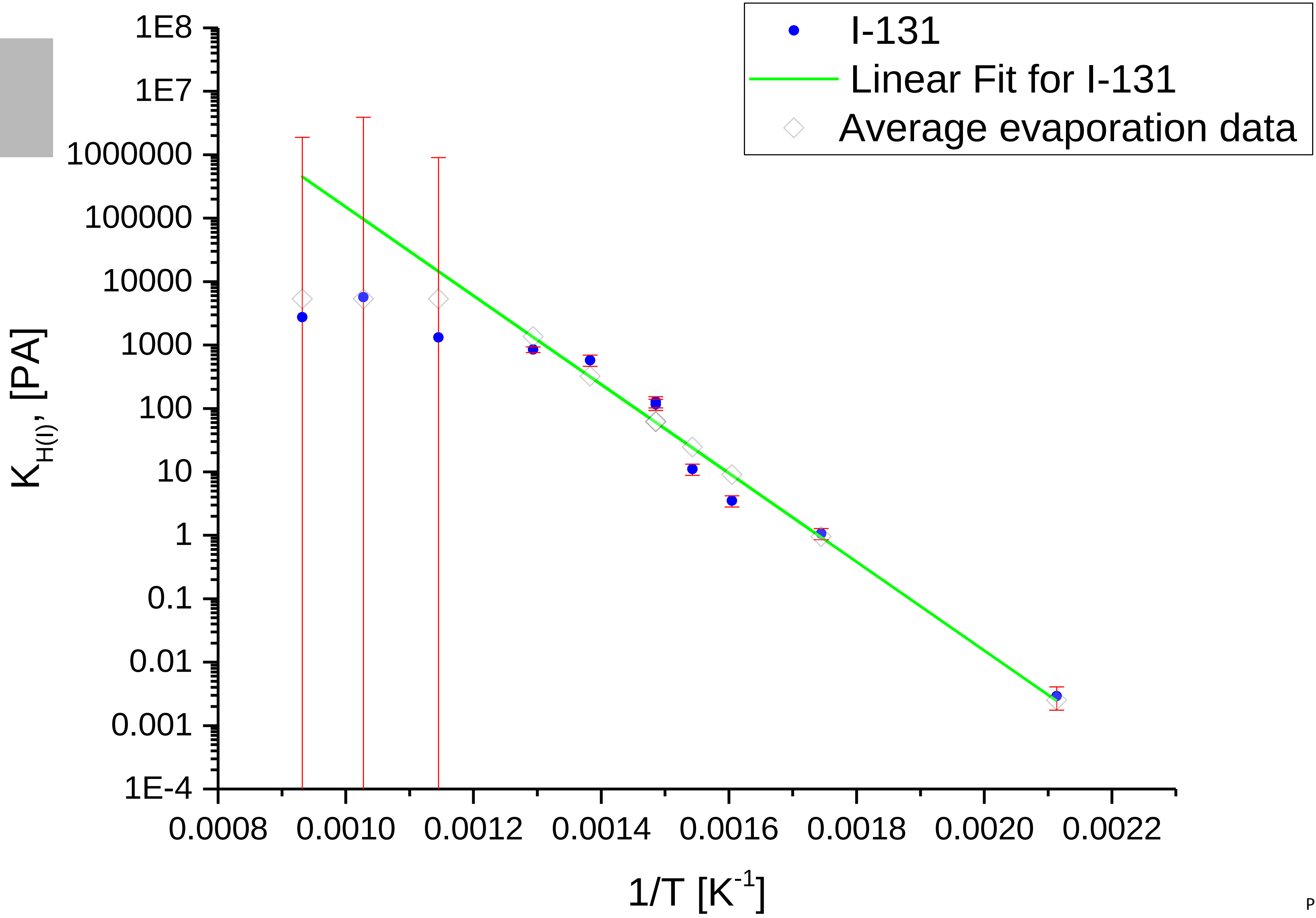
- **Twice the activity at top compared to bottom part of the sample**



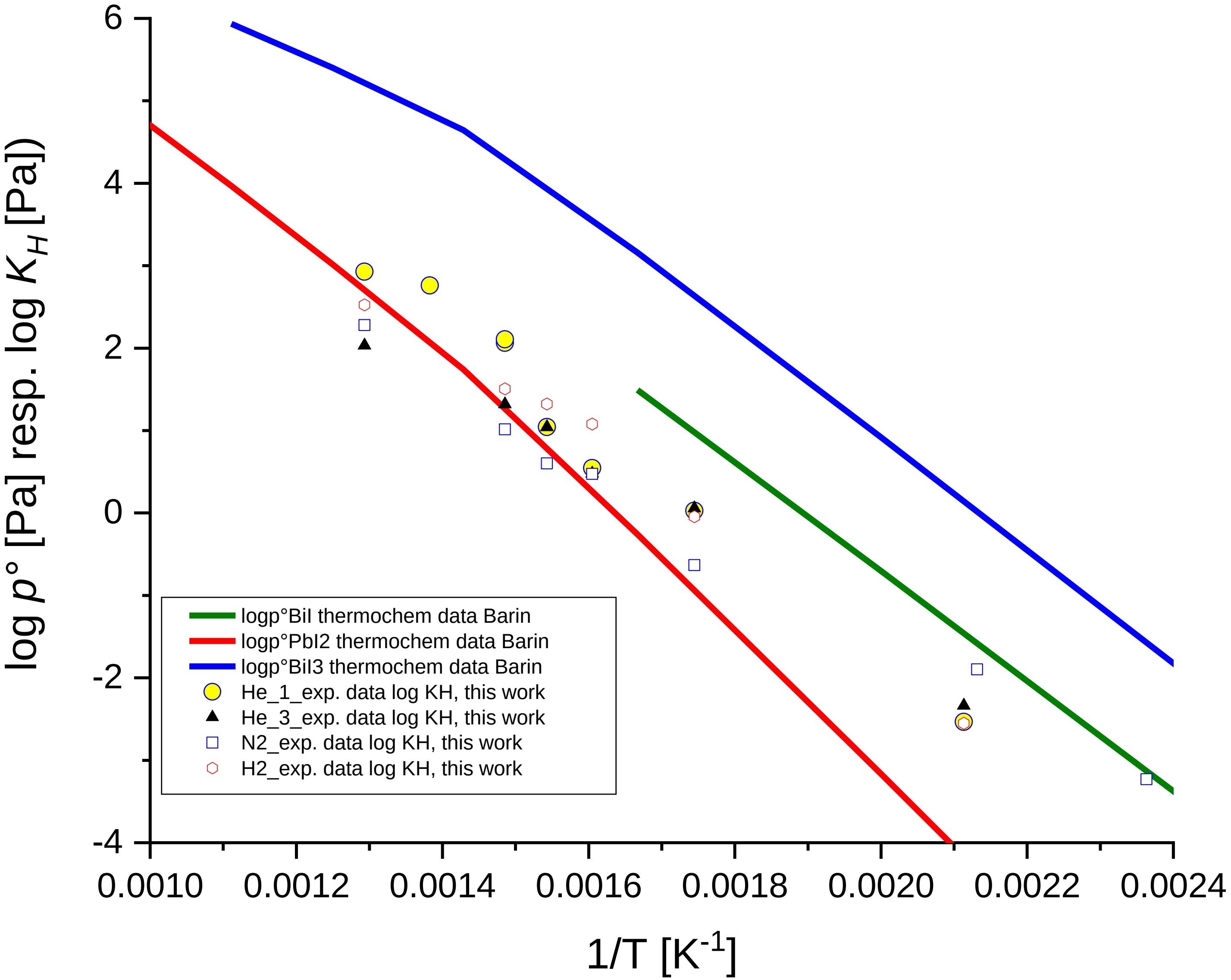
Forced cooling:

- **1-5% difference in activity between top and bottom part of the sample**

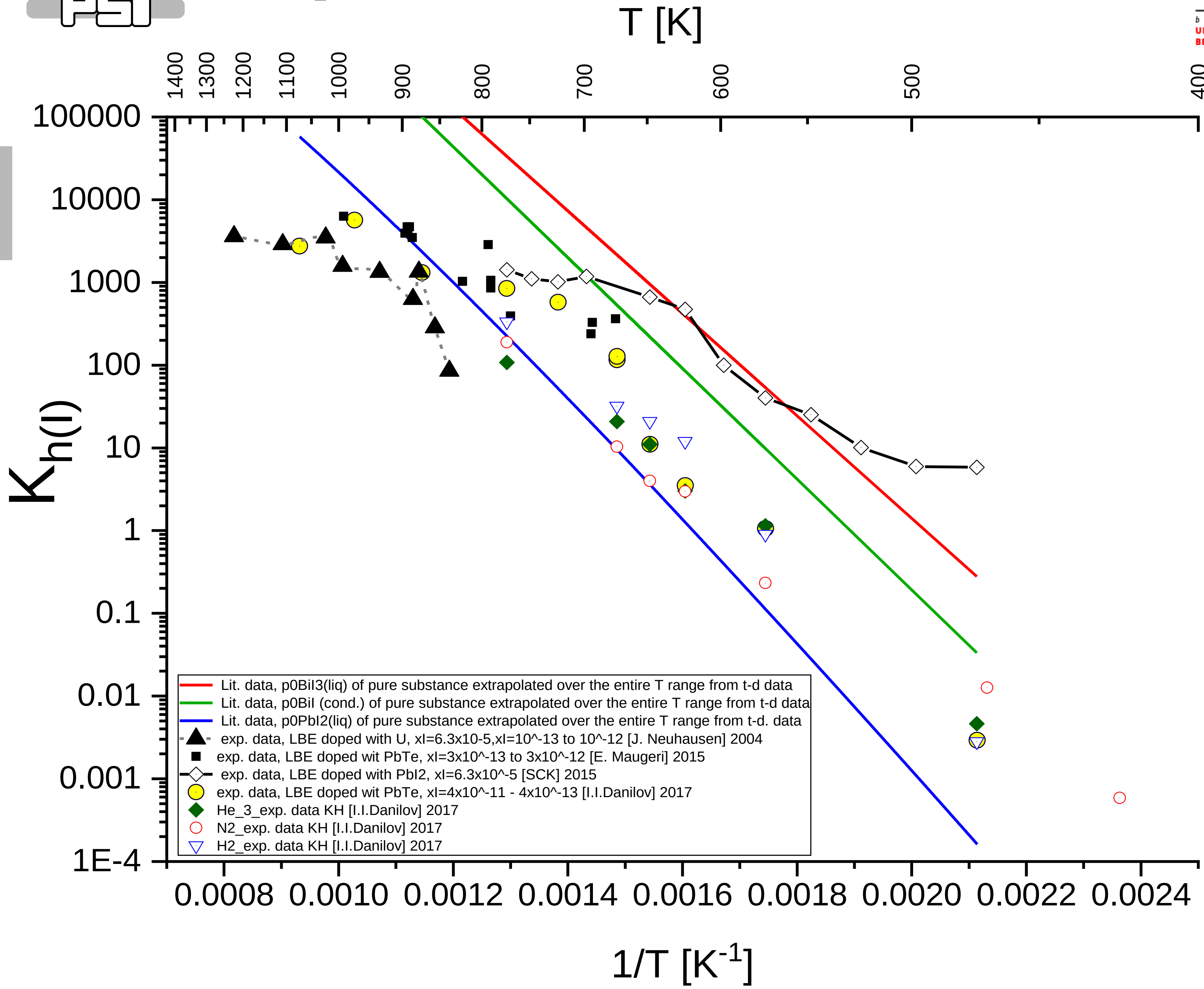
# Results for I-131 compared with simulation data



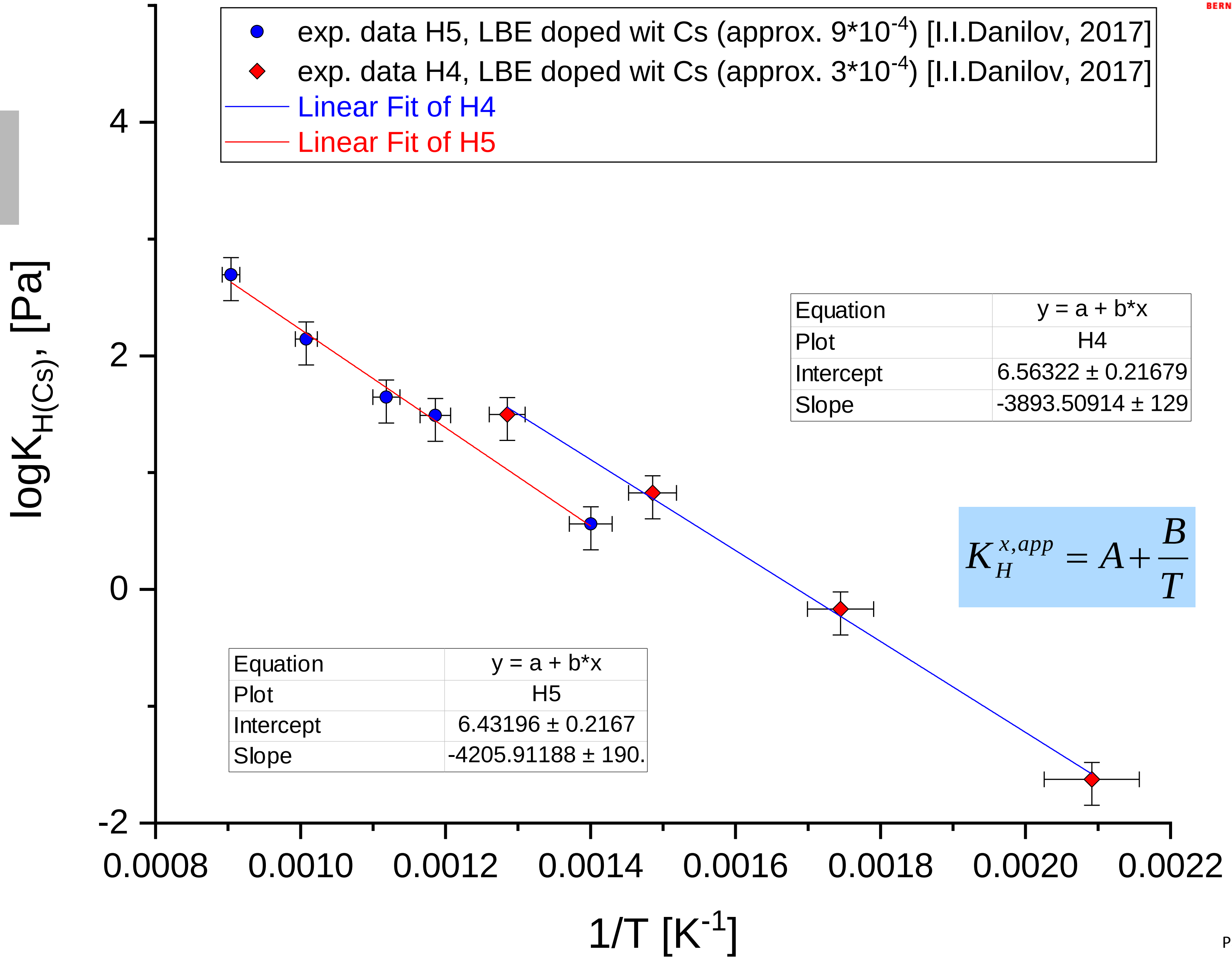
# Results for I-131 compared with literature data



# All experimental and literature data for I-131



# Experimental results for Cs-134



| Equation | y = a + b*x |
|---|---|
| Plot | H4 |
| Intercept | 6.56322 ± 0.21679 |
| Slope | -3893.50914 ± 129 |

| Equation | y = a + b*x |
|---|---|
| Plot | H5 |
| Intercept | 6.43196 ± 0.2167 |
| Slope | -4205.91188 ± 190. |

$$K_H^{x,app} = A + \frac{B}{T}$$

Государственная корпорация «Росатом»

Государственный научный центр РФ – Физико-энергетический институт имени А.И. Лейпунского

# POLONIUM ACTIVITY RELEASE FROM HEAVY LIQUID METAL COOLANT INTO GASEOSUS PHASE

N.I. Gonchar, D.V. Pankratov

# Alpha-active isotopes into HLMC

HLMC containing Pb and Bi form alpha-active isotopes: **Bi-210m, Po-209 и Po-210.** Po-210 ($T_{1/2}$ =138,4 days, $E_{\alpha}$=5,3 MeV) is the most radiotoxic one. Po-210 produces insignificant gamma-radiation and isn't dangerous as an external radiation source. There is no significant radiation danger in normal operation until the primary coolant circuit is pressure-tight. Howerever, when designing the reactor gas system and refueling system polonium radiotoxity and alpha-activity presence in the coolant should be considered.

The most dangerous case of organism exposure is caused by polonium intake into organism through food, water and inhalation. Contact of polonium with skin and mucous tunics is also dangerous.

It should be also taken into account that accidents, accompanied by the first circuit coolant leakage or significant depressurization of the gas system may result in formation of alpha-active aerosols in the air and highly radioactive surface contamination upon their precipitation. For this reason while simulating polonium activity migration and developing staff-protection means there is a need to pay special attention aerosols and gaseous polonium compound – $PoH_2$.

To substantiate radiation safety and forecast the aftermath of such accidents is essential to develop a model of polonium activity migration through the first circuit in normal operation and under conditions resulting in accidents. The model must be tested by experimental date. Polonium activity release from HLMC into gas is main element of this model.

# Evaporation velocity of polonium activity

- Thermal evaporation velocity of i-isotope activity (Bq/c) could define using Langmuir equation and Raoult law

$$Q_i^{evp} = 4{,}38 \cdot 10^{-3} a_i M_0 S\beta \cdot \sum_j \frac{P_{ij}^{sat}(T)\xi_j}{\sqrt{M_{ij}T}}$$

- Polonium can have some chemical states into HLMC: Po, $Po_2$, PbPo, BiPo и $PoO_2$ . If polonium chemical states distribution is unknown should use polonium thermodynamic activity coefficient into HLMC

$$p_i^{eff} = p_{\mathrm{i}}^{\mathrm{sat}} \cdot \gamma \cdot \mathrm{X}$$

# Experimental study of polonium release from irradiated HLMC samples. IPPE, 1995

- The samples: lead, lead-bismuth and lead-lithium eutectics
- Temperature : 300, 500 и 800 $^{o}$C
- Medium over the sample: vacuum (0,1÷1 Pa) or argon (1,33·10$^{4}$ и 8,65·10$^{4}$ Pa)
- The time of exposure: 8 hours
- Polonium activity quantity (Bq) evaporated from the sample was measuring
- Initiale date: mass and activity of the sample, evaporation surfice area, measured quantity of evaporated activity. Polonium atomic quota was (2,7÷3,7)·10$^{-11}$ into Pb-samples and ~ 2,7·10$^{-8}$ in LBE-samples

# Estimate of effective evaporation velocity and thermodynamic activity coefficient

- An amount of Po-210 activity $A_{evp}$ evaporated into vacuum during exposure $t_{exp}$ was measured. Effective evaporation velocity and mass flux were calculated as

$$Q^{eff}_{Po-210} = A_{evp} / t_{exp} \qquad G_{Po-210} = \frac{Q^{eff}_{Po-210}}{\lambda \cdot S} \cdot \frac{10^{-3} \cdot M_{Po-M}}{N_A}$$

- Po-210 effective pressure over smelting

$$P^{eff}_{Po-210} = \frac{G_{Po\text{-}210}}{4{,}38 \cdot 10^{-3} \sqrt{M_{Po-M} / T}}$$

- And in another terms $p^{eff}_{Po}(T) = p^{sat}_{Po}(T) \cdot \gamma_{Po/M}(T) \cdot X_{Po}$

# Polonium/HLMC thermodynamic activity coefficients derived from IPPE experimental date

- Evaporation into argon atmosphere

$$Q^{k}_{эфф} = Q_k / \beta_k \qquad \beta = \nu_k / \nu_{vac} \qquad \nu_k = Q_k / A^{исх}_k$$

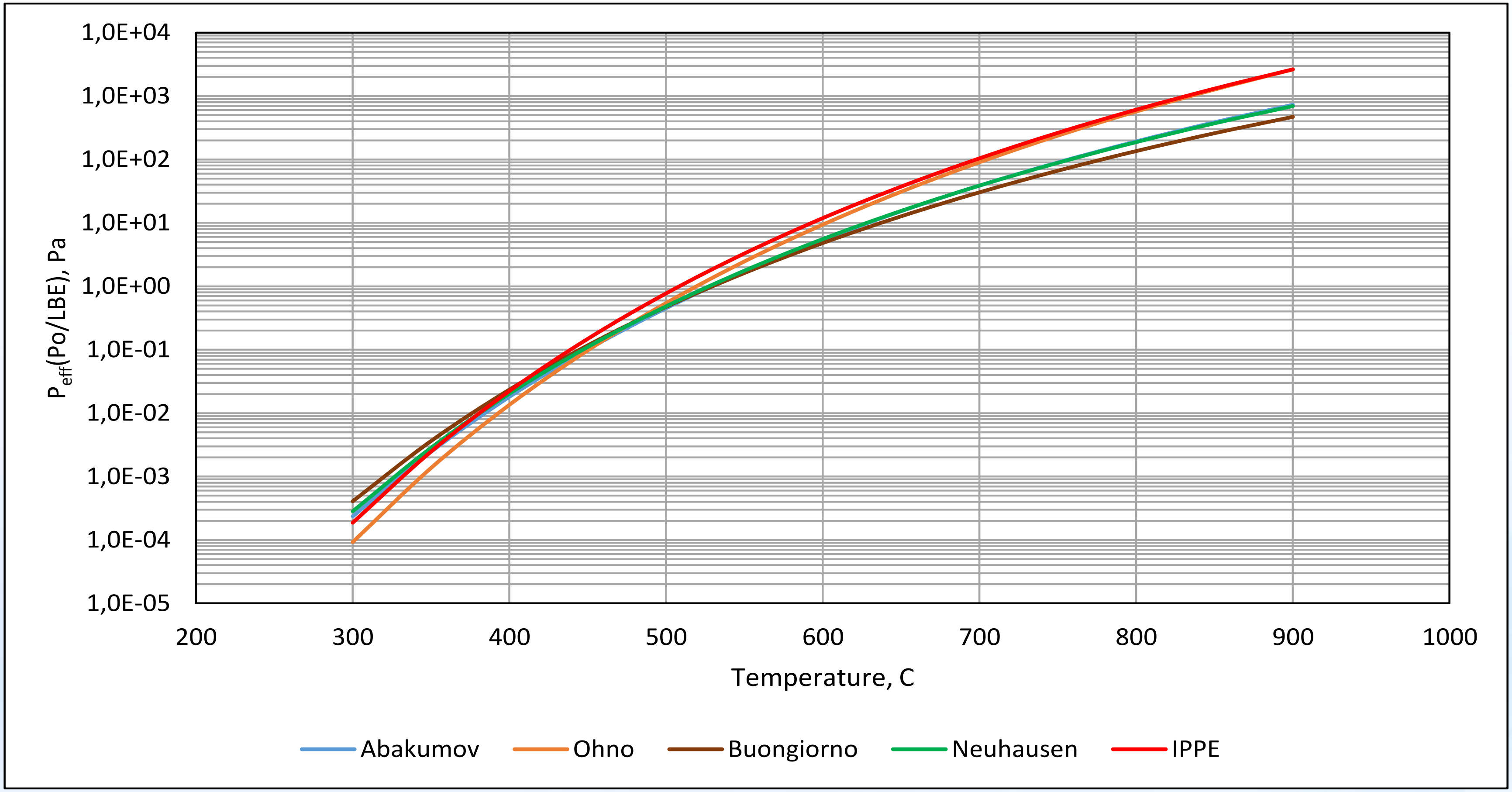
- Polonium thermodynamic activity coefficients estimated using IPPE-date

- Into lead $$Lg(\gamma_{Po/Pb}) = -0,0946 - \frac{2401}{T}$$

- Into LBE $$Lg(\gamma_{Po/Pb-Bi}) = 0,788 - \frac{2568}{T}$$

- Into LLE $$Lg(\gamma_{Po/Pb-Li}) = 3,062 - \frac{5299}{T}$$

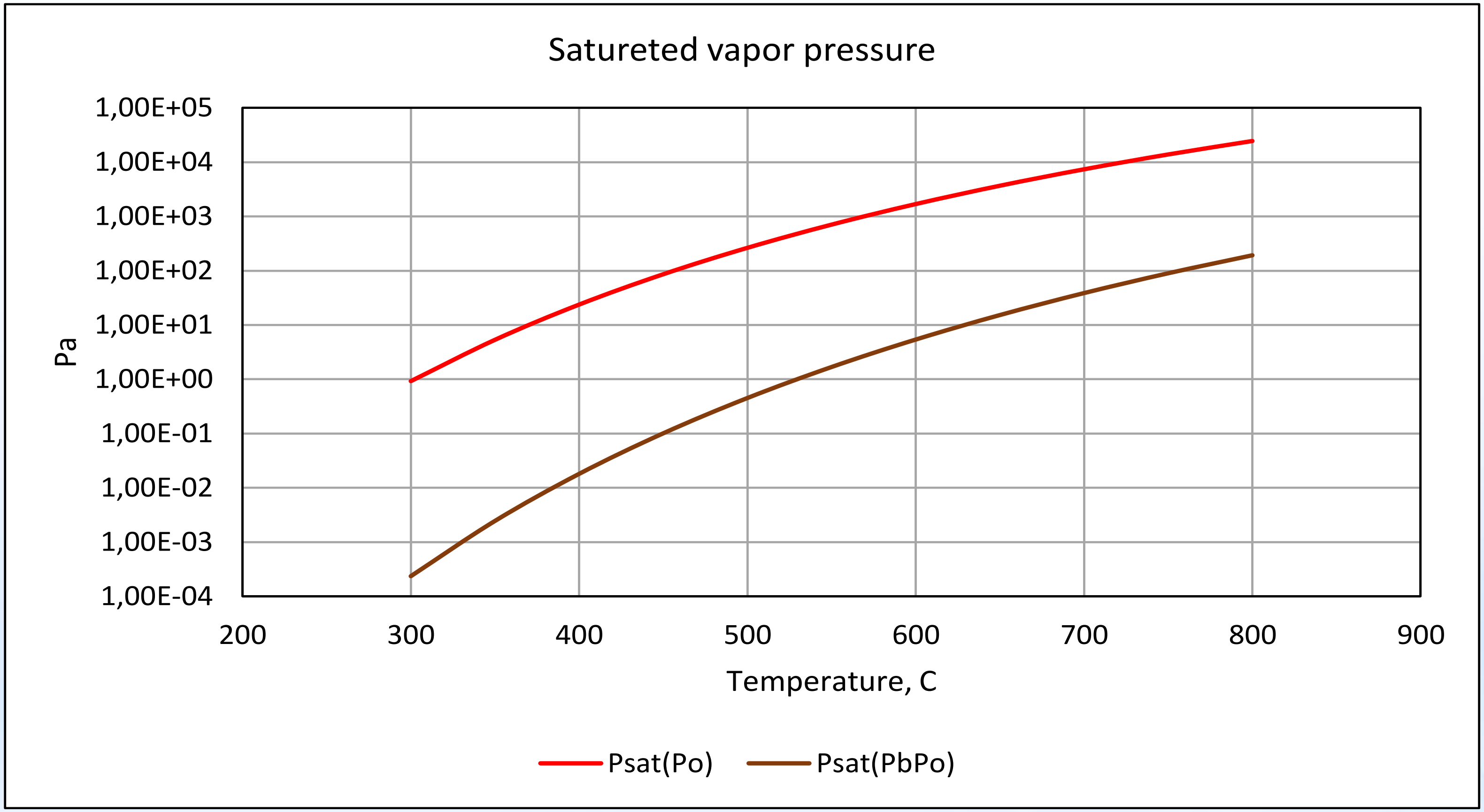
# Extrapolation of $P_{eff}$(Po/LBE) normalized at Po atomic quota



# Abnormal polonium volatilization at low temperature is mentioned in the number of sources

- Also IPPE experiment registrated abnormal large polonium release velocity at T=300 $^{o}$C. For lead (solid) the relation $Q_{meas}/Q_{calc}$ is 100÷200, for LBE (liquid) one is from 0,8 to 3,6.
- The reasons of abnormal volatility may be: aggregate recoil/sputtering, selfheating by α-decay, polonium diffusion and accumulation at sample surface, PbPo and humid air chemical interaction forming high volatile $PoH_2$ . One of reasons may be appreciable quota of pure polonium. It's commonly accepted polonium evaporate from containing lead smelting only as PbPo. A forming PbPo begin at 350 $^{o}$C and decomposition at 600 $^{o}$C. (Witteman et al)

# Extrapolation of Psat(T) Po and Psat(T)PbPo, calculated by Abakumov equations

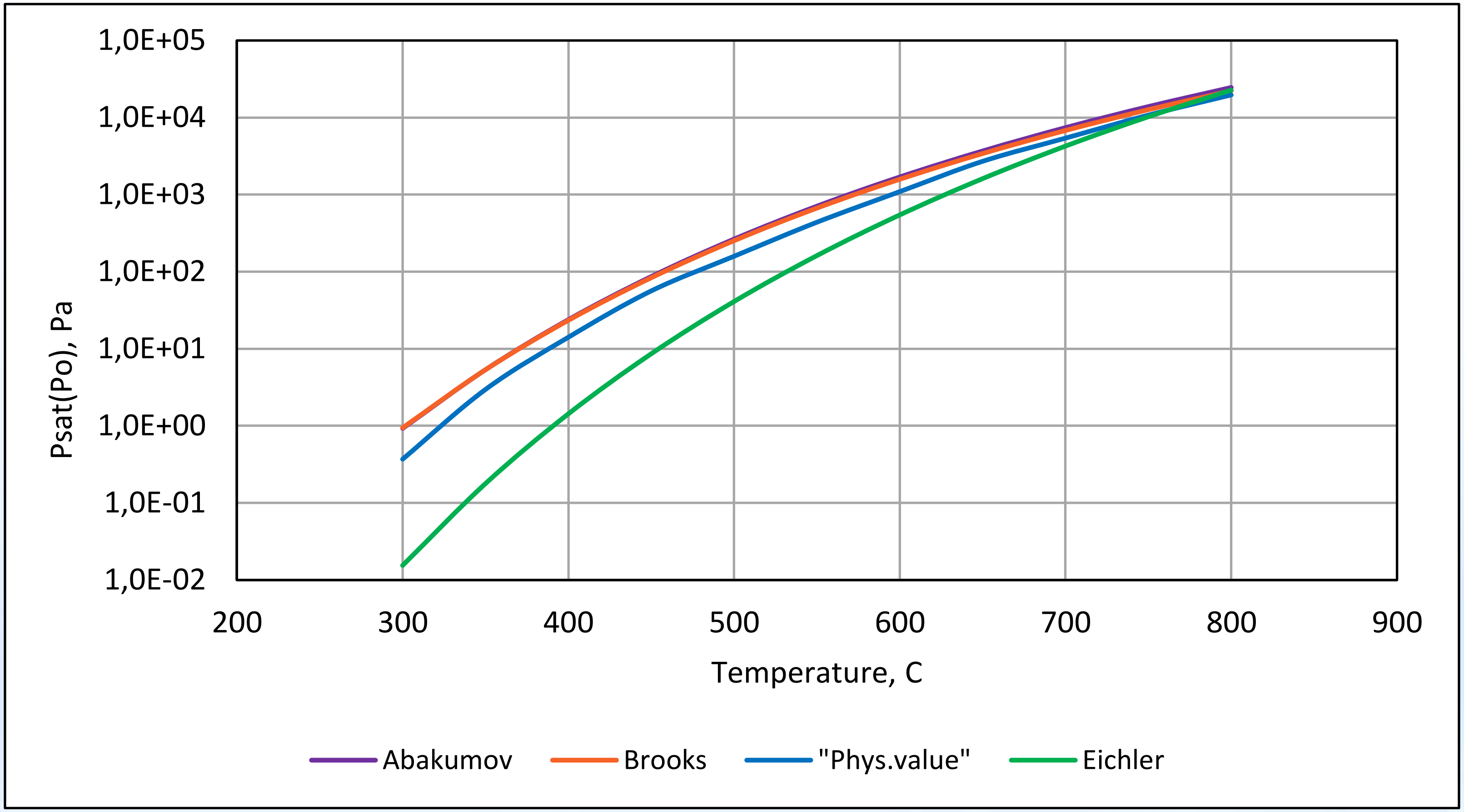


- If HLMC polonium activity contain 1 % of pure polonium and 99 % PbPo then at a temperature about 300 $^{o}$C the effective evaporation velocity would tenfold the PbPo thermal one. Let’s polonium activity contained into our samples pure polonium quota equal X and PbPo one – 1-X. Then equation of thermal evaporation velocity would have only one unknown variable

$$Q_i^{evp} = 4{,}38 \cdot 10^{-3} a_i M_0 S\beta \cdot \sum_j \frac{P_{ij}^{sat}(T)\xi_j}{\sqrt{M_{ij}T}}$$

- Pure polonium quota value calculated by this equation depend on polonium saturated vapor pressure that value has significant deviation at low temperature mentioned in different sources

# Polonium saturated vapor pressure, calculated by different sources



# Conclusion

- Polonium release velocity from HLMC into gas is the main factor of polonium migration model through the primary circuit of nuclear power plant cooled by HLMC

- Polonium release into cover gas of primary circuit at normal operation temperature should consider as lead polonide thermal evaporation. The pure polonium quota should be taken into account under conditions resulting in accidents accompanied by the first circuit coolant leakage. Polonium compound chemical interaction with operation room atmosphere should be considered too.

- Pure polonium quota in lead and LBE samples at 300 $^{o}$C was estimated using IPPE experimental date. In lead samples it is from 3 to 9 % depending on value of pure polonium vapor pressure using for calculation. In LBE samples it is ~ $10^{-2}$ %.

- At 500 $^{o}$C polonium activity evaporated from lead and LBE as PbPo

Thank you for your attention!

PAUL SCHERRER INSTITUT


WIR SCHAFFEN WISSEN – HEUTE FÜR MORGEN

Erik Karlsson :: Paul Scherrer Institut :: HLMC 2018 Obninsk :: 10th October 2018

# *Evaporation and Adsorption Behaviour of Iodine Released from Irradiated Tellurium-Doped LBE*

SCK•CEN
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

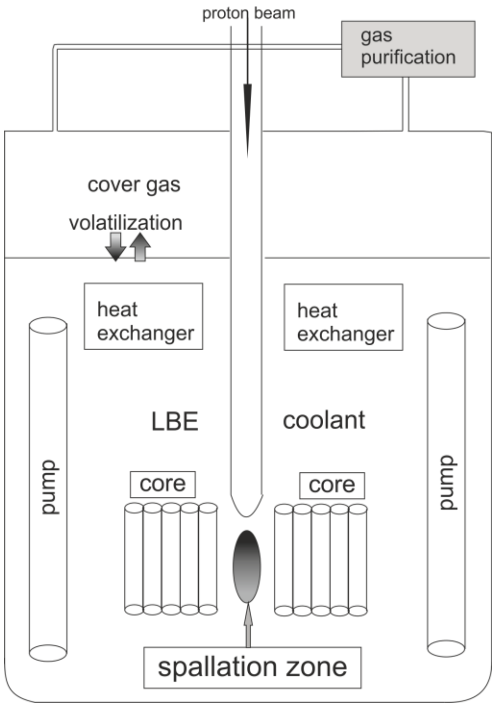
European Commission

Horizon 2020
European Union funding
for Research & Innovation

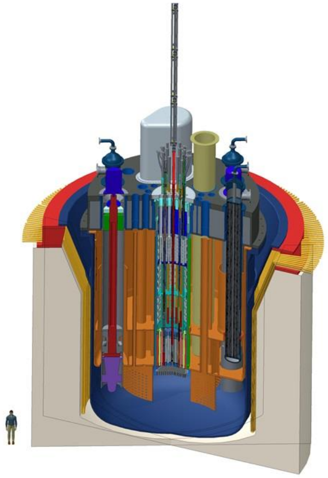
Myrte
MYRRHA Research
and Transmutation
Endeavour

# Introduction and Scope

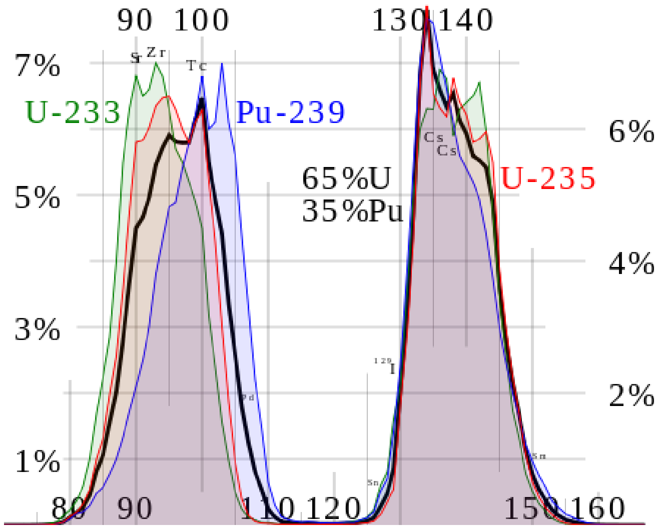
## MYRRHA reactor - Multi-purpose hYbrid Research Reactor for High-tech Applications



- Accelerator driven
  → Subcritical (k<1)
- HLM-coolant (lead-bismuth eutectic, LBE)
- Large ΔT safety margin
- Natural seal against enviroment
- A possible solution to the nuclear waste problem



→ Requires investigation regarding release in the event of an accident



Main volatile elements

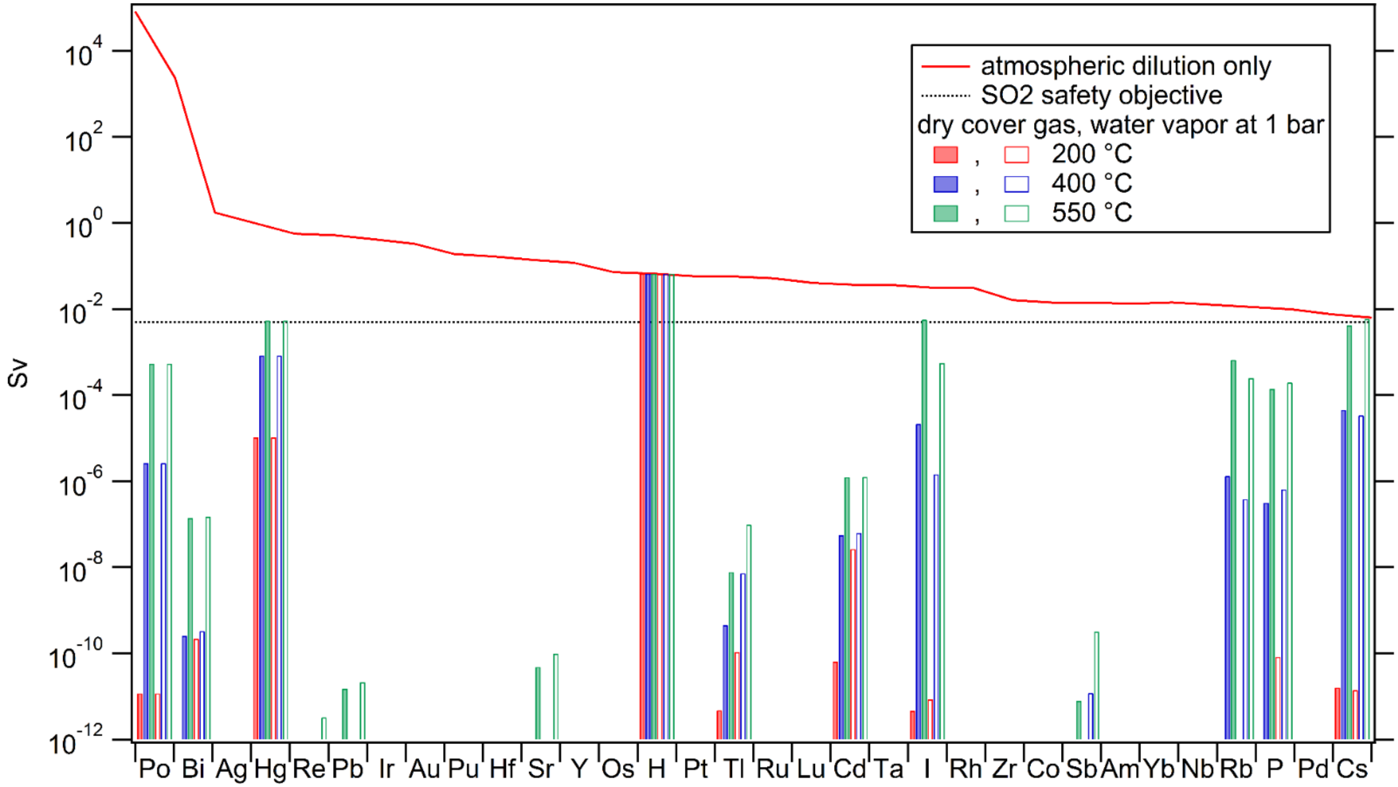
**Iodine**

Mercury

Cesium

Polonium

# Introduction and Scope

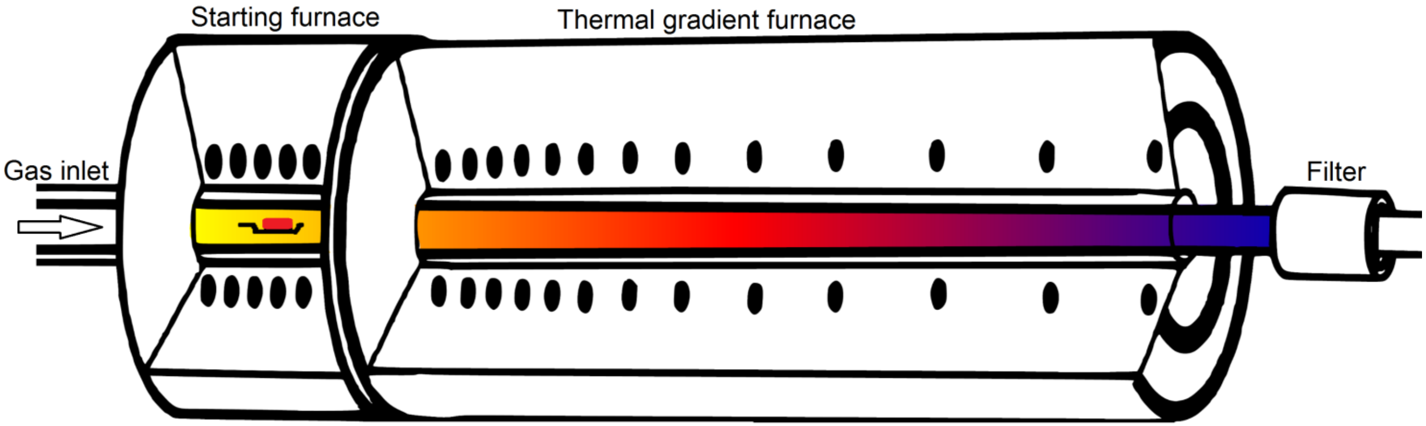


*A.Aerts (SCK-CEN)*

# Method

- Main experimental method : Thermochromatography

The separation or distinguishing of gaseous chemical species according to the strength of their interaction with a stationary phase.

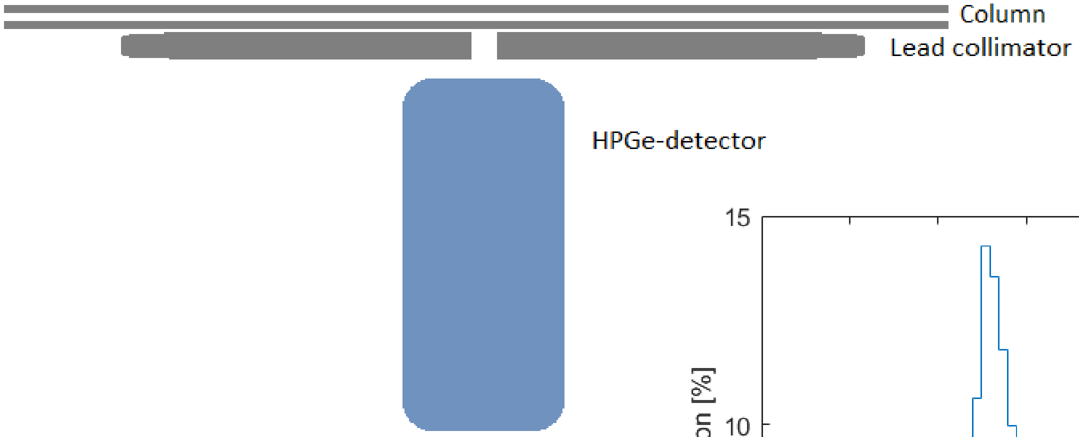


Samples prepared by neutron irradiation of tellurium doped LBE

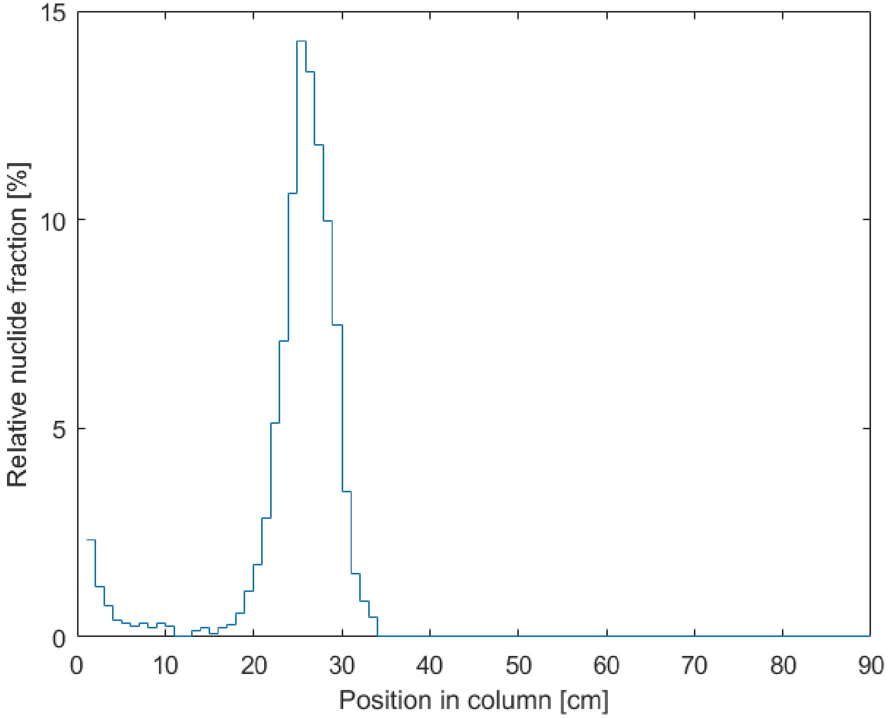
$^{130}$Te + n -> $^{131}$Te -> (~25 min, $\beta^-$) $^{131}$I

# Method

## Measuring



Column measured in 1 centimetre steps on HPGe-detector

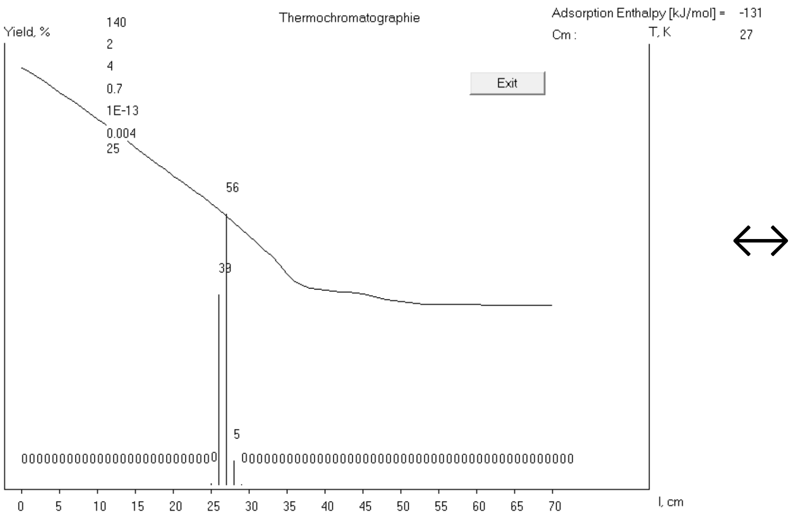


# Method

Evaluation of experimental results

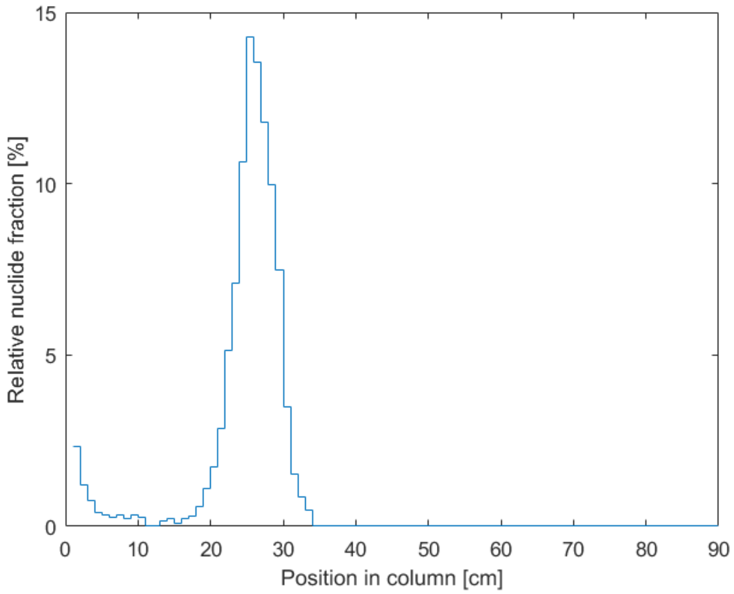
→ Monte Carlo simulation

- One atom at a time
- Simulation is provided experimental data as well as a guess for $\Delta H_{ads}$



Adsorption Enthalpy [kJ/mol] = -131

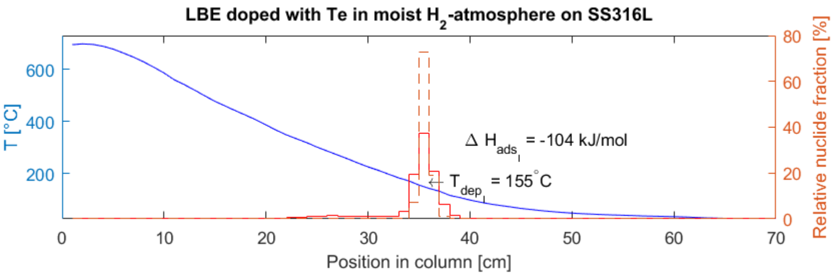
↔

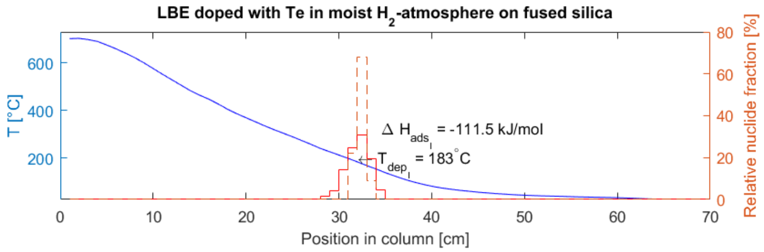


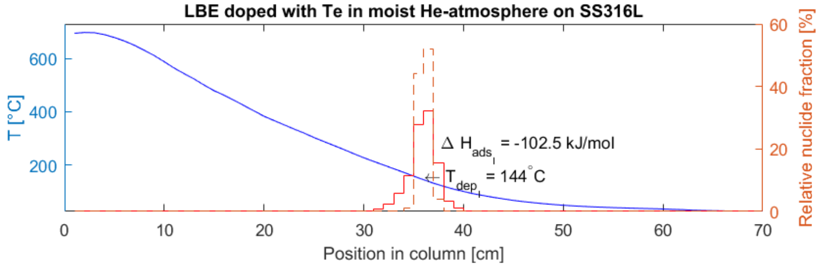
→ $\Delta H_{ads}$ = -131 kJ/mol

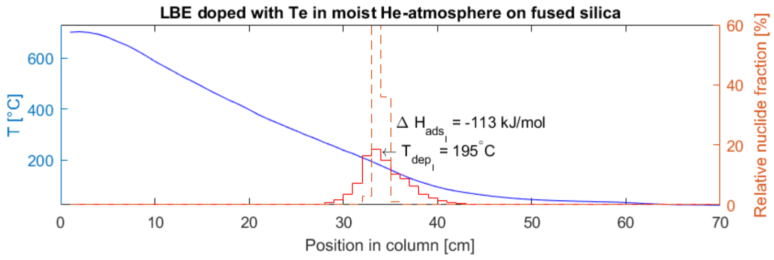
# Results

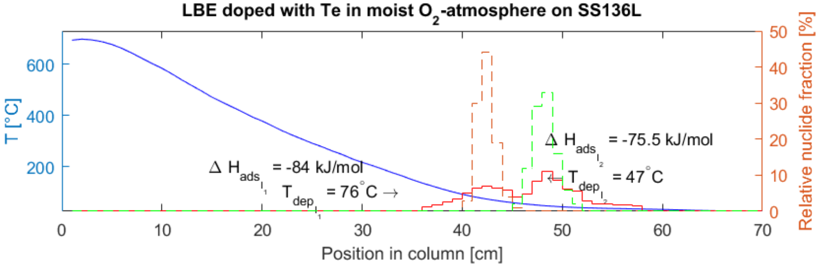
## $^{131}$I Moist conditions

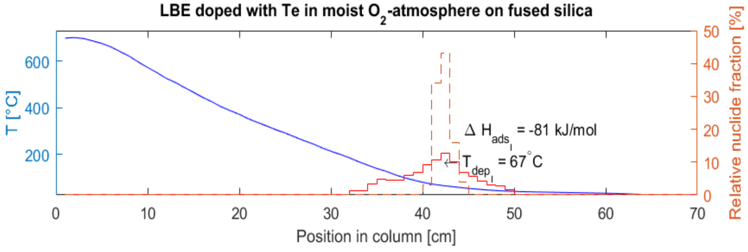








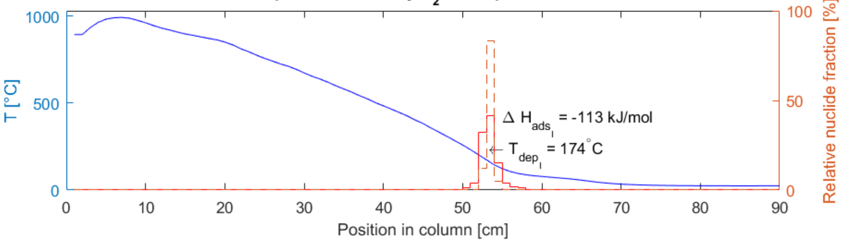




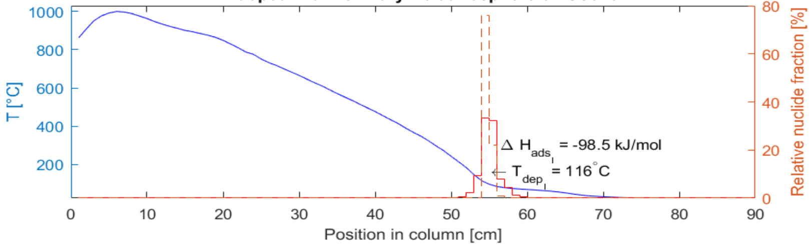
# Results

## $^{131}$I Dry conditions

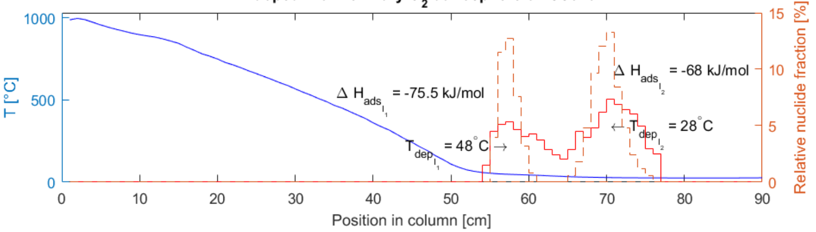
LBE doped with Te in dry $H_2$-atmosphere on SS316L



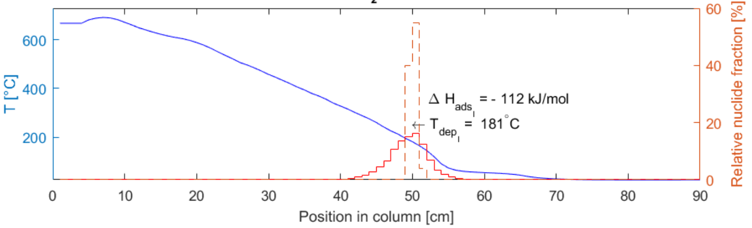
LBE doped with Te in dry He-atmosphere on SS316L



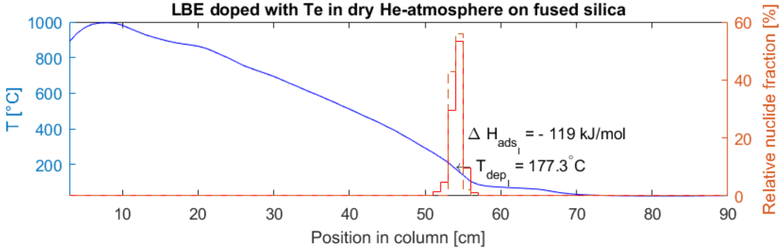
LBE doped with Te in dry $O_2$-atmosphere on SS316L



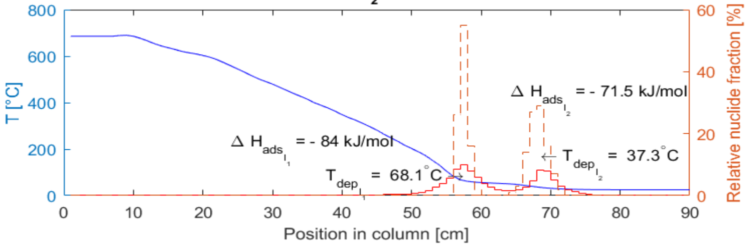
LBE doped with Te in dry $H_2$-atmosphere on fused silica



LBE doped with Te in dry He-atmosphere on fused silica



LBE doped with Te in dry $O_2$-atmosphere on fused silica



# Interpretation

Evaluation

What remains :
- Speciation!

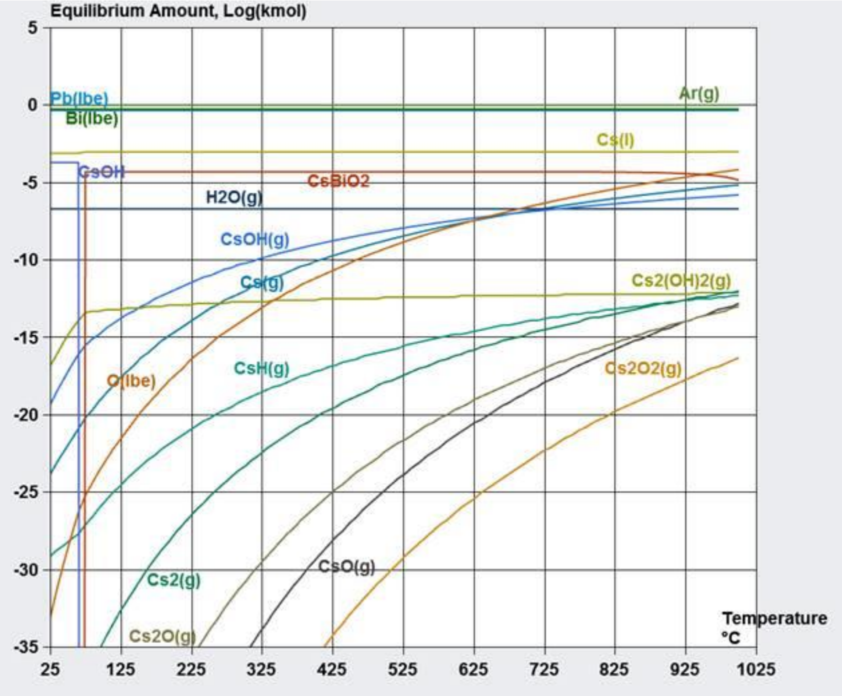
Methods

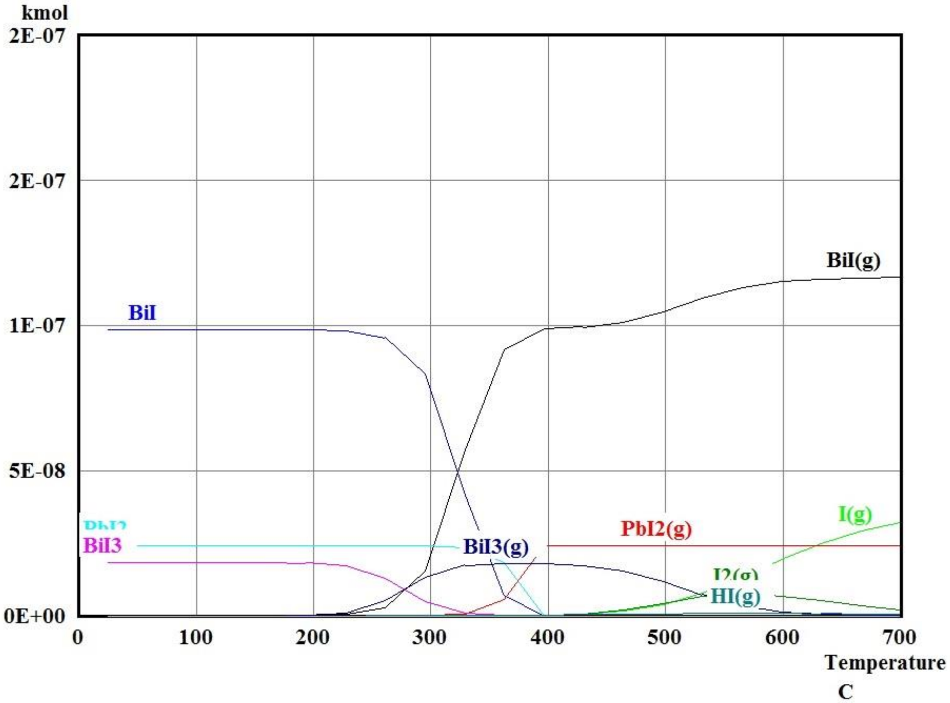
- Gibbs energy minimization
- Irradiating known compounds and comparing results
- Thermogravimetric analysis of decomposition
- Empirical correlations
- Common sense (partly complicated by impurities)

# Interpretation

- Gibbs energy minimization

- Calculates the most stable composition of the system
- Has no regard for time or energy barriers





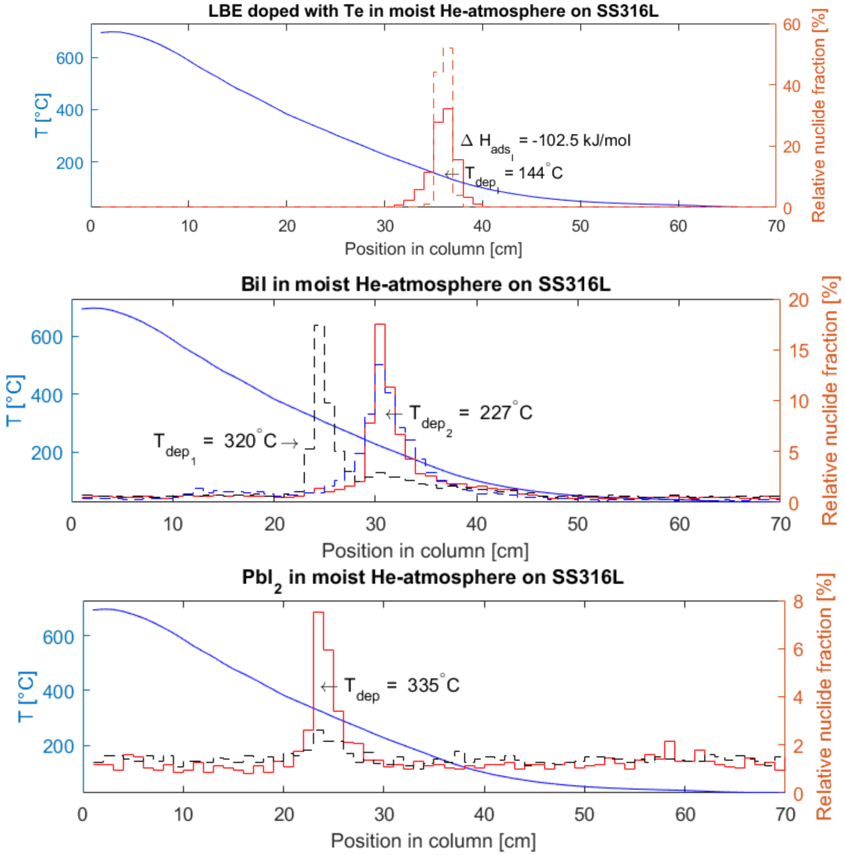
(A.Aerts - SCK)

# Interpretation

- Irradiating known compounds and comparing results

Examples : BiI, $PbI_2$

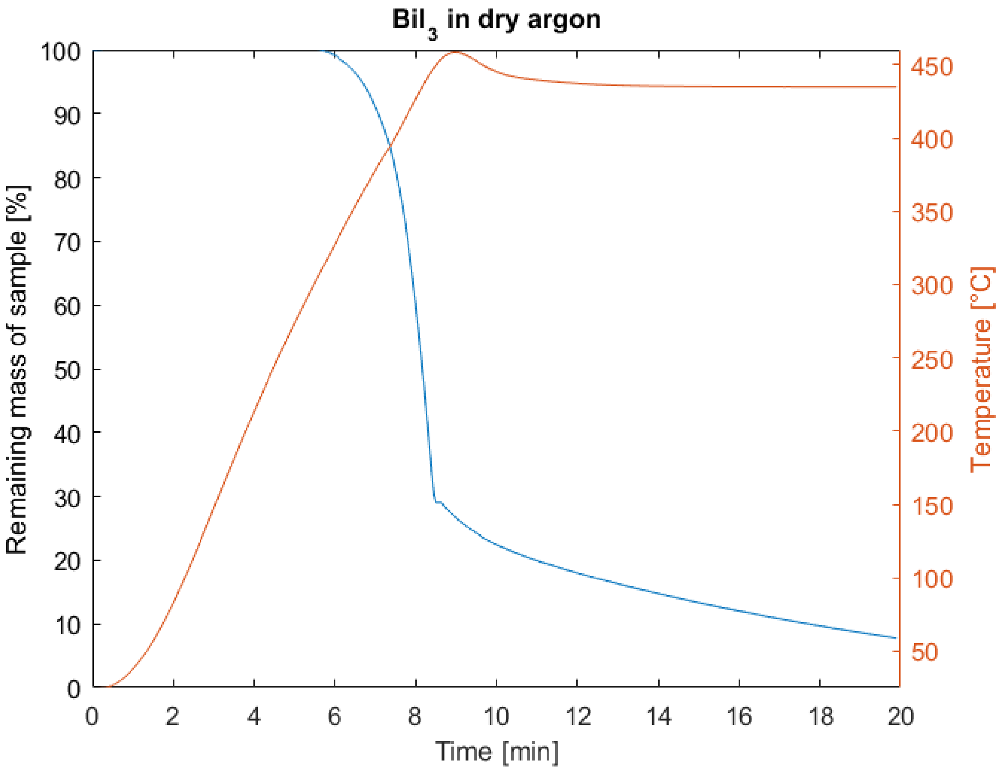
- ”True” comparison impossible in thermochromatography experiments
- Can extract information on behavior (reactions, decomposition etc.)



# Interpretation

- Thermogravimetric analysis of decomposition

Example : $BiI_3$

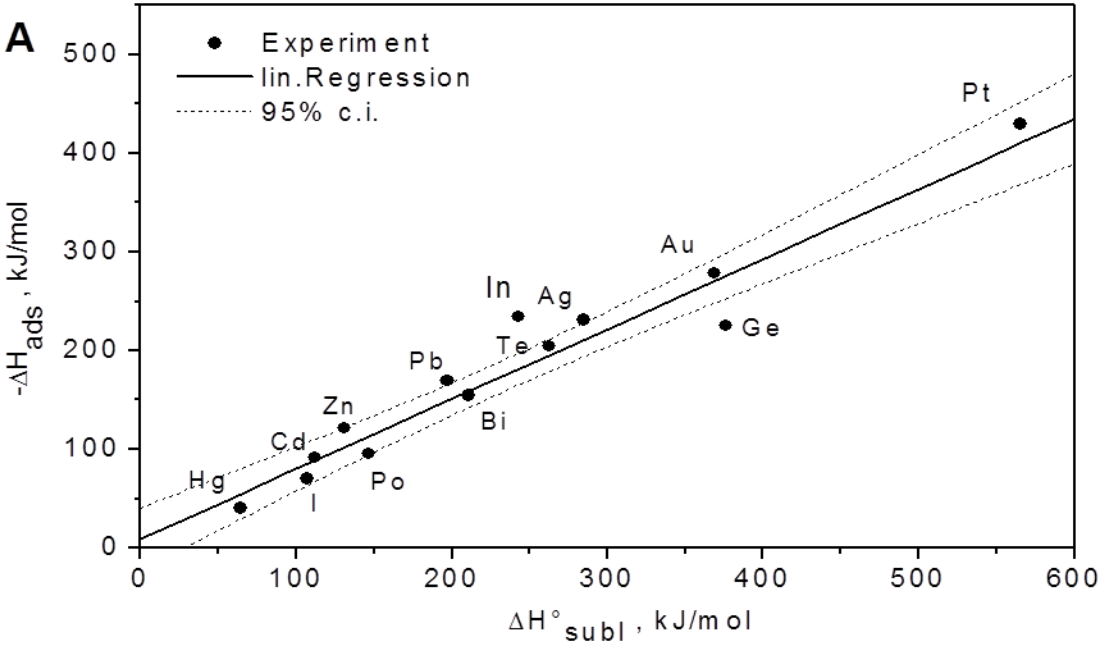


TGA shows decomposition in inert gas around ~400-450°C

# Interpretation

- Empirical correlations

- Useful in conditions the correlation has been developed for



$$-\Delta H_{ads} = (4.2 \pm 15.8) + (0.71 \pm 0.06)\,\Delta H_{sub}$$

(R.Eichler)

# Interpretation

- Common sense

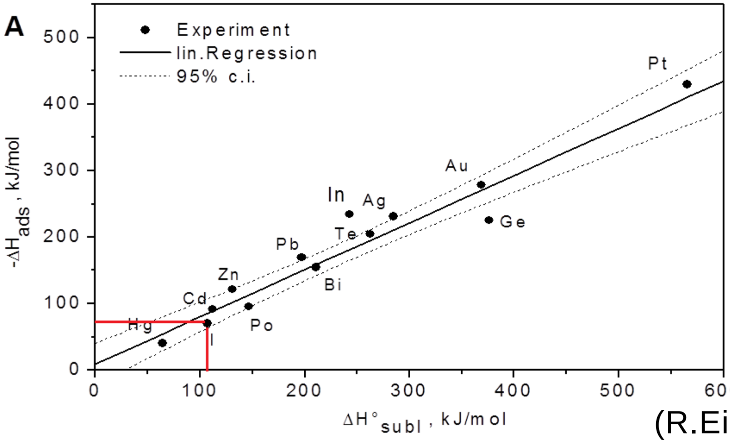
- What elements are present?
- What are the expected outcomes of the mixture?
- Would heat dissociate the compounds/make parts react to form compounds?

This method is effective to produce inputs and interpret output for GEM-methods (Gibbs energy minimization)

# Conclusions

$^{131}$I

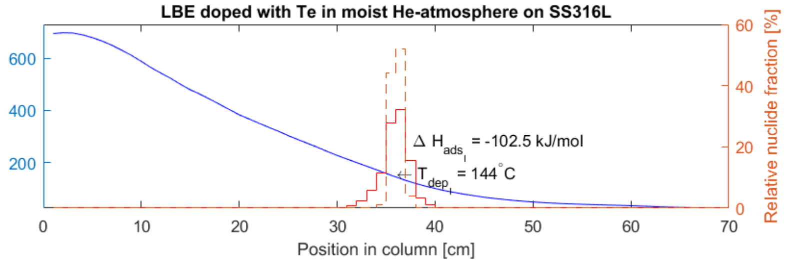
- Empirical correlation for fused silica surfaces holds
- Forms volatile compounds, iodine found in filters in all experiments

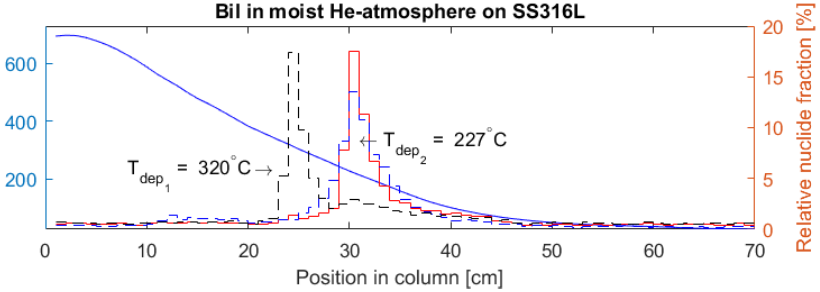


(R.Eichler)

$$-\Delta H_{ads} = (4.2\pm15.8)+(0.71\pm0.06)\,\Delta H_{sub}$$

Binary iodide experiments deposition patterns suggest similar species present in LBE-matrix experiments (likely BiI)





- Preparing homogeneous doped LBE samples with controlled levels of impurities as well as oxygen may be of importance to get predictable behaviour

- In the case of SS316L, surface state is very important (oxidized, reduced) with so many potentially participating elements and compounds

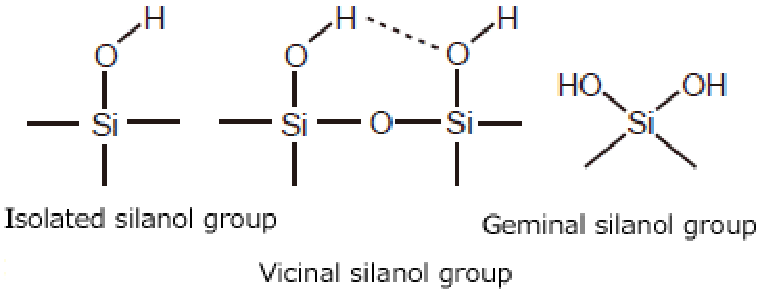
- Oxygen seems to impede the evaporation of iodine from LBE (oxide scale formation?)

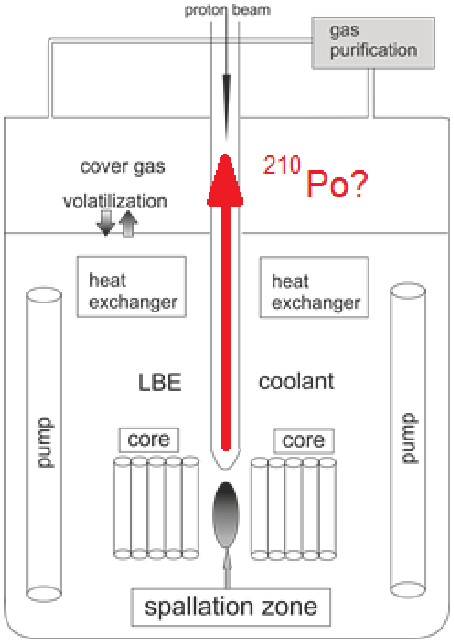
# Future work

- Perform some experiments with carrier free iodine evaporated from irradiated Te or TeO2 and deposited on gold foil
  - Do this in both stainless steel and Ag columns

- Pretreating surfaces by pre-reduction in isothermal furnaces under hydrogen flow (both SS316L & fused silica)

In the case of the steel to reduce the surface oxidation and with the silica to remove silanol groups which may introduce oxygen and water into an otherwise dry and inert gas





## Acknowledgements

- Jörg Neuhausen
- Robert Eichler
- Ivan Danilov
- Alexander Aerts (SCK-CEN)
- Alexander Vögele

Lastly I would like to thank EURATOM for funding the MYRTE project under HORIZON 2020.

**Thank you for listening!**

**Questions?**

РОСАТОМ

ГНЦ РФ-ФЭИ

HLMC - 2018

# LEAD-BEARING COOLANTS IN PERSPECTIVE TECHNOLOGIES OF SOLID, LIQUID AND GASEOUS RAW MATERIALS PROCESSING

**Ulyanov V.V., R.Sh. Askhadullin, V.P. Mel'nikov,**
**V.A. Gulevskiy, M.M. Koshelev, A.N. Storozhenko**

JSC "SSC RF – IPPE“
Obninsk, 2018

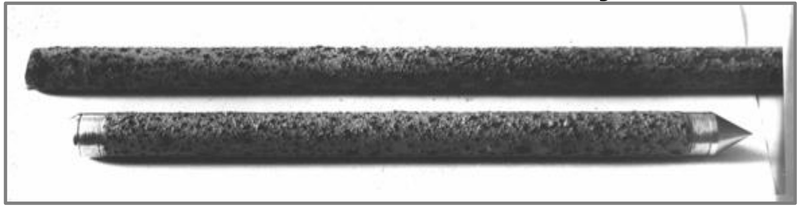
# First experience of HLMC technology development in Russia

**First K-27 submarine** (November class) with LBE.
Commisioning – 1963.
Accident – 1968.
**Cause of accident** – fusion power rod of the reactor because of deterioration in heat exchange, caused by deposits of slags.

## Typical examples of slag deposits at the initial stage of LBE development (1968 – 1972)

Slag deposits on the pipe internal surface

Slag deposits in the heat-exchange assembly



Slag deposits on the surface of the recuperator’s heat-exchange tubes

| Typical composition of slags,% | | | | | |
|---|---|---|---|---|---|
| Fe | Cr | Ni | $O_2$ | Pb | Bi |
| $4{\cdot}10^{-4}\div6{,}9$ | $2{\cdot}10^{-4}\div1{,}7$ | $2{\cdot}10^{-4}\div0{,}2$ | $0{,}9\div2{,}4$ | $47\div76$ | $14\div46$ |

# Slag formation at the loop depressurization

$$\{Pb\} + \tfrac{1}{2}(O_2) \rightarrow \langle PbO \rangle$$

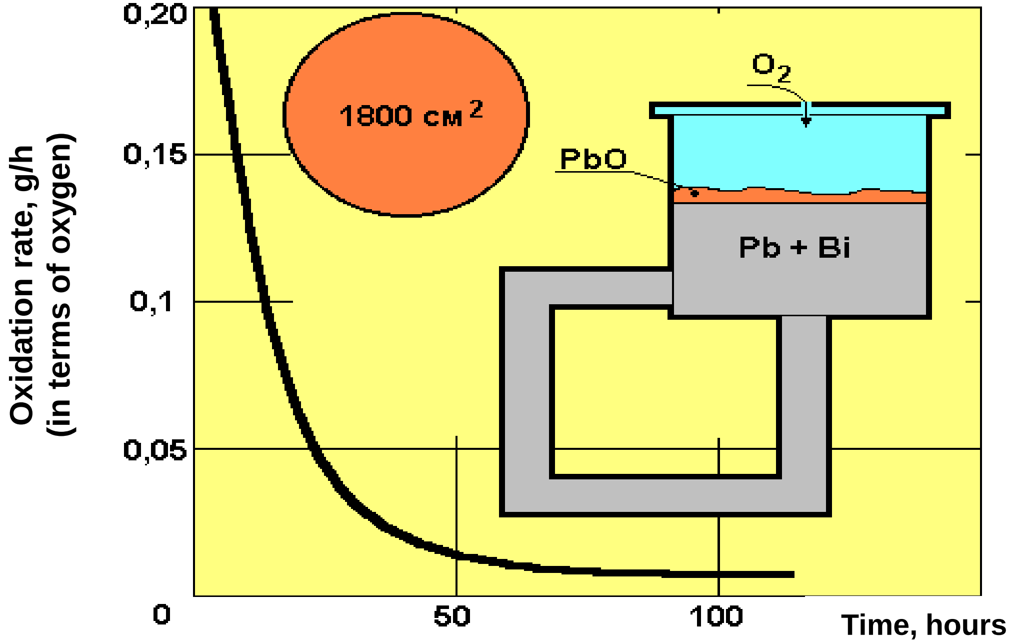
**A) without removal of HLMC from a loop – the minimum accumulation of slags**

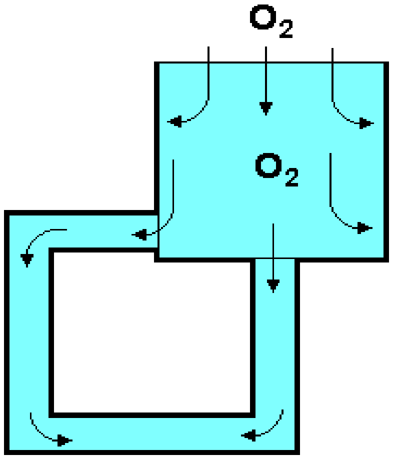
**B) during removal of HLMC from a loop – the maximum accumulation of slags**

$M_{PbO}/M_{HLMC} \sim 10^{-3} \div 10^{-4}\ \%_{wt.}$

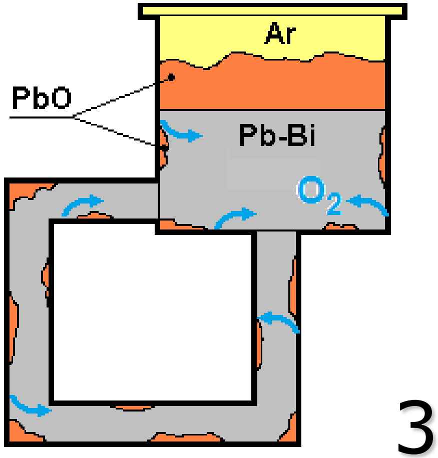
$M_{PbO}$ (with A) << $M_{PbO}$ (with B)

$M_{PbO}/M_{HLMC} \sim 10^{-2} \div 5\ \%_{wt.}$





Sorption of $O_2$ a "cold" surface of a contour when carrying out repair and reloading works

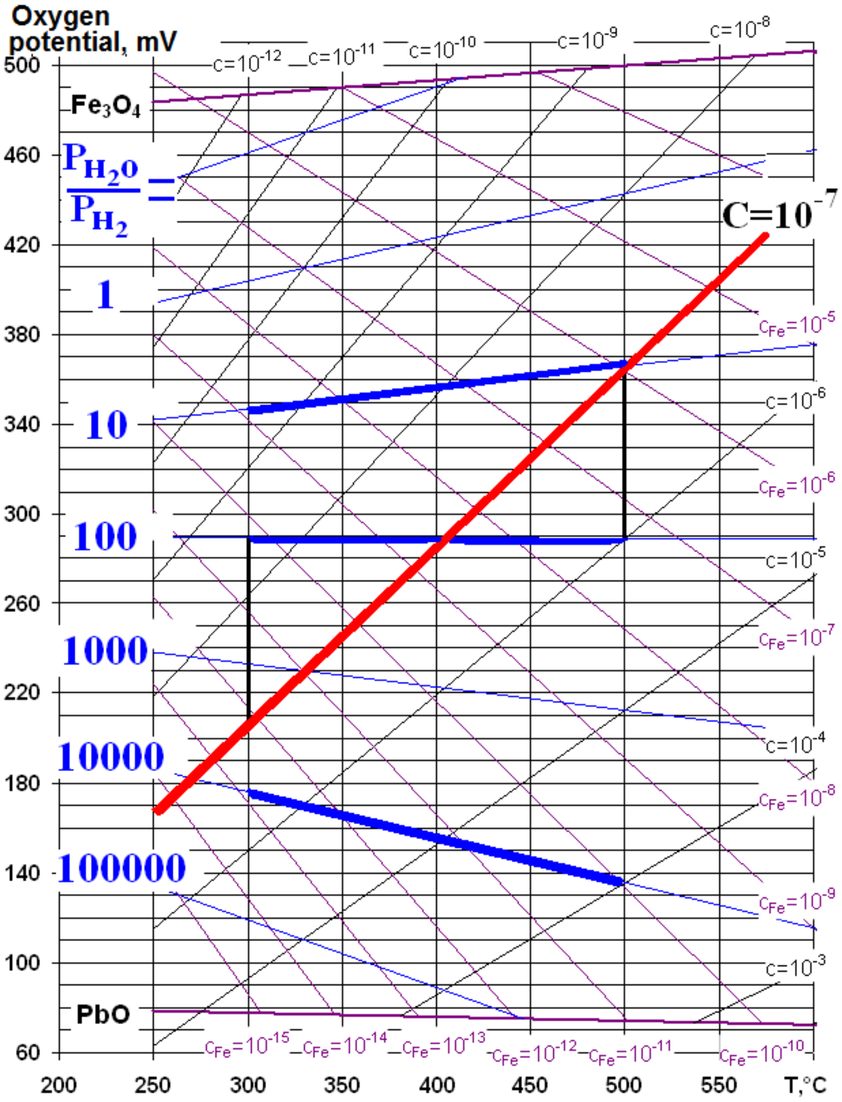


Desorption of $O_2$ and oxidation of the coolant

$$\{Pb\} + \tfrac{1}{2}(O_2) \rightarrow \langle PbO \rangle$$

**Minimization of contact of the coolant with oxygen of air is important for the solution of tasks of prevention of formation of slags on the basis of oxide PbO.**

# HLMC interaction with “$H_2$–$H_2O$” mixtures



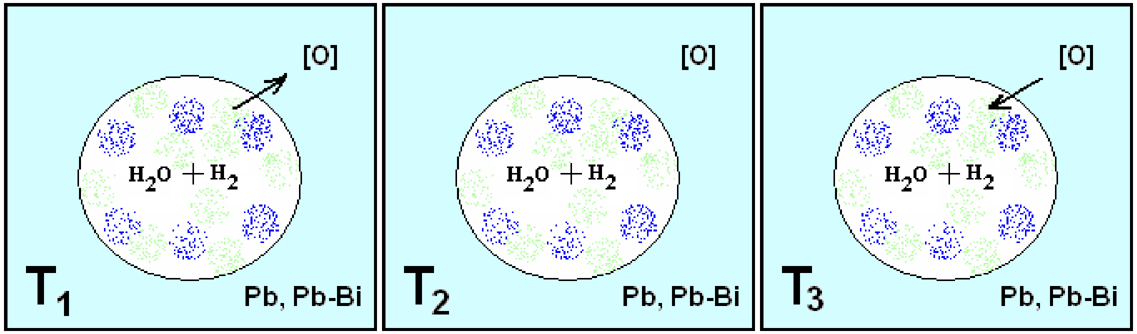
$$(H_2O) + \{Pb\text{-}Bi\} \leftrightarrow (H_2) + [O] + \{Pb\text{-}Bi\}$$

**Diagram E – T – C – $p_{H_2O}/p_{H_2}$**

**for LBE**

$$E\ (V) = 0.13 - 1.5\cdot10^{-5}\cdot T\cdot(1+6.6\cdot \lg a_O) - Pb$$

$$E\ (V) = 0.09 - 1.8\cdot10^{-5}\cdot T\cdot(1+5.6\cdot \lg a_O) - Pb\text{-}Bi$$



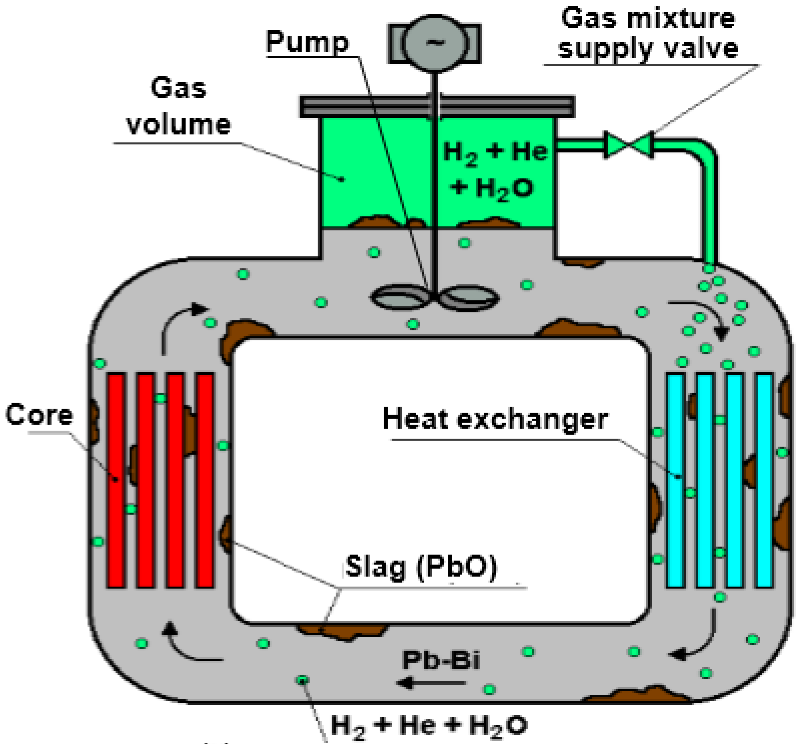
$$C_O = f\ (V_{HLMC},\ V_{gas},\ T_{cold},\ T_{hot},\ F_{cold},\ F_{hot},\ \ldots)$$

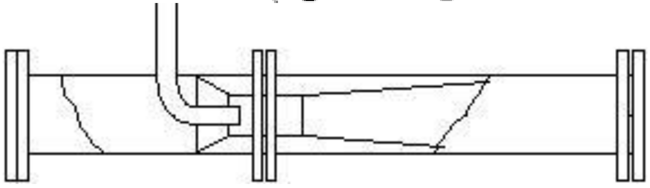
Thermodynamic properties of “$H_2$ – $H_2O$” and HLMC differ from each other. Different interaction scenarios (oxidation, deoxidation, equilibrium) are possible during their transportation along different temperature zones of loop.

# Hydrogen purification of loop design facilities

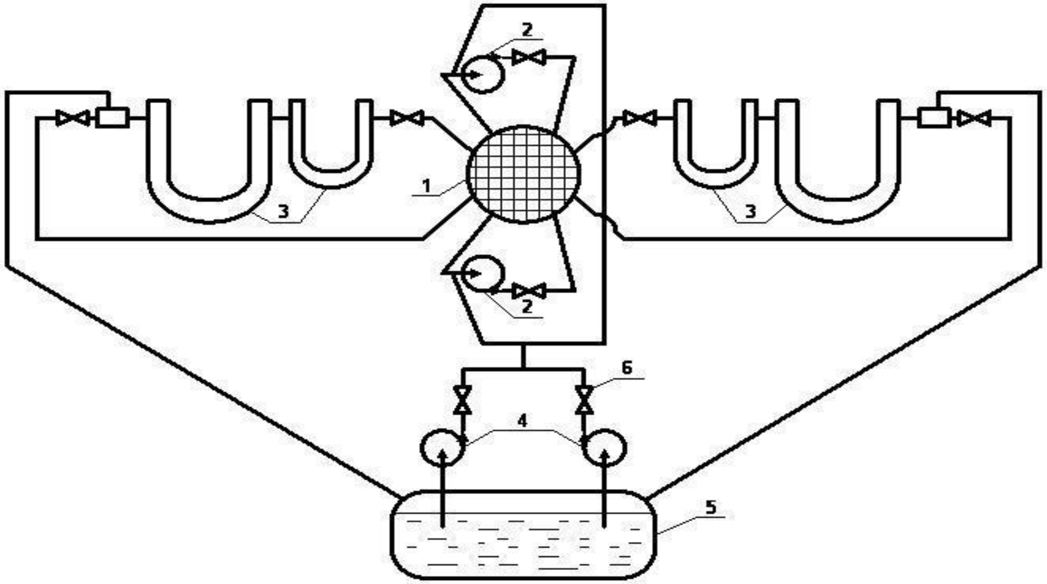
$$(H_2) + \langle PbO \rangle \rightarrow (H_2O) + [Pb]$$

$$(H_2)+[O] \rightarrow (H_2O)$$

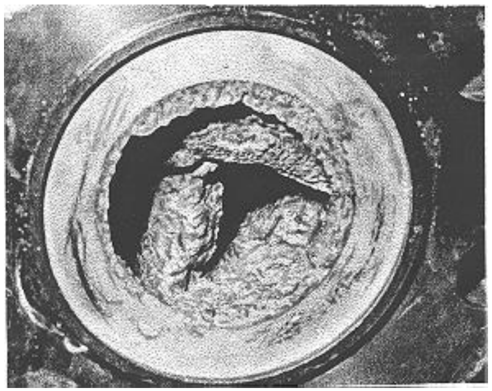




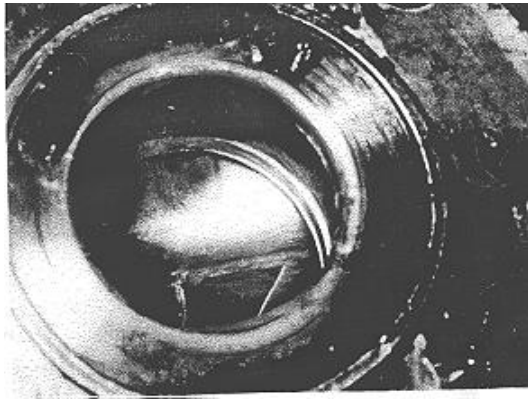
Ejector scheme



1. Core. 2. Pump. 3. Steam generator. 4. Auxiliary pump. 5. Tank. 6. Gates.

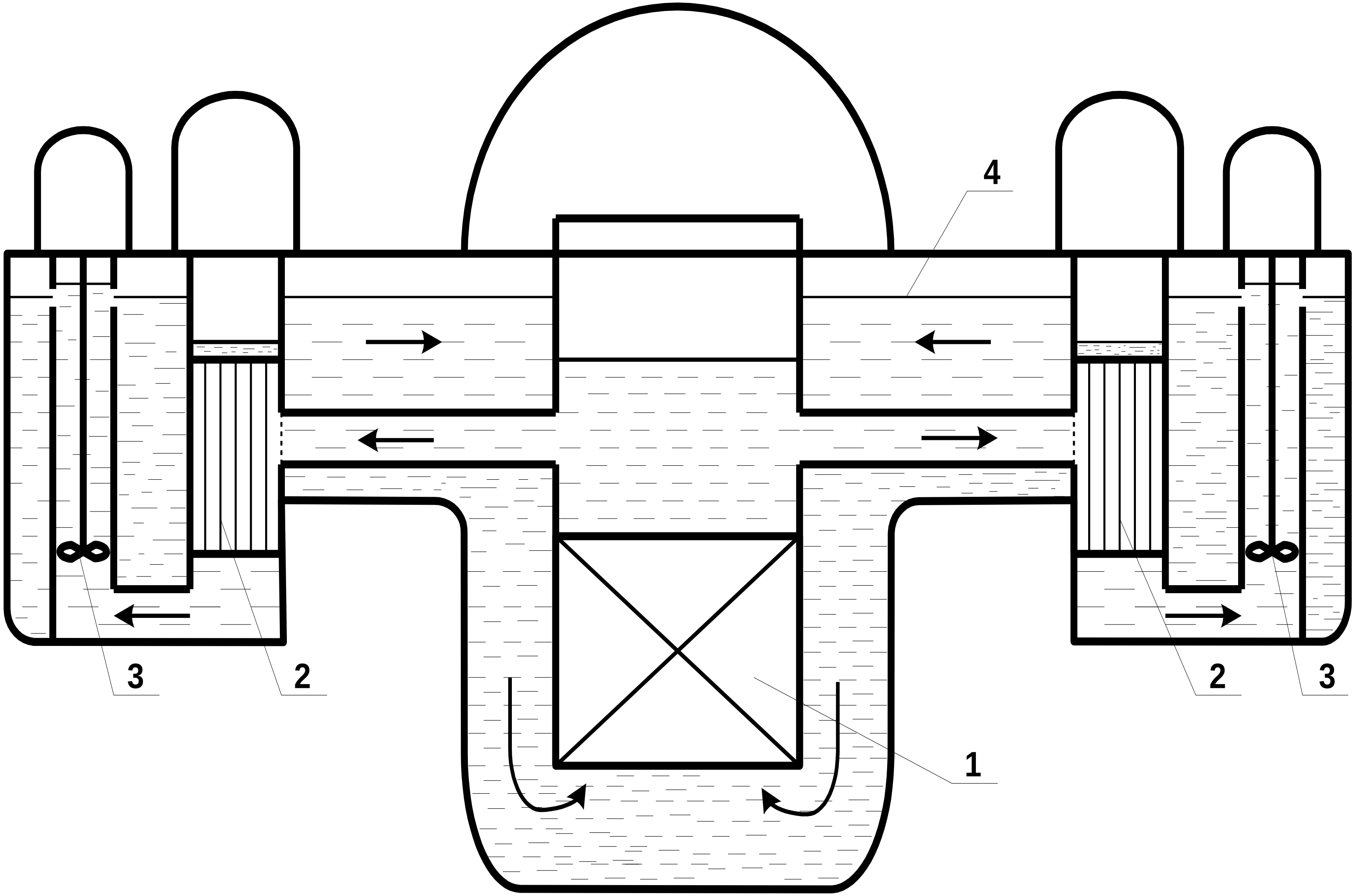


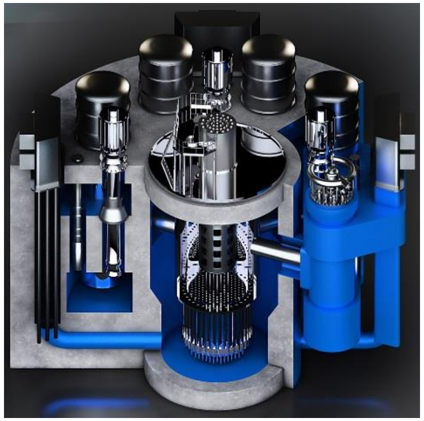
Loop section before purification

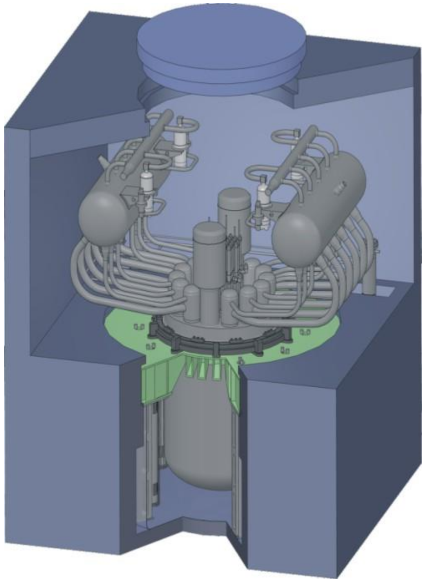


Loop section after purification

# Advanced loopback design reactor facility



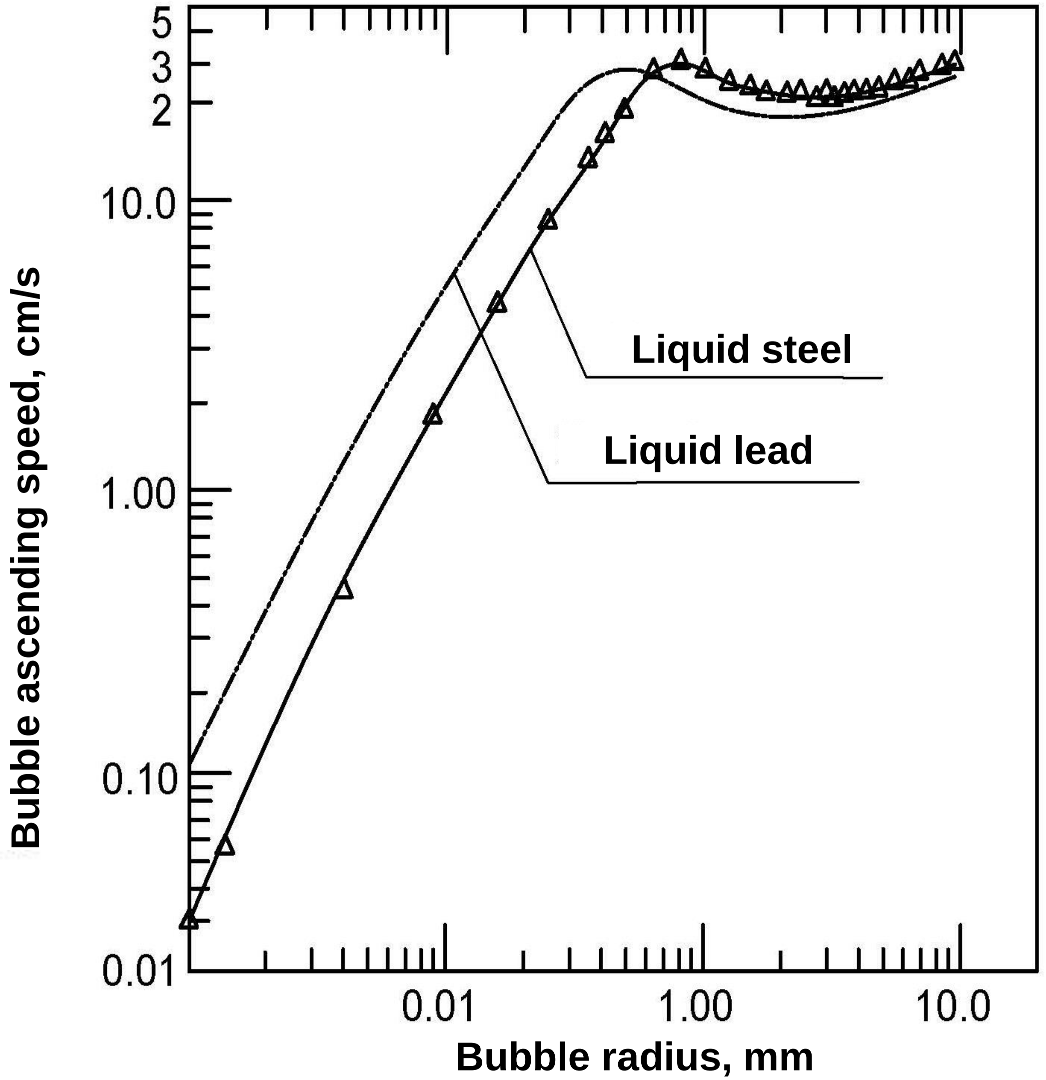




**1 – core, 2 – steam generators, 3 – pump, 4 – “coolant-gas” boundary**

# Dependence of gas bubble floating rate on radius

**$(H_2) + \langle PbO \rangle \rightarrow (H_2O) + \{Pb\}$**



In designs of reactor facilities there are sites promoting gas separation, i.e. they are calculated on removal of bubbles of water vapor from a contour that, however, complicates carrying out hydrogen cleaning.

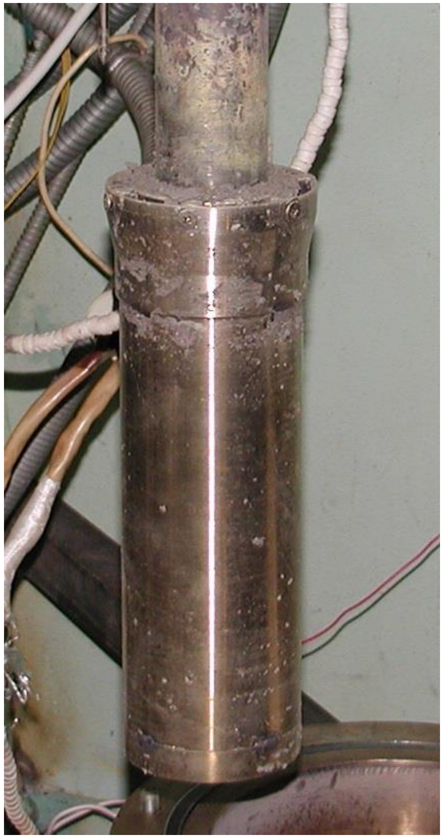
Slags on the basis of PbO can be formed in any site of a contour.

For their removal only one decision – a dispergation of gas bubbles and introduction to the volume of HLMC of a fine gas phase is possible.

**The design of real reactor installation or the stand requires the principle of input of gas.**

# Tests of gas handler (GH) on the working site with Pb (∅300мм)

1 – GH; 2 – oxygen sensor;
3 – gas contour; 4 – heaters; 5 – gate

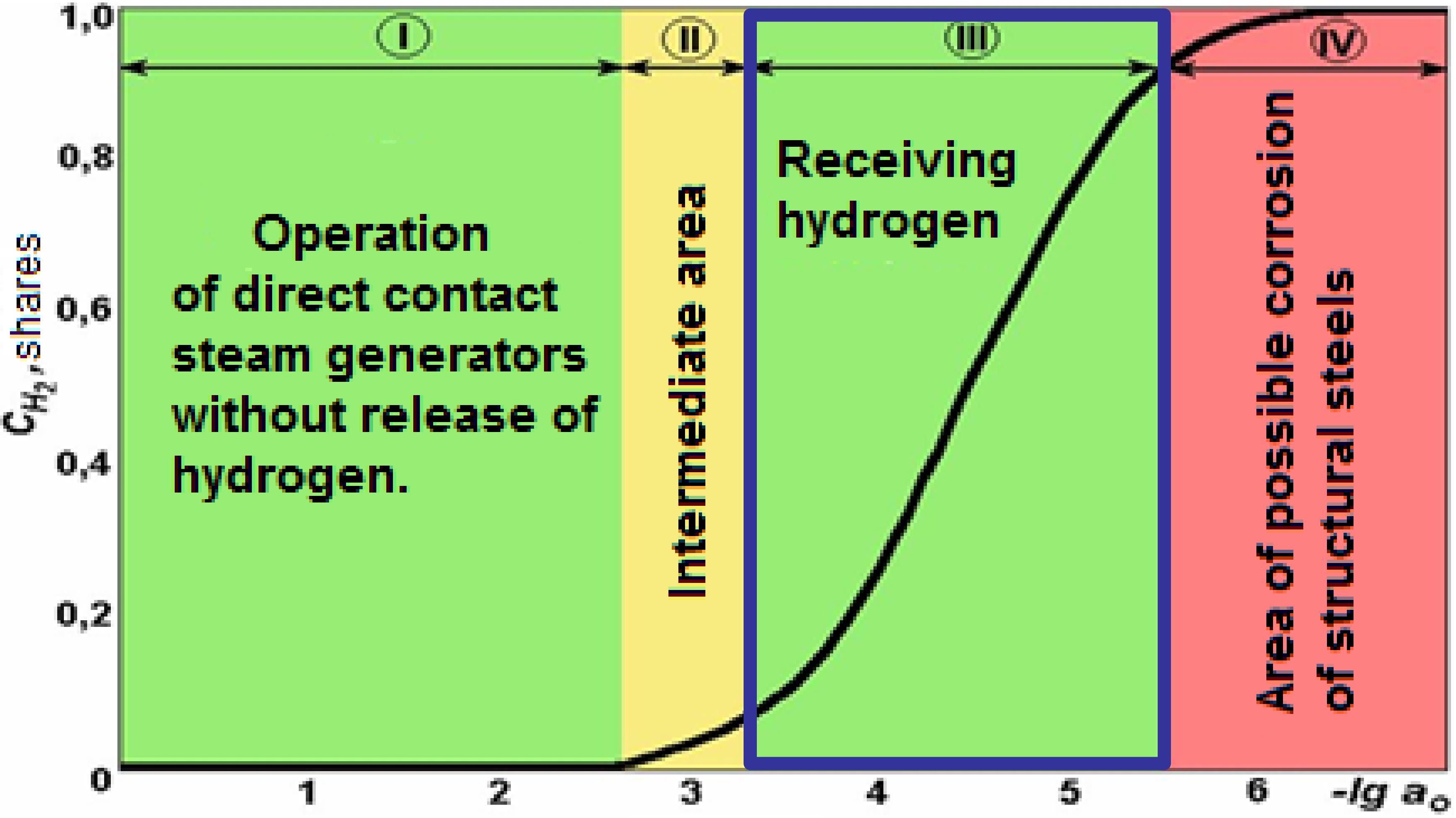


GH fragment
before cleaning

GH fragment
after cleaning

# Thermodynamics of LBE interaction with the "$H_2$-$H_2O$" mixes

$$(H_2O) + \{Pb\text{-}Bi\} \rightarrow (H_2) + [O] + \{Pb\text{-}Bi\}$$



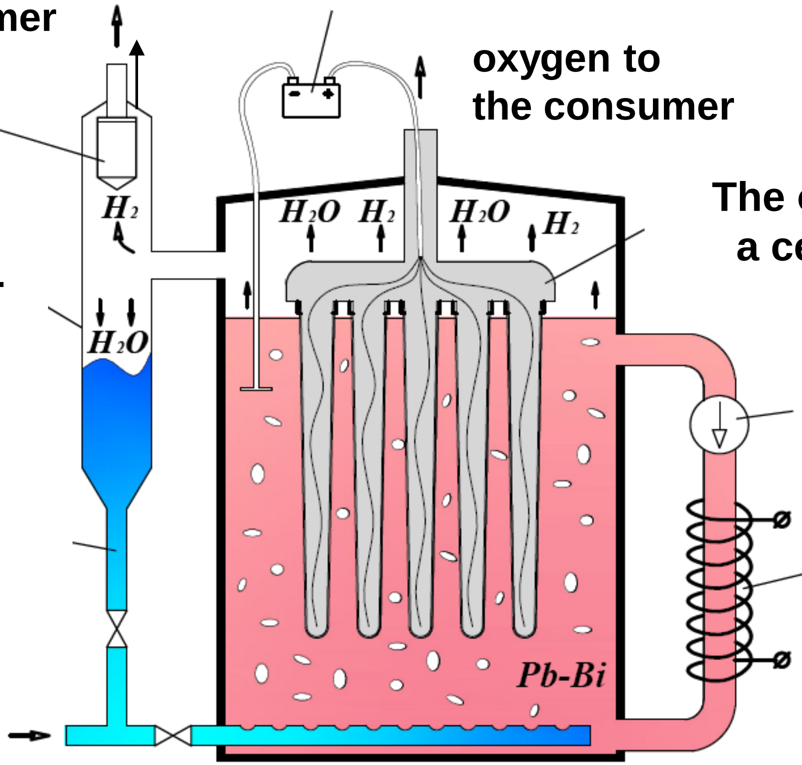
$$a = \frac{C_O}{C_{OS}}$$

Zone I – optimum conditions for operation of direct contact steam generators.

**Zone III – the optimum content of oxygen for hydrogen generation.**

# High temperature water decomposition in HLMC

$$(H_2O) + \{Pb\text{-}Bi\} \leftrightarrow (H_2) + [O] + \{Pb\text{-}Bi\}$$



$H_2$ to consumer

power supply of the oxygen pump

oxygen to the consumer

Gas filter

The oxygen pump with a ceramic membrane

Refrigerator-condenser

Pipe

Not reacted water back in the reactor

Warmly from any possible source

Water supply

During the work in "zone III" water interacts with Pb-Bi with formation of $H_2$ and increase in content of the dissolved oxygen. The oxygen pump continuously "pumps out" the dissolved oxygen from the heat carrier, deoxidating it. On an internal cavity of the pump high-pure oxygen is formed.

# Oxidic conversion of hydrocarbons in HLMC

Zone 1: $4Pb+2O_2=4PbO+Q_1$

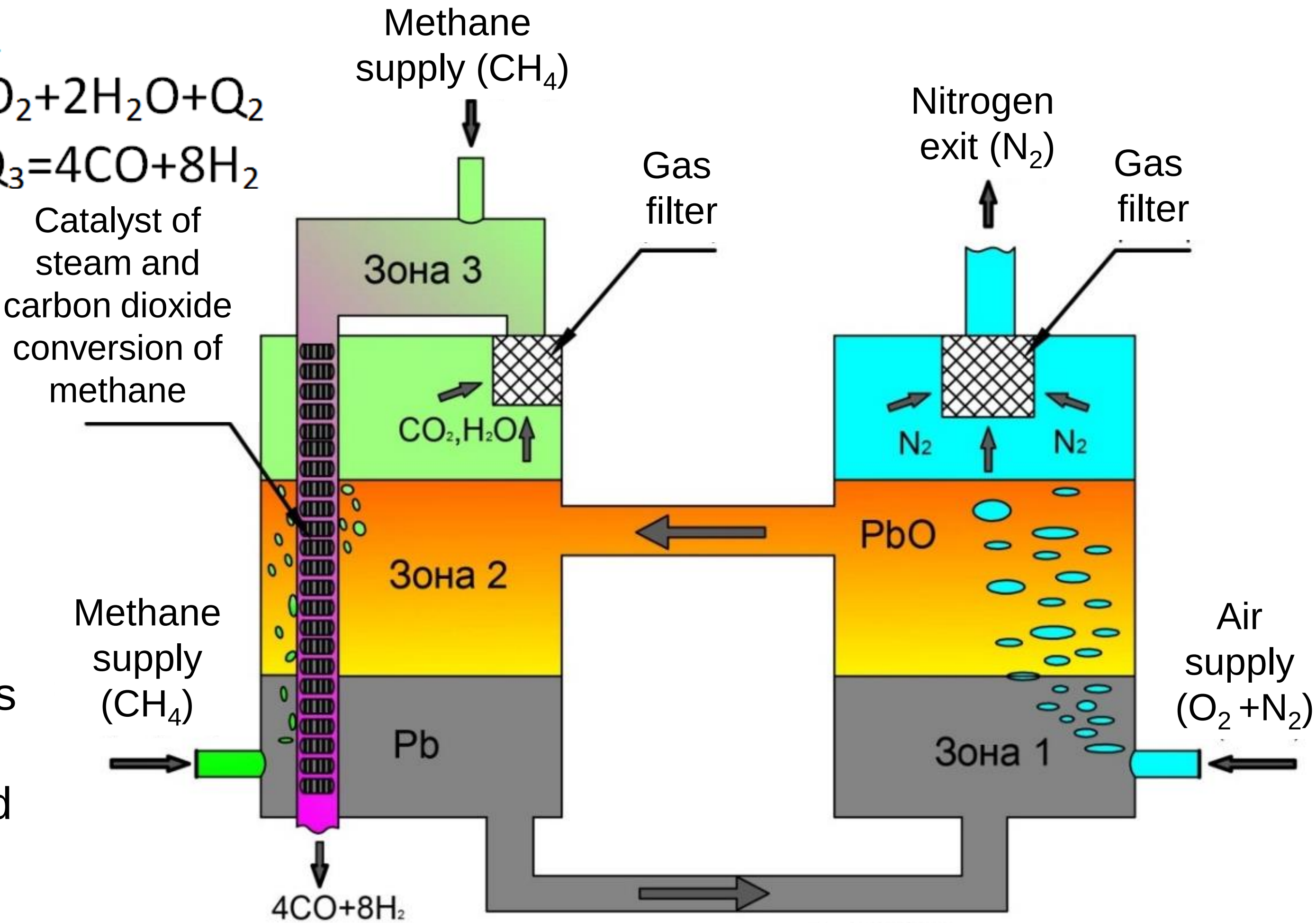
Zone 2: $4PbO+CH_4=4Pb+CO_2+2H_2O+Q_2$

Zone 3: $3CH_4+CO_2+2H_2O+Q_3=4CO+8H_2$

Zone 1 – an air divider.

Zone 2 – oxidizer of organic raw materials.

Zone 3 – the proofreader of structure synthesis gas. Methane is added to $CO_2$ and $H_2O$. On the catalyst they interact with receiving synthesis gas. Reaction takes place with the absorption of heat allocated in a zone 1 and a zone 2 (total reaction - an exothermic).



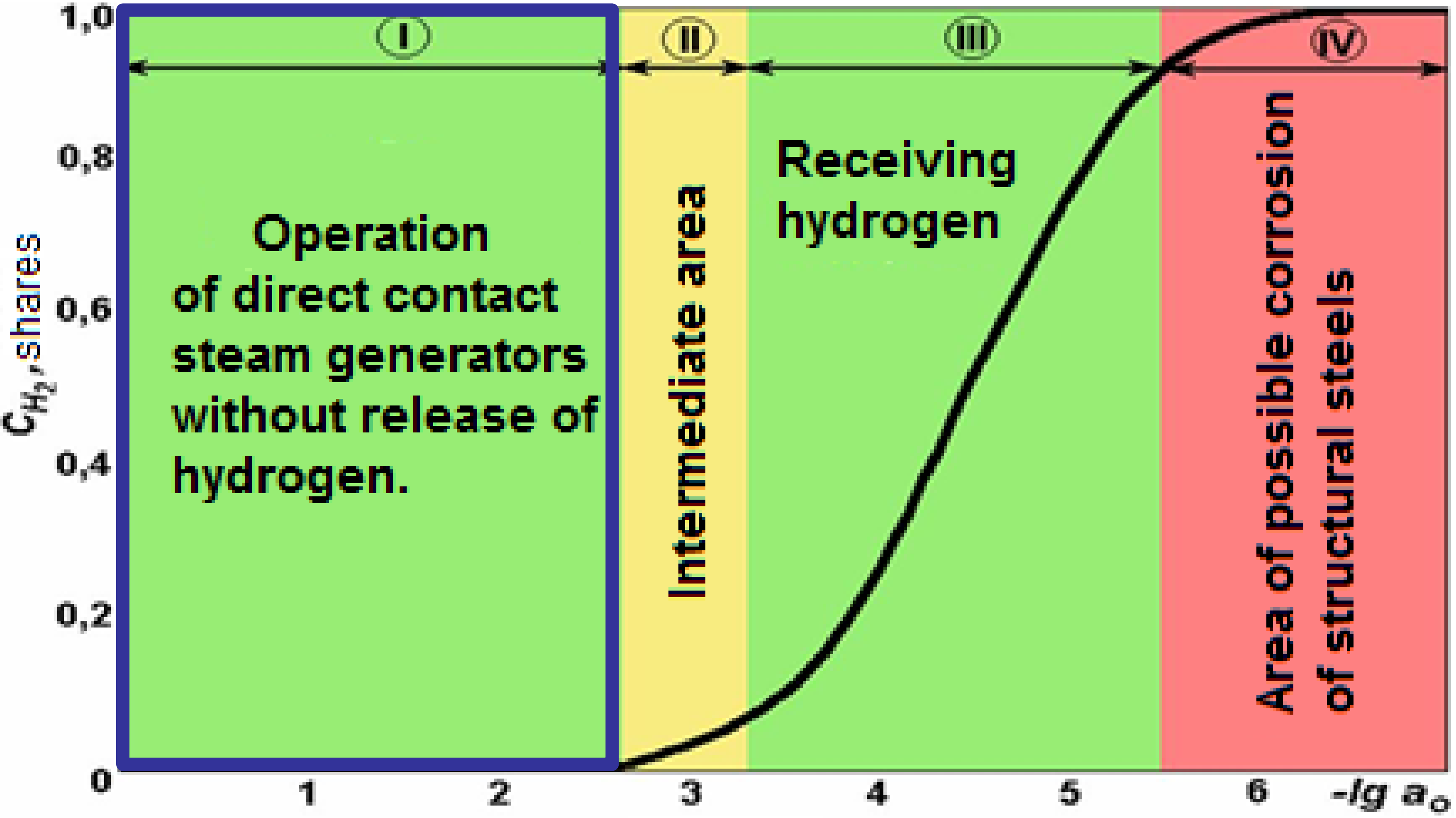
$4CO+8H_2$ on Fischer-Tropsh's synthesis

$4CO+8H_2=2C_2H_4+4H_2O+Q_{сфт}$

$$2O_2+4CH_4\xlongequal[\text{Pb, Catalyst}]{t=1000°C}4CO+8H_2+Q$$

# Thermodynamics of LBE interaction with the "$H_2$-$H_2O$" mixes

$$(H_2O) + \{Pb\text{-}Bi\} \rightarrow (H_2) + [O] + \{Pb\text{-}Bi\}$$

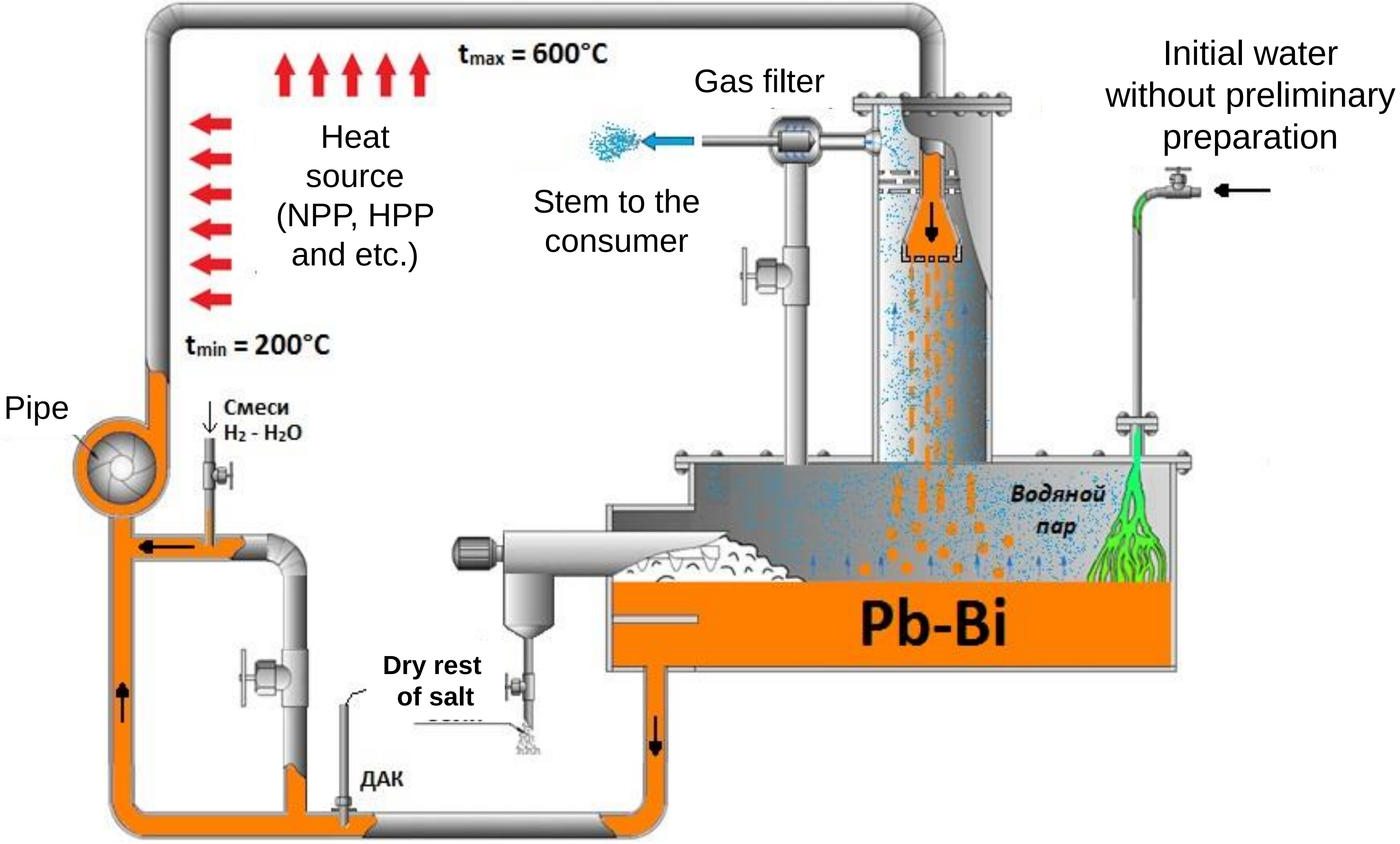


$$a = \frac{C_O}{C_{OS}}$$

**Zone I – optimum conditions for operation of direct contact steam generators.**

Zone III – the optimum content of oxygen for hydrogen generation.

# Direct contact distillation of water without preliminary preparation



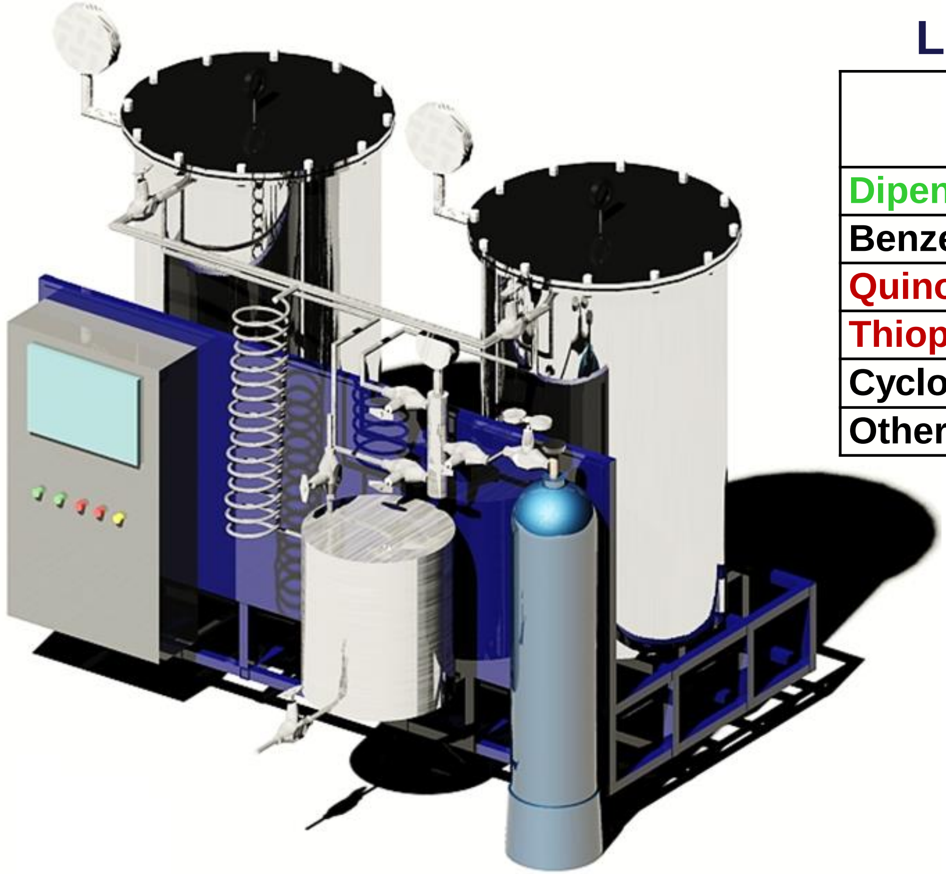
During the work in "zone I" LBE is chemically inert for water. LBE just the highly effective heat carrier. Direct contact distillation of water till the dry rest is perspective for fields of slate hydrocarbons and as a finishing step of desalting together with the return osmosis.

# Content of impurity in water condensate

| The defined indicator | Units of measure | Incoming water | Water after desalting | Hygienic standard, no more |
|---|---|---|---|---|
| **pH value** | pH | 6,01±0,20 | 5,2±0,20 | 6-9 |
| **General mineralization (dry rest)** | mg/dm³ | 39400±8200 | 469±42 | 1000 (1500) |
| **Permanganatny oxidability** | mgO/dm³ | 1,20±0,24 | 35,8±7,16 | 5,0 |
| **Alkalinity** | mmol/dm³ | 0,40±0,05 | < 0,1 | (0,5-6,5) |
| **Total hardness** | °H | 0,50±0,08 | < 0,1 | 7,0 (10) |
| **Iron (Fe totally)** | mg/dm³ | 0,29±0,06 | < 0,1 | 0,3 (1,0) |
| **Fluorides ($F^-$)** | mg/dm³ | 0,93±0,13 | < 0,1 | 1,5 |
| **Sulfates ($SO^{2-}_4$)** | mg/dm³ | 11±2 | < 10 | 500 |
| **Manganese (Mn totally)** | mg/dm³ | 0,035±0,0009 | < 0,01 | 0,1 (0,5) |
| **Lead** | mg/dm³ | - | 0,025±0,003 | 0,03 |

The results of researches of tests of water in the center of hygiene and epidemiology, Obninsk

# Pyrolysis of car tires in HLMC



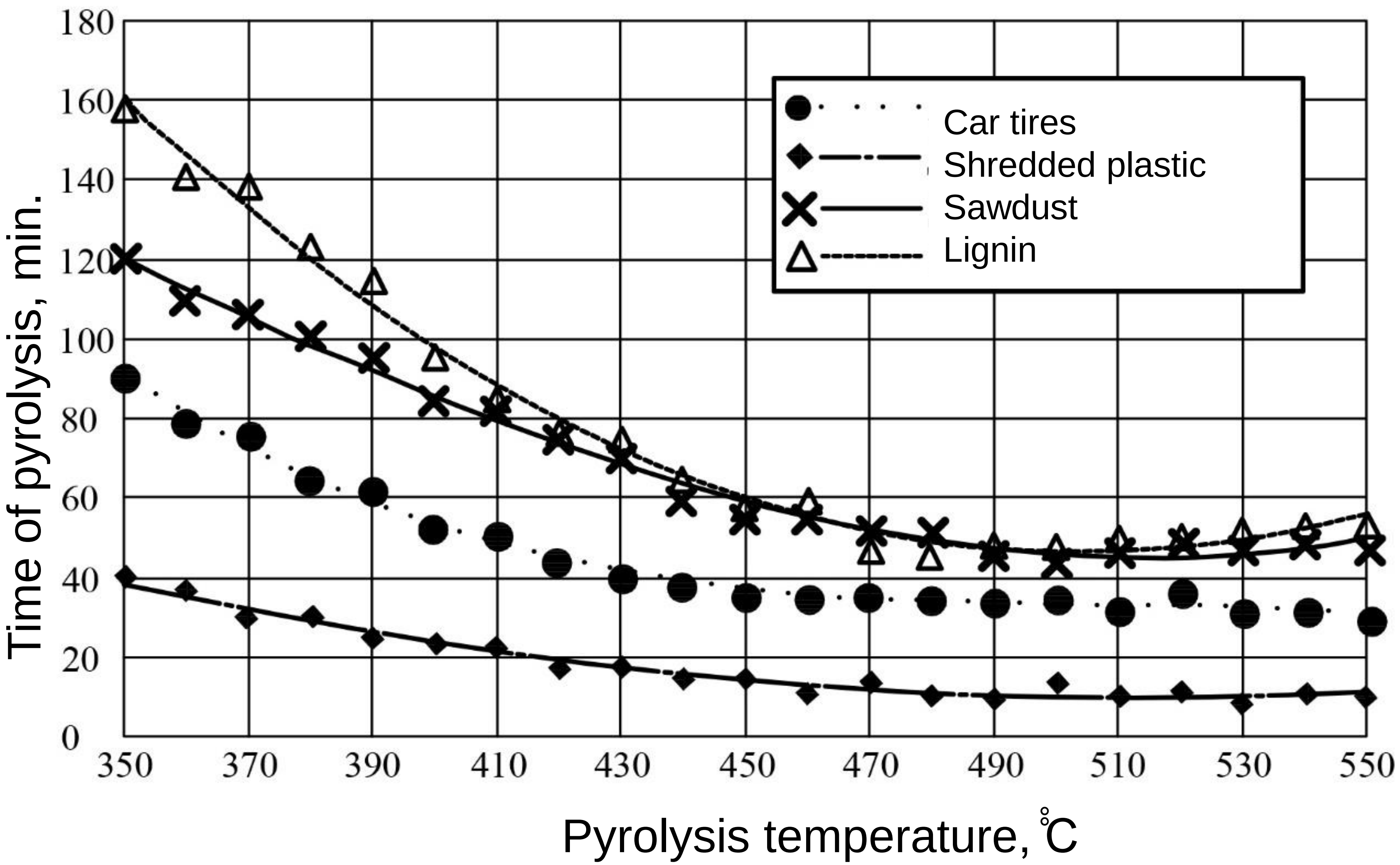
## Liquid products of pyrolysis of car tires, %mass.

| Chemical compound | Pyrolysis in lead | Traditional pyrolysis in gas |
|---|---|---|
| Dipentene | 5,3 | 0,3 |
| **Benzene** | 25,4 | 29,9 |
| **Quinoline $C_9H_7N$** | 0,3 | 3,3 |
| **Thiophene $C_4H_4S$** | 0,2 | 6,7 |
| **Cycloalkanes, alkanes, C8-C20** | 18,3 | 18,2 |
| **Others** | 50,5 | 41,6 |

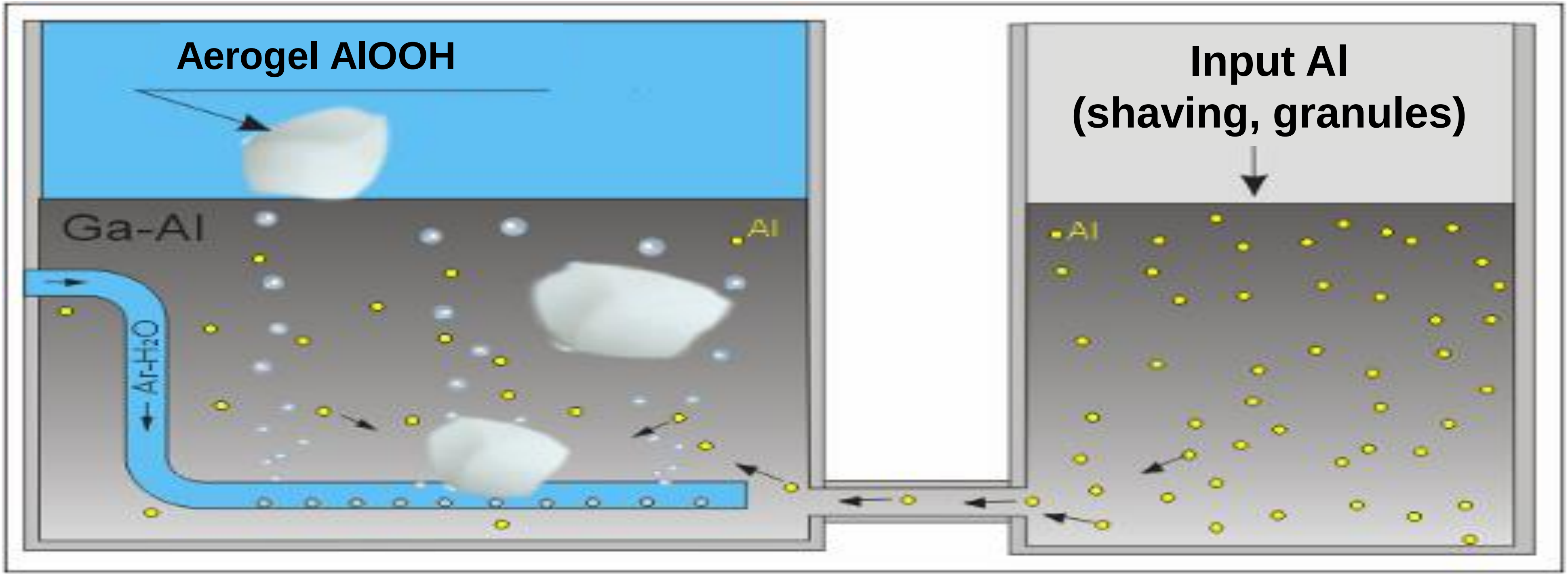
## Dipenten at primary to distillation, %mass.

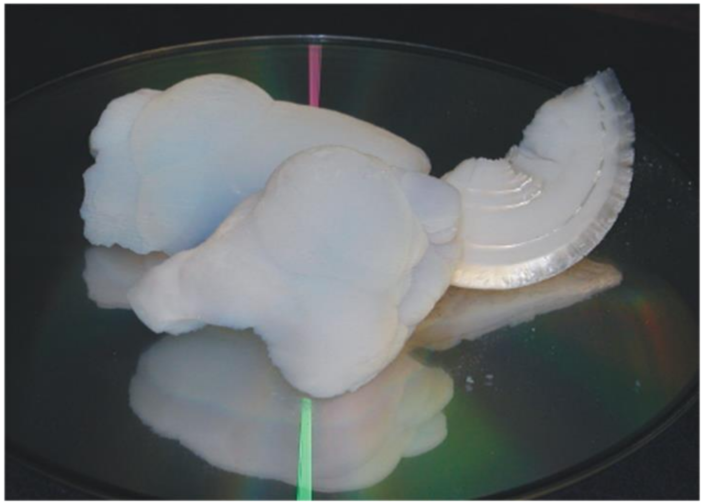
| T, °C | At traditional pyrolysis in gas | At pyrolysis in lead |
|---|---|---|
| **340** | - | 17,4 |
| **370** | 0,4 | 22,7 |
| **400** | 0,6 | 25,2 |
| **420** | 0,7 | 26,1 |
| **450** | 0,9 | 25,8 |

# Pyrolysis of solid organic waste in HLMC



# Receiving oxidic nanomaterials in liquid metals



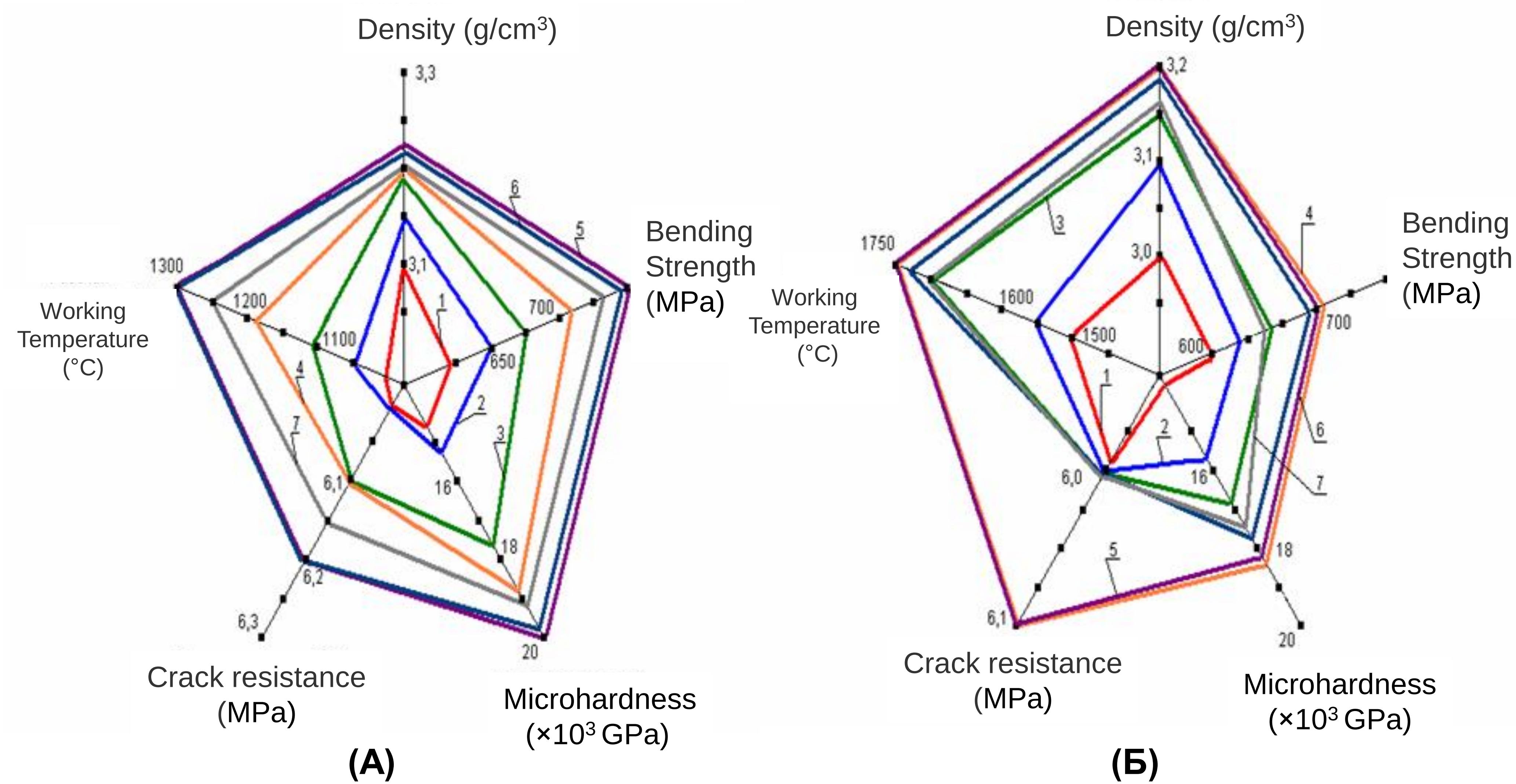


***1 stage.*** Dissolution in liquid metal (matrix) of metal (reagent), **{Me'}+ [Me'']**

***2 stage.*** Oxidation of the dissolved metal water vapor:

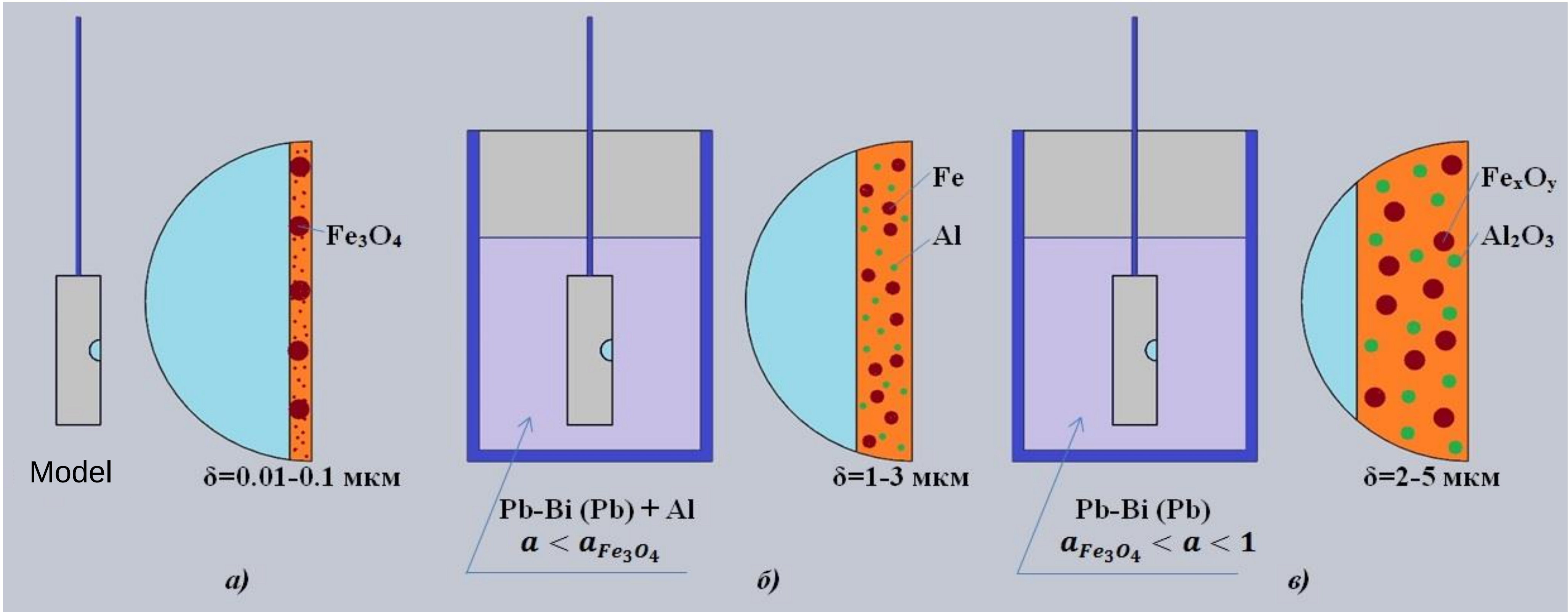
$$\{Me'\}+[Me'']+H_2O = \ =\{Me'\}+<Me''_xO_y> +H_2$$

# Influence of additives of AlOOH aero gel in the powders $Si_3N_4$ (A) and SiC (B) on properties of the received ceramic materials

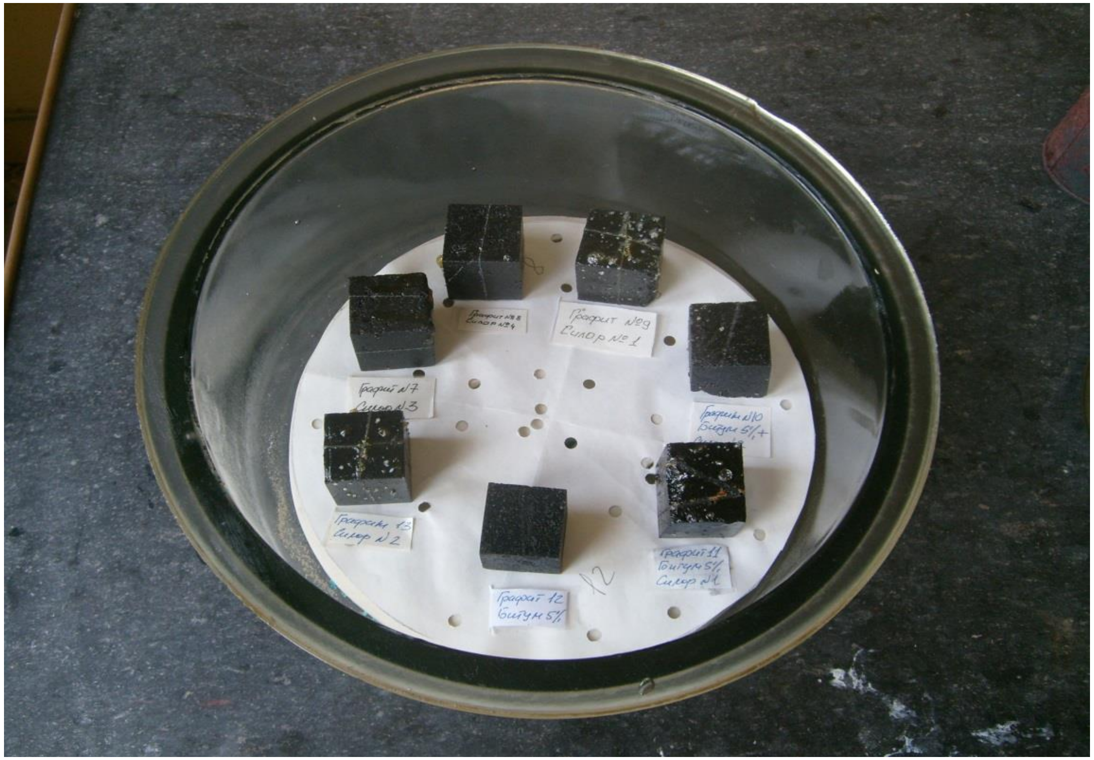


**1 – additive is absent; 2 – 0,5 % mas.; 3 – 1,0 % mas.; 4 – 1,5 % mas.; 5 – 2,0 % mas.; 6 – 2,5 % mas.; 7 – 3,0 % mas.**

# Creation of protective anticorrosive films



# Use of liquid metal for modifying of coal anodes of aluminum electrolyzers

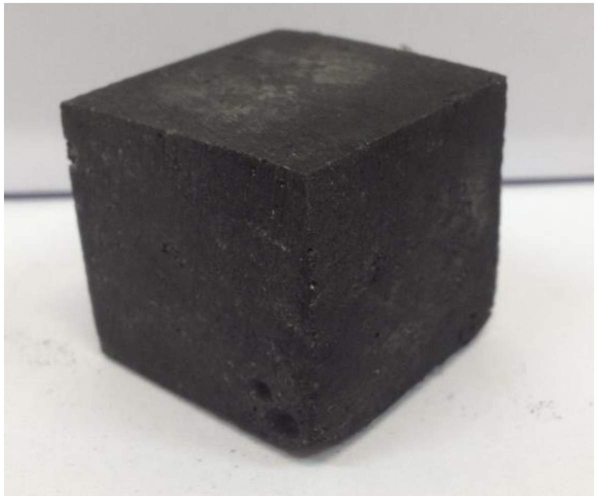


## The impregnated samples of anodes

**The impregnating organic liquids:**

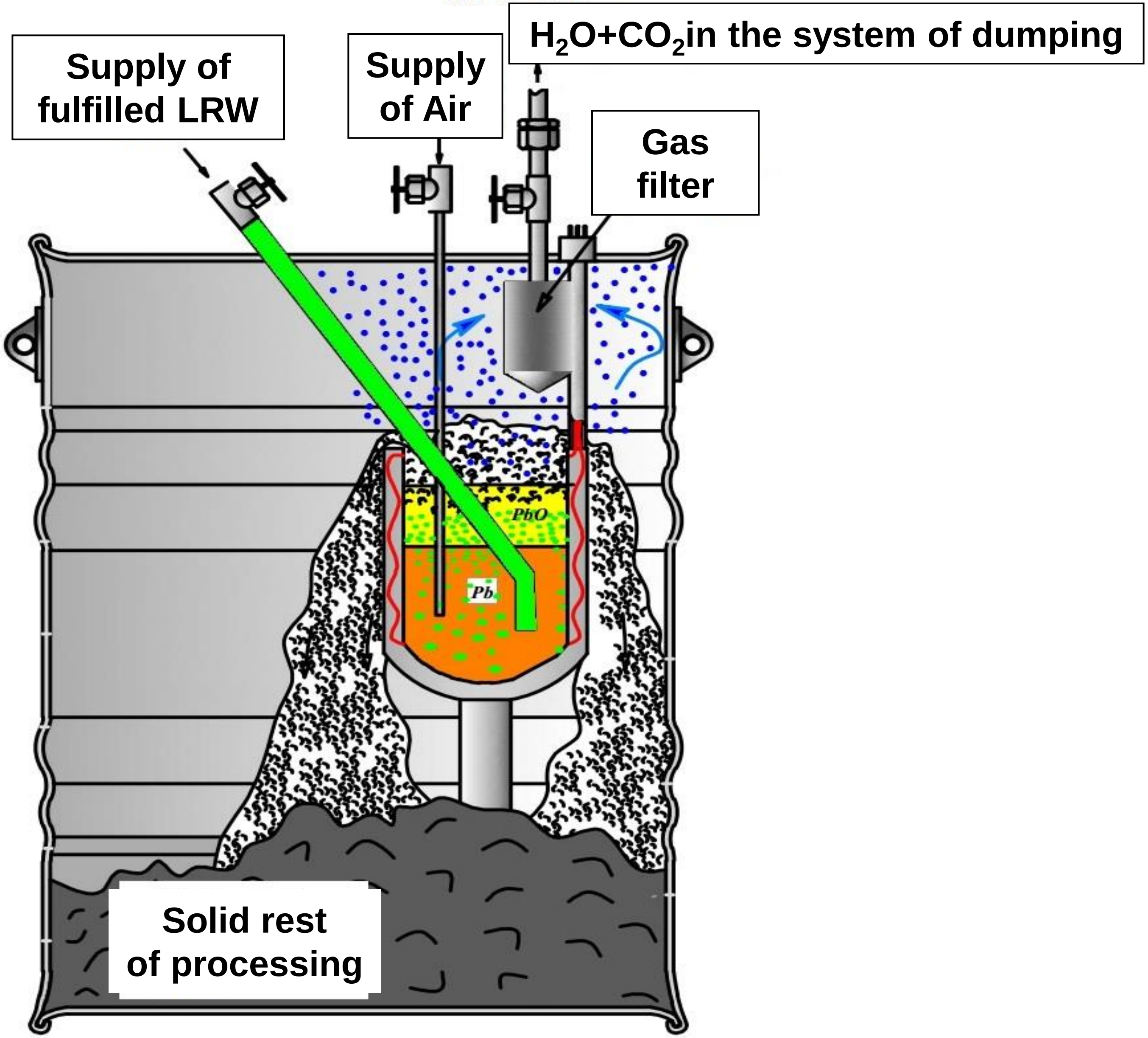
- **bitumen,**
- **compositions of the Silor — Ultra brand,**
- **carbide - phenolformaldehyde,**
- **epoxy, polyester resins**

**Anode sample after pyrolysis in the deoxidated Pb-Bi**

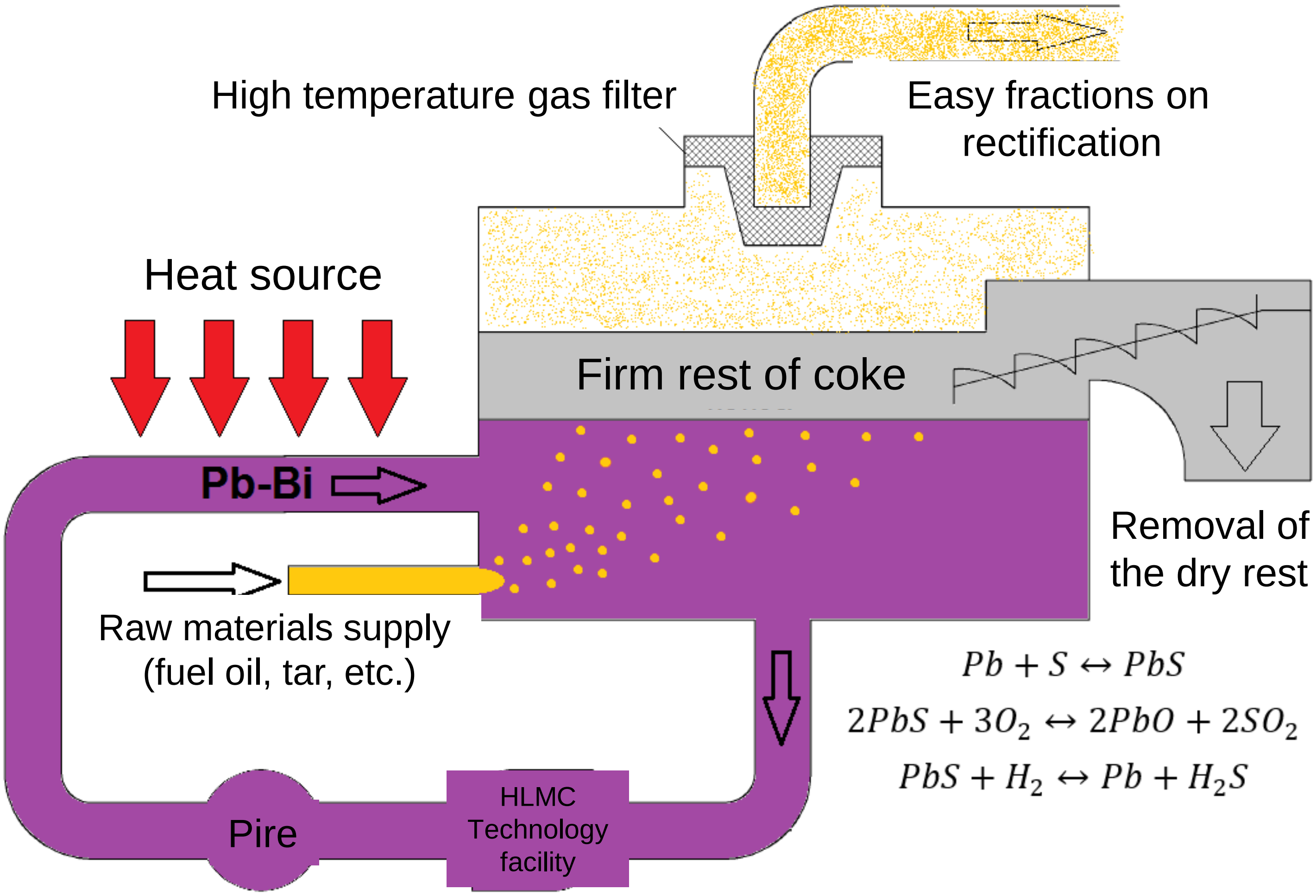


**Anode sample after pyrolysis in the oxidized Pb-Bi**

# Liquid metal copper – an immobilizator of waste



# Installation of direct contact processing of oil products



$$Pb + S \leftrightarrow PbS$$

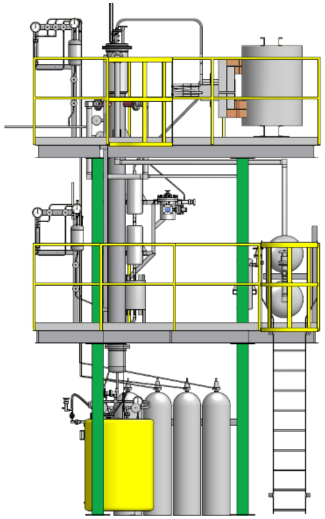
$$2PbS + 3O_2 \leftrightarrow 2PbO + 2SO_2$$

$$PbS + H_2 \leftrightarrow Pb + H_2S$$

In Russia depth of oil refining doesn't exceed 68-70%, against 90% to the USA and 80% in the European Union.

Increase in depth of processing from 65% to 70% provides saving 30 million t of oil.

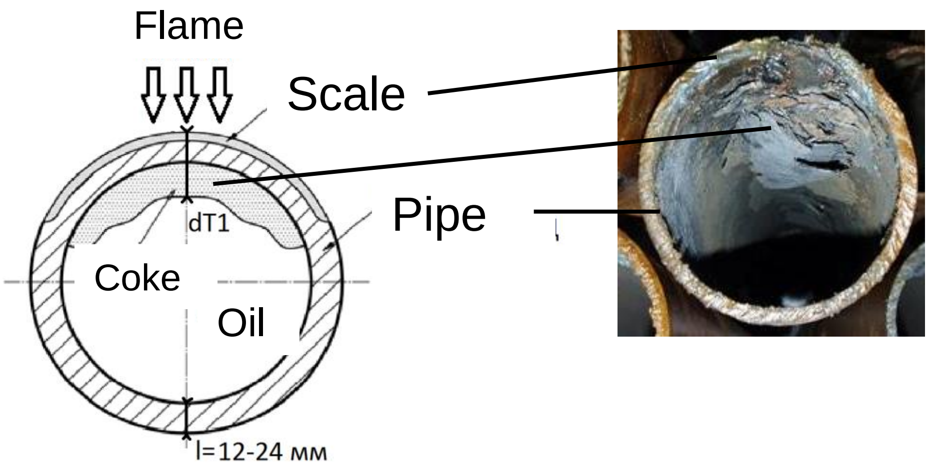
The Russian oil contains a lot of sulfur that does it less valuable.

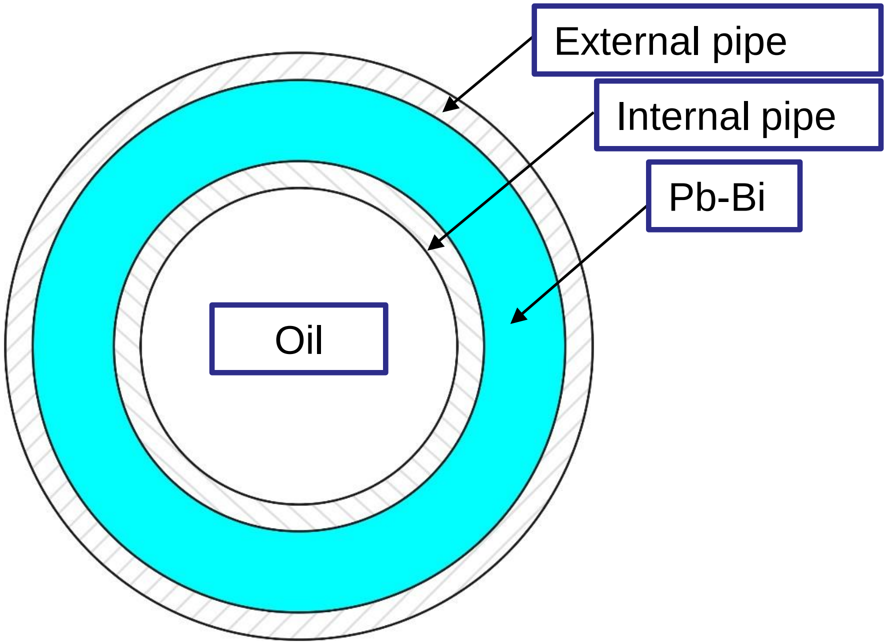


Settlement and pilot researches are conducted. The engineering design of Installation of direct contact processing of oil products in relation to conditions of concrete oil refineries is created.

# Tubular furnaces of oil fire heating

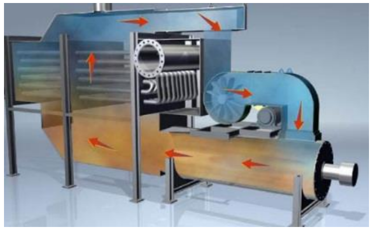
The tubular furnace is used in oil-processing industry. It is intended for heating of hydrocarbons raw materials up to the temperatures of 350÷500 ℃. Heating of pipes occurs due to the combustion of liquid or gaseous fuel in the combustion chamber.





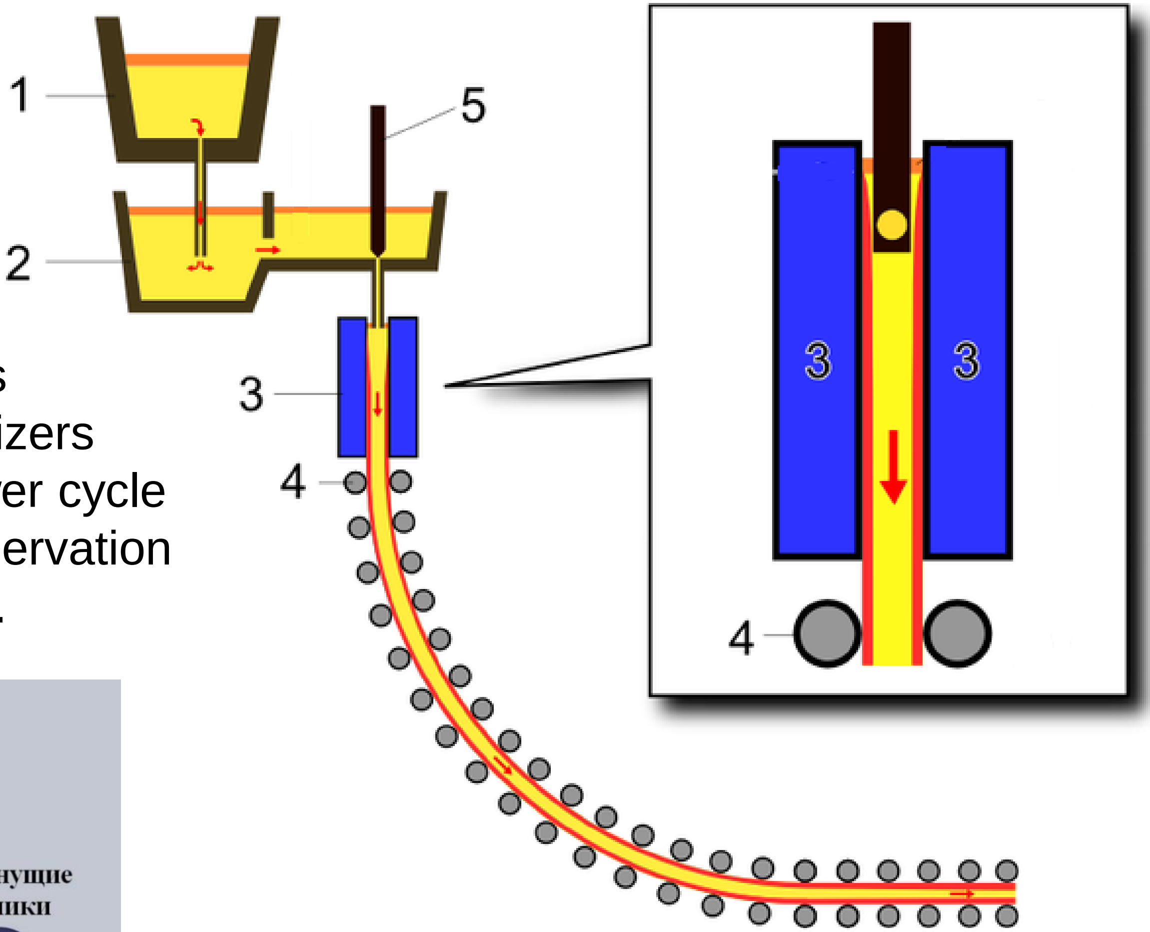
The main problem at operation of such furnaces – providing uniform (on the section of a heat exchange pipe) heating of raw materials for prevention of local coke production.

*The offered design of a heat exchange pipe for furnaces of fire heating of oil*

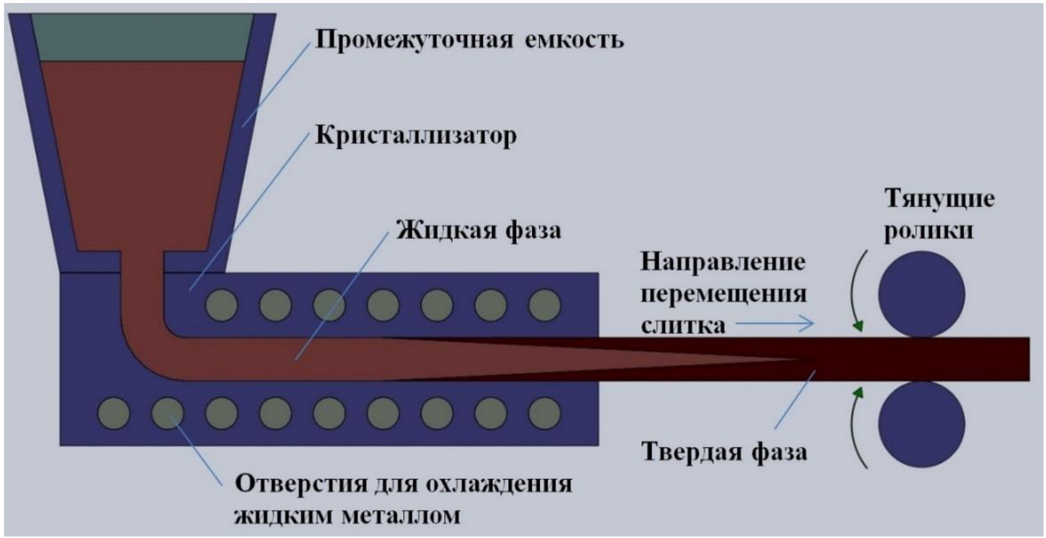


# Utilization of heat of crystallizers of steel

The crystallizer serves for primary cooling of the spilled steel. The heat removal flow is about 430 MJ per one ton of liquid steel. Water acts as coolant of a crystallizer. Water temperature at the inlet of a crystallizer is 20÷45°C. Water temperature at the outlet of a crystallizer is 60÷95°C. Transition to the lead for crystallizers coolant will allow to carry out a steam-power cycle for generation of the electric power at preservation of the minimum pressure to a cooling loop.



***Scheme of installation of continuous casting.***
***1 — the Ladle of supply of liquid metal.***
***2 — the Intermediate ladle.***
***3 — the Crystallizer.***
***4 — the Pulling rollers.***
***5 — the Stopper.***



# Conclusion

1) For maintenance of purity of the first contours of reactor installations and research stands with lead-bearing coolants use of hydrogen containing gas mixes is proved.
2) The greatest efficiency of cleaning is reached at input of gas mixes in heat carrier volume. Designs of the input equipment of gas in heat carrier volume for various designs of reactor installations and research stands are proved.
3) The scientific reserve created at justification of technology of lead-bearing heat carriers has allowed to pass to development of new technologies of processing of solid, liquid and gaseous organic raw materials at his direct contact with lead-bearing fusion.
4) The prospects of liquid metal technologies of distillation of water without preliminary preparation, thermoelectrochemical water decomposition, receiving synthesis gas from organic raw materials, creation of nanomaterials, processing of oil products, pyrolysis of solid organic waste are proved.
5) The possibility of use of intermediate lead coolant heat exchangers in crystallizers of steel and at oil refineries is studied.

# Thank you for your attention

РОСАТОМ

V International Scientific and Technical Conference Heavy liquid metal coolants in nuclear
(HLMC-2018)

ГНЦ РФ-ФЭИ

# Application of HLMC in the technology of metal radioactive waste processing

**Authors: Voronin I. A., Melnikov V. P., Yagodkin I. V., A. Posazhennikov M., Lung, A. Yu., Nikolaev A. N.**

**Obninsk**
**9-11 October 2018**

# The purpose and objectives

**Purpose**

Approbation of the method of pyrometallurgical melting of MRO at the experimental melting unit.

**Objectives**

Development of an experimental melting unit including a liquid metal cooling circuit, a melting unit and a gas cleaning system.

Working out the mode of processing of the metal radioactive waste (MRW)

# Relevance

During the operation of nuclear power facilities, materials containing radioactive substances, including various metal structures, are formed. In this case, the classification of the material to radioactive waste excludes reuse, and such materials are subject to disposal. At the nuclear power plant in the normal mode of operation accumulates about 1-2 thousand tons of metal radioactive waste (MRO) per year. They are also formed during the decommissioning of power units, while their volume during the decommissioning of one power unit with a capacity of 1000 MW is not less than 15 thousand tons. In addition, during the repair and modernization of existing facilities, a significant number of MRW are also formed.

To date, nuclear power plants have accumulated about 600 thousand tons of MRW.

The main share of radionuclides 54Mn, 51Cr, 59Fe, determining the radiation situation, is concentrated in corrosion products covering the inner surfaces of the circuit. In case of damaged fuel rods in a VVER-type reactor, the surface activity will be mainly determined by nuclides of fragmentation origin (95Zr, 106Ru, 131I, 137Cs, 140Ba, etc.).

# Existing technology for the processing of MRW

JSC "ECOMET-S" (Pine forest) uses a complex for processing and recycling of metal raw on the basis of an induction furnace, production capacity up to 6000 t/year.

RC "Crystal" (Krasnoyarsk) developed a project of pilot industrial complex on the basis of gas-lift technology, capacity up to 2080 t / year

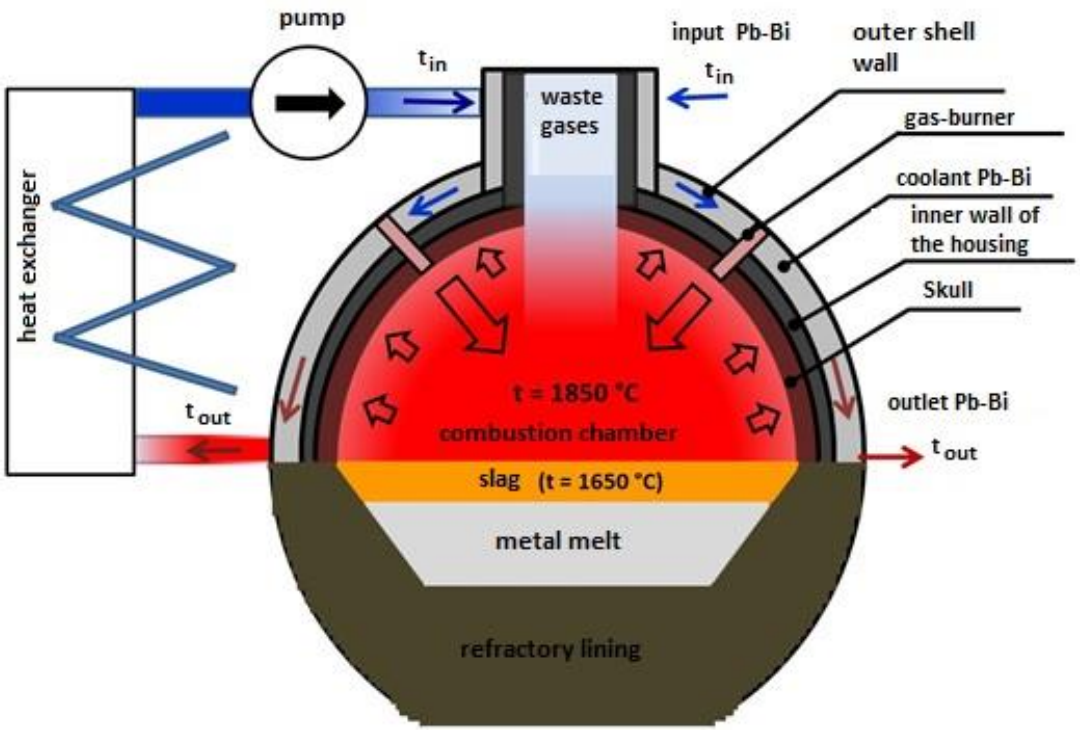
In FSUE "Radon" (Moscow) designed the installation for plasma processing of radioactive waste of complex composition "Pluto", the annual production capacity of 200-250 kg/h.

In OJSC IC«CIPT" (Moscow) the proposed pyrometallurgical plant for the decontamination of MRW on the basis of the fuel and oxygen burners, a design capacity of 50-250 MT/year.

(Industrial partner in Agreement with the Ministry of education and science 2014-2016 years.)

# Substantiation of the possibility of using a heavy liquid metal coolant to cool the melting unit body

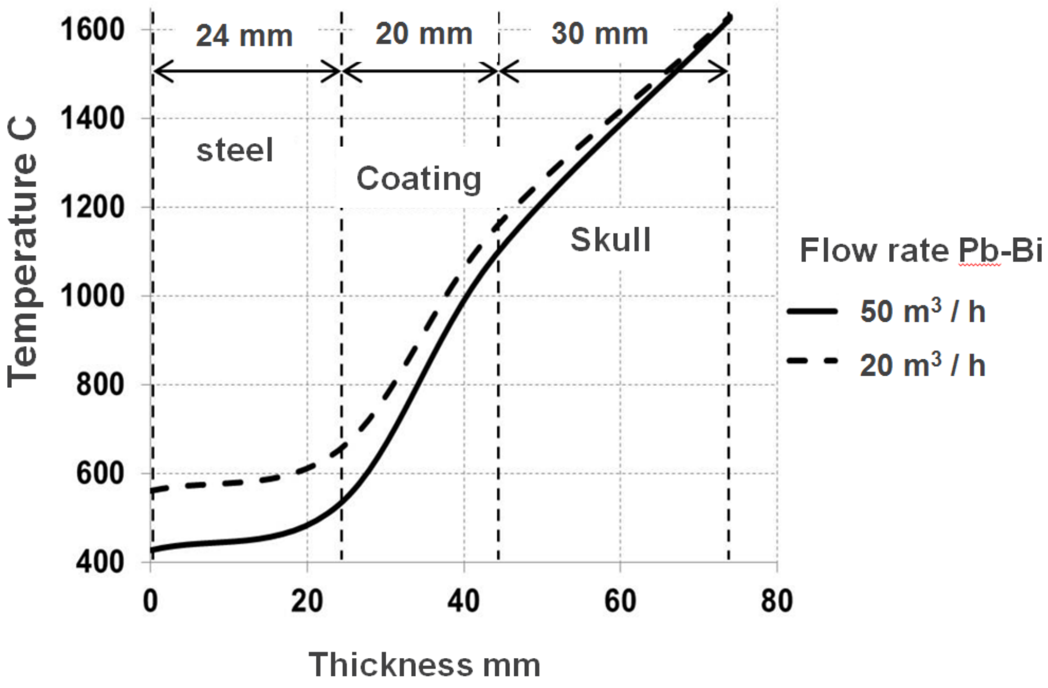
**The cooling system of the steel body of the melting unit eutectic lead bismuth**



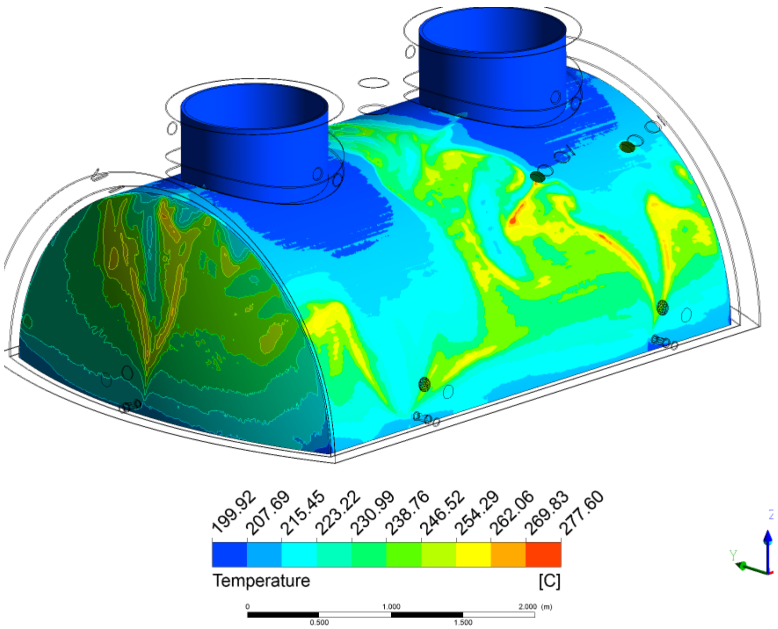
To cool the melting unit, a liquid-metal coolant is used, for example lead-bismuth eutectic. Advantage of application:

- this coolant is effective, allowing heat to be removed at high temperatures and low pressures;
- high boiling point (~ 1670 ° C) the heat-removal crisis and dangerous situations associated with steam explosions are practically excluded;
- lead-bismuth coolant is explosive and fireproof because of its chemical inertness in relation to water and air;
- has a relatively low melting point (~ 125 ° C)

# Calculated estimates of the temperature distribution during cooling of the melting unit



The distribution of surface temperature inner body



1. Calculated estimates of the temperature distribution during cooling of the melting unit with lead-bismuth coolant are made.
2. 2. When the steel body of the melting unit is cooled by a lead-bismuth coolant, it is possible to maintain the temperature on the inner surface of the body within the permissible range of values.

# Gas cleaning system

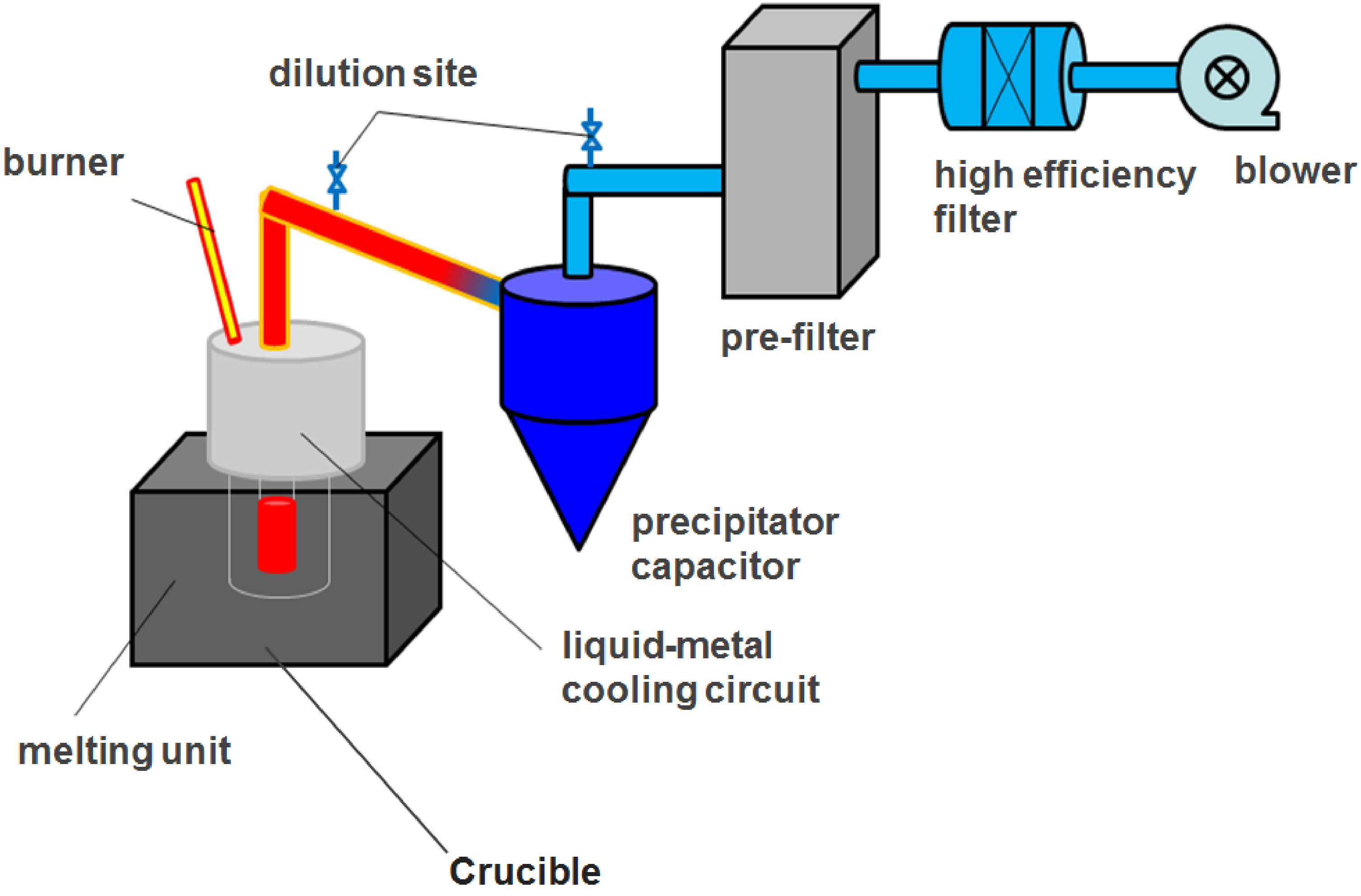
The most widely used in metallurgy methods for cleaning gas media can be divided into mechanical purification, sorption, electrostatic cleaning and purification by means of sound and ultrasonic coagulation.

**Characteristics of gas cleaning devices used at metallurgical plants**

| Device | Dimensions of trapped particles, µm | Cleaning efficiency,% | Upper limit of gas temperature, ºC |
|---|---|---|---|
| Dust suppression chambers | 5 - 20000 | 40-70 | 350-550 |
| Centrifugal dust precipitators | 3 - 100 | 45-85 | 350 - 550 |
| Electrofilters | 0,005 - 10 | 86-99 | 300-450 |
| Hydraulic dust collectors | 0,01 - 10 | 85-99 | 350 - 500 |
| Pocket Filters | 2-10 | 85-99 | up 150 |
| Highly effective aerosol filters | 0,3 | 99,95 | up 150 |

To contain radioactive aerosols contained in the waste gases, it is necessary to use a multicomponent purification system, the components of which operate on different principles.

# Experimental facility



# Test result

| № | Isotope | Specific activity, Bq/g | Specific activity, Bq/g | Decontamination rate |
|---|---|---|---|---|
| 1 | Cs-137 | 216 | ≤0,1 | ≥2160 |
| 2 | Am-241 | 68,6 | ≤0,1 | ≥686 |
| 3 | U-235 | 20 | ≤0,1 | ≥200 |
|  | Total | 322 | ≤0,1 | ≥3220 |

At the outlet from the melting unit, the temperature of the gaseous medium was not less than 1600 ° C, at the exit from the high-efficiency filter no more than 130 ° C, while the efficiency of the final filter was 99.95%

Experimentally shows the implementation of the regime of processing of the MRW to allow the coefficient of reduction – coefficient of 5.35 and decontamination 3220, which exceeds the design value

# Conclusion

1. Confirmed the possibility of using HLMC in the technology of cooling the housing of a melting unit for pyrometallurgical processing of metal radioactive waste.
2. The implementation of the MRW processing regime is experimentally shown to provide a volume reduction factor of 5.35 and a decontamination factor of 3220, which is more than 3 times higher than the design values.
3. It is shown that the average temperature on the surface of the steel from the coolant side will not exceed 600°C in the considered range of coolant flow rates when using the cooling of the melting unit body with lead-bismuth eutectic.
4. A gas cleaning system was developed, which allowed to provide cooling of exhaust gases with a temperature of 1600-1900ºC to 130ºC.
5. The efficiency of the gas cleaning system was 99.95% for the most penetrating particles (0.3 µm).

For preparing this paper we used the results that had been obtained the course of implementation of the project of the Russian Ministry of Education and Science - “Development of a technology of utilization of metal radioactive waste on the basis of melting units with liquid-metal heat removal”. The unique identifier of PNIER (Applied Research and Experimental Developments) is RFMEFI62614X0002.

# Thank you for your attention

# The immobilization of the ash residue produced as a result of processing radioactive ion-exchange resins in a lead melt

**Skomorokhova S.N., Trifanova E.M., Sitnikov I.V., Nikolaev A.N., Askhadullin R.Sh.**

**«Heavy liquid metal coolants in nuclear technology» (HLMC-2018)**

**October 8-10, 2018, Obninsk**

**Joint Stock Company "State Scientific Centre of the Russian Federation – Institute for Physics and Power Engineering named after A.I. Leypunsky"**

# Relevance

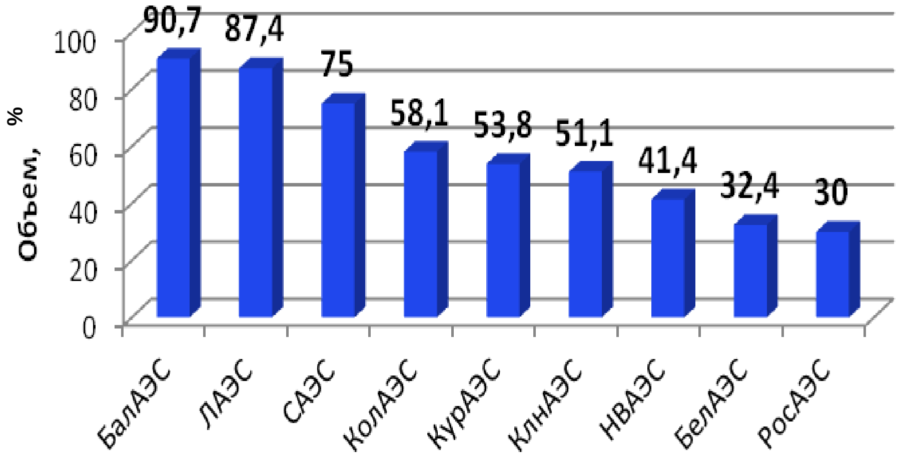
Annually with 1MV 60-70 liters IER

**Total accumulated radioactivity IER - 28,664 $m^3$, which is 65% of the projected volume of existing storage facilities.**

**On average over the past 5 years, nuclear power plants generate 617 $m^3$ of radioactive IER per year.**

**Consumption of IER in SC “Rosatom” in 2012 is 1780 tons/year, in 2016-2020 - 3500 tons/year.**

**Filling of liquid radioactive waste storage facilities ***



**The mass placement of IER at the station already creates additional costs associated with servicing temporary storage facilities. When decommissioning, the IER will be recycled in accordance with the acceptance criteria.**

* From the presentation of A.Yu. Savkin, FSUE «RADON»

# The main methods of processing radioactive IER

Inclusion in matrix materials:

- Cementing;
- Incorporation into the polymer matrix;
- Deactivation.

Destructive ways of processing:

- Pyrolysis;
- Drying;
- Supercritical water oxidation.

- **Direct solidification of the spent IER by cementation or bitumization has been accepted by present as the major processing method.**
- **And cementation is a preferred one, as a rule, due to high radiation stability and noncombustibility of cement binding materials and cement matrix.**
- **A relatively low level of incorporation (usually not more than 10 %wt. in terms of a dry resin for Portland cement matrices) is referred to as the main shortcomings of the IER direct cementation on the basis of traditional binding systems; and it results in the increase of a volume of the solidified products being delivered for storage.**

# Processing of IER in the melt of heavy metals

## 1.Piroliz

- ✓ step-by-step process of removal of unbound and bound water, destruction, pyrolysis of IOS;
- ✓ burned in the presence of lead oxide of hydrocarbons in the off-gas to produce carbon dioxide and water;
- ✓ after the accumulation of a sufficient amount of metallic lead on the surface of the lead oxide pellets, the backfilling of the lead oxide with a stream of air

## 2. Purification of gases

Cleaning of waste gases and condensate from radionuclides and toxic impurities

## 3. Confirmation

Ash, along with the air flow is transported to the mixer.

When filling the mixer add slag-alkaline binders and water.

The resulting solution is mixed and sent to a container for curing and subsequent long-term storage.

The conditions of processing in a melt of heavy metals and their oxides fasten chemical processes of polymer destruction due to the close contact of reagents and stable heat exchange in the reaction mass.

Chemical inertness of lead in contact with water, which concentration in the IER is significant (up to 50-60 %wt.), provides maximum efficient separation of water and discharge of it as a steam to the air conditioning system.

The IER thermal destruction using heavy metal oxides as oxidizers and the absence of the contact with air provides the decrease of a volume of gaseous discharges containing residual components of the air mixed with toxic and radioactive substances.

# The alkali-slag binders

**The alkali-slag binders (geopolymers, geocements) or the cements activated by alkali are unburned binders based on industrial waste. The operational performance of the materials created on their basis is better than that of the Portland cement (PC). They are some of the most efficient versions of clinkerless cements. The extensive raw material base for the production of alkali-slag binders consists mainly of industrial waste of the alumosilicate composition with a high concentration of the amorphous phase – metallurgical slags, ashes, construction waste. The materials combining some properties of glass, ceramics, and artificial neoformations based on traditional inorganic binders are formed as a result of their alkaline activation in the finely dispersed state. The alkali compounds, when their optimum amounts are added, not only play the role of slag activators but also serve as an independent component of an alkali-slag binding system**

The operational advantages of the alkali-slag binders:
strength,
water impermeability,
corrosion resistance,
frost resistance,

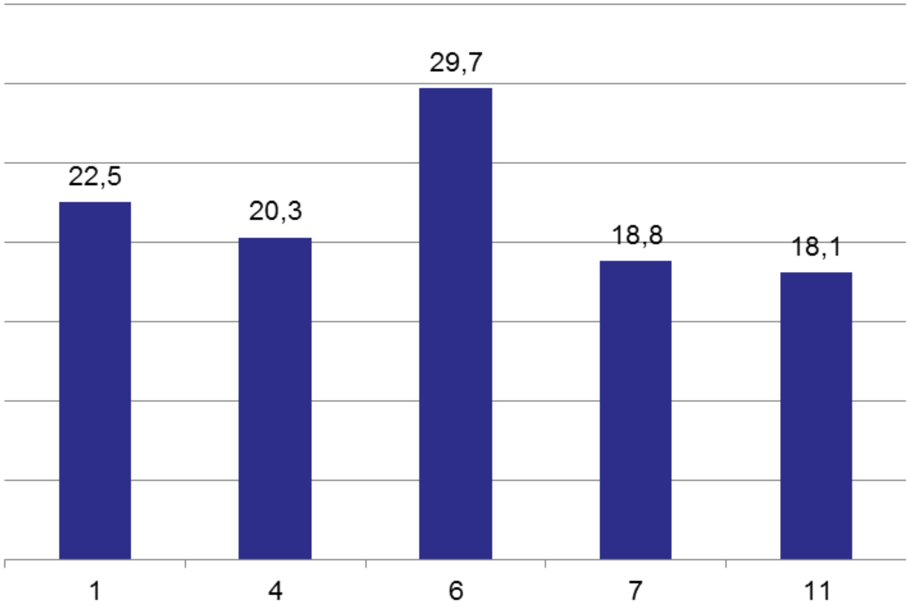
# Methods

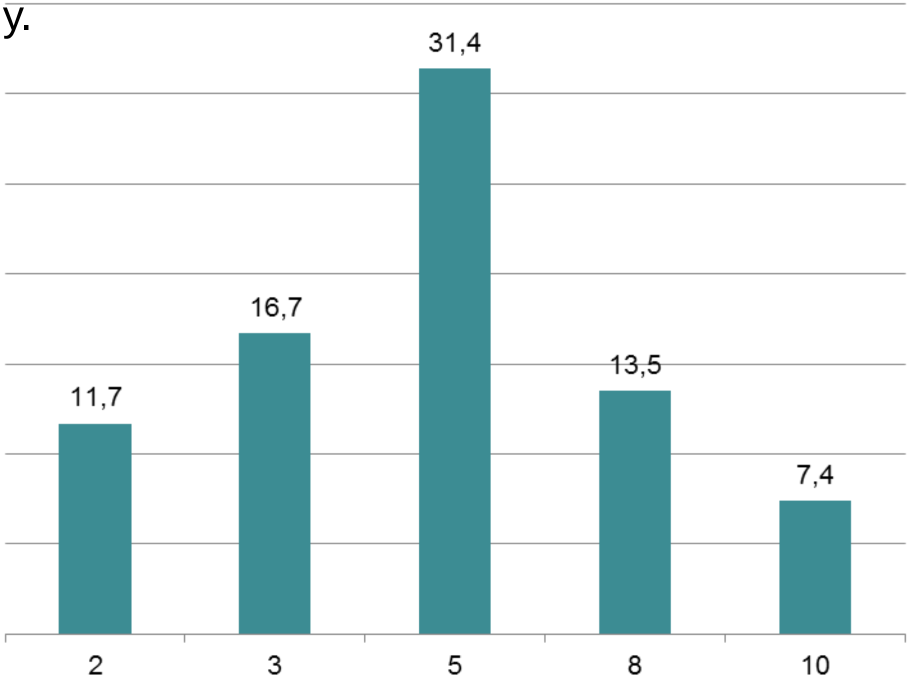
A simulated composition of the spent IER of NPPs was used for the experiments. It was prepared on the basis of KU-2-8 and AB-17 resins by their transition to corresponding salt forms ($Na^+$- and $NO_3^-$-forms as well as $K^+$-, $NH_4$- and $BO_3^{3-}$-forms) by standard techniques – by processing KU-2-8 cationite in $H^+$-form and AB-17 anionite in $OH^-$-form with the saturated solution of a corresponding salt.

- Recipes were developed for the ash residue immobilization into a cement compound, and a batch of materials was prepared for making two types of the alkali-slag binding systems on the basis of slag-Portland cement (Portland cement of “PC-500”) and blast-furnace slag (granulated slag of the blast-furnace process.

# Test results for mechanical strength

The samples synthesized on the base of two types of alkali-slag binding systems with the ash residue concentration from 36.0%wt. to 46.4%wt. feature mechanical compression strength, which exceeds considerably the value specified by regulations (≥5 MPa). The mechanical strength of the samples with the highest achieved capacity for the ash residue (46.4%wt. and 45.6%wt.) features the values of 18.1 MPa and 13.5 MPa, respectively.





**Specifications of samples of the compounds based on slag-Portland cement**

| Sample No. | 1 | 4 | 6 | 7 | 11 |
|---|---|---|---|---|---|
| Ash concentration in the compound composition, %.wt. | 44,1 | 40,9 | 41,4 | 42 | 46,4 |

**Specifications of samples of the compounds based on the granulated blast-furnace slag**

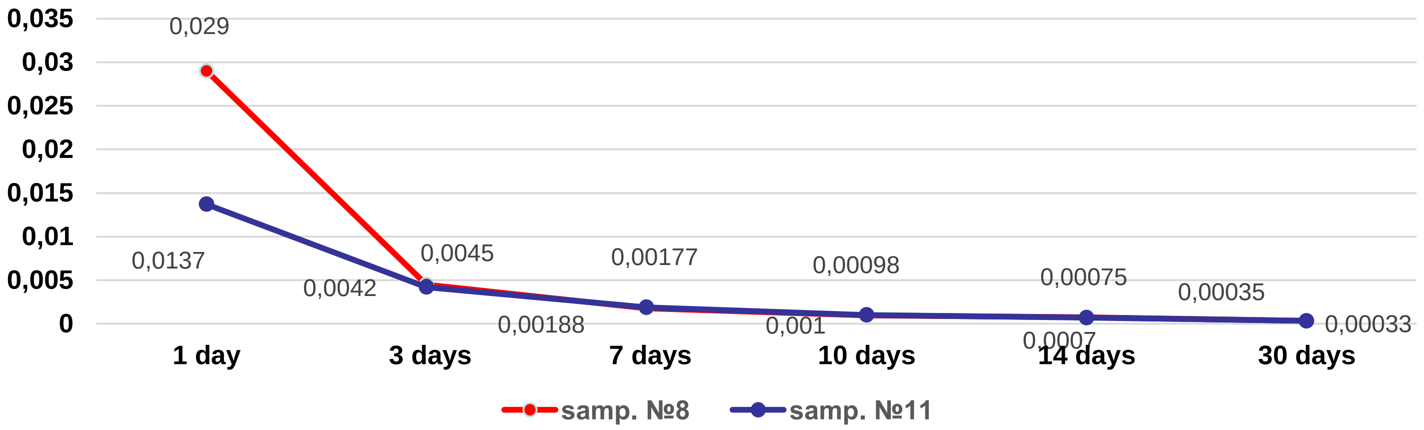
| Sample No. | 2 | 3 | 5 | 8 | 10 |
|---|---|---|---|---|---|
| Ash concentration in the compound composition, %.wt. | 36,0 | 41,6 | 43,4 | 45,6 | 40,4 |

# Leach rate

- The results of measurements of a rate of $^{137}$Cs leaching from the studied samples of alkali-slag compounds of two types with the highest capacity for the ash residue (45.6%wt. and 46.4%wt.) are given in figure. They reflect high water-resistance of the synthesized compounds featuring the values of ≤1.10$^{-3}$ g/cm$^2$.day already at the forth experimental point (after 10 days storage in the contact solution). This result complies with the regulatory requirements.

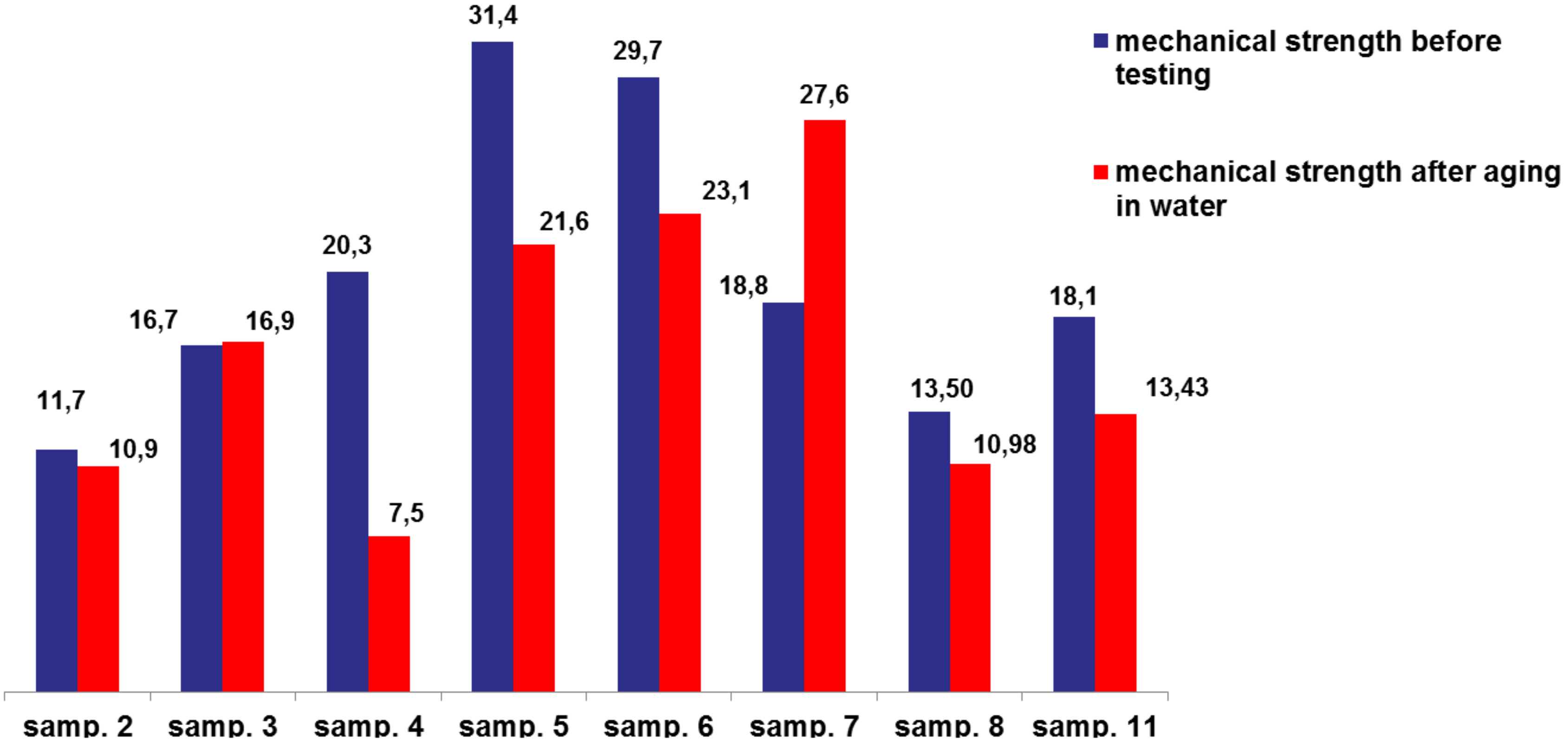
| **No. of samples and recipes** | **№ 8 samples based on the granulated blast-furnace slag. (45.6%wt.)** | **№ 11 – samples based on slag-Portland cement (46.4 % wt.)** |
|---|---|---|

A rate of $^{137}$Cs leaching from the samples of two types of alkali-slag compounds containing 45.6%wt. and 46.4%wt. of the ash residue produced as a result of processing the simulated IER in a lead melt



# The results of testing waterproofness of the alkali-slag compound samples based on blast-furnace slag and slag-Portland cement

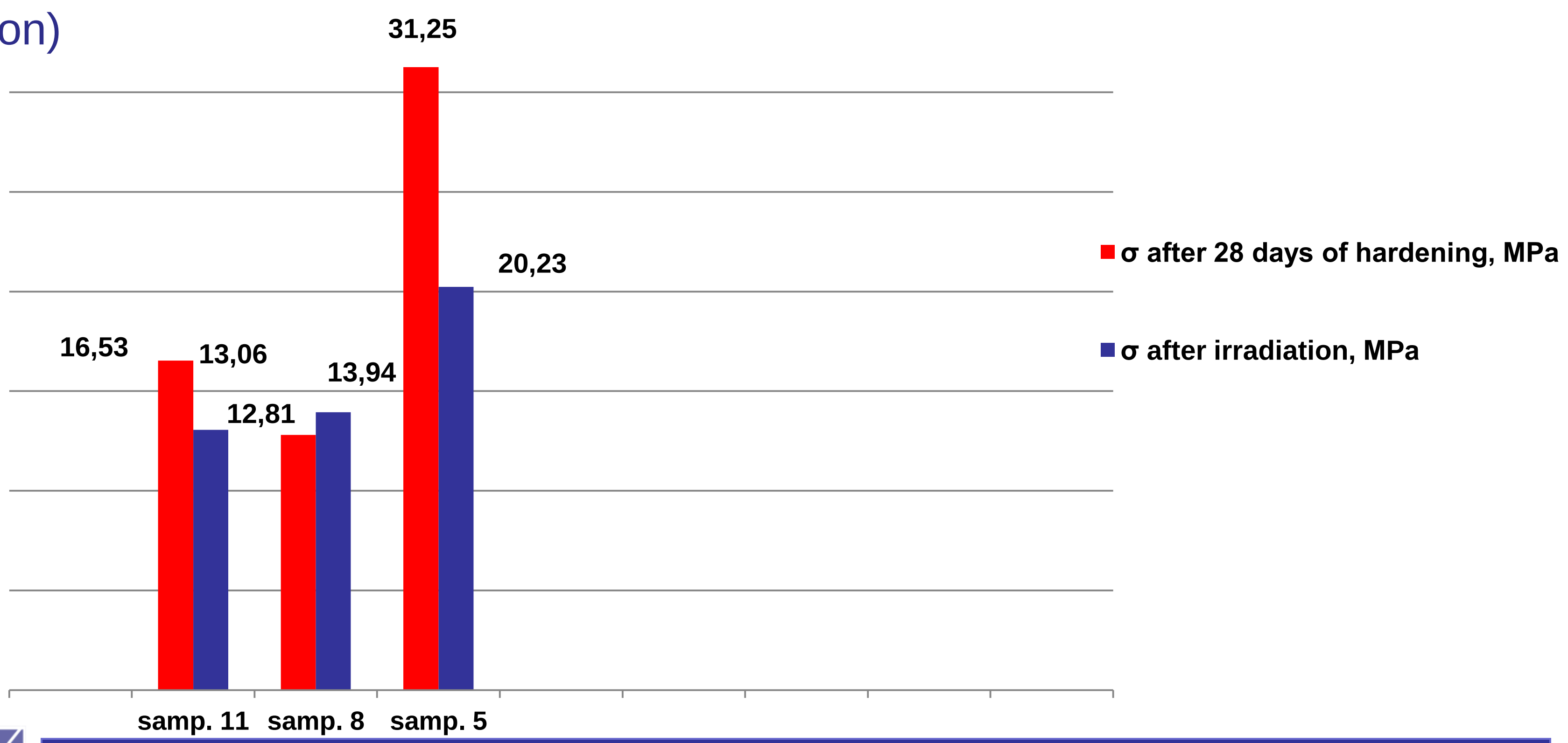
•It follows from the immersion test results that waterproofness of the samples after 90 days storage in water complies with the regulatory requirements for both groups under study and features the values of mechanical compression strength, which exceed the value specified by the regulations by 1.5-4 times.



# Radiation resistance

For the tests for radiation resistance, samples of slag cement alkaline cement compounds, including the ash residue from IER processing, made according to the developed formulations, with a mechanical strength of ≥5 MPa (after 28 days of hardening) were placed in the working chamber of the ‘Kinetik’ facility for irradiation with a $^{60}$Co power source 25 x-ray/sec to a dose of $10^6$ Gy.

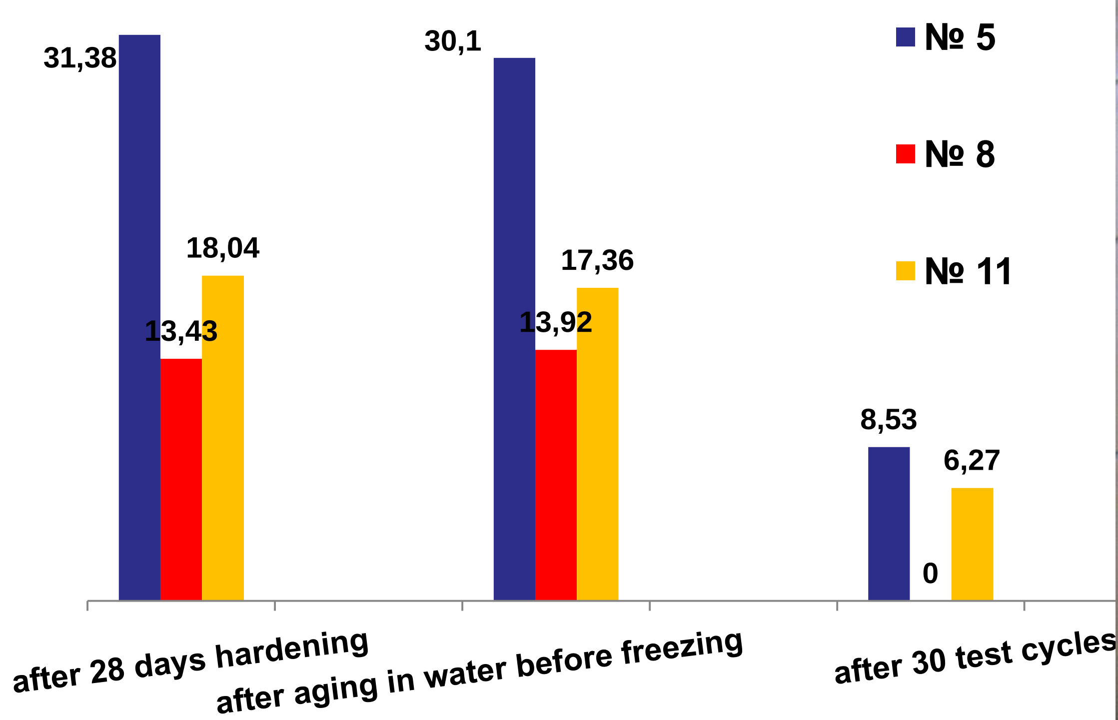
The results of tests of samples of slag-alkali compounds with ash included from the processing of IER, the mechanical strength for compression (before and after irradiation)



# Resistance to thermal cycles

- For carrying out tests for the resistance to thermal cycles in accordance with GOST 10060.1-95, special laboratory samples of slag-alkali waterproof compounds No. 5, 8 and 11, which have the greatest achieved filling of the ash residue from the IER processing according to the adopted method, have been made.
- The produced samples for the strength test were conditioned in normal-humidity conditions for 28 days (temperature 20-25 ° C, relative humidity 100%).

| No. of samples and recipes | № 5 on the basis of a granular slag (43.4% by weight of ash) | № 8 on the basis of a granular slag (45.6% by weight of ash) | №11 on the basis of slag-portland cement(46.4% by weight of ash) |
|---|---|---|---|



- Samples of the series No. 8 did not pass the thermocycling test due to their destruction (shedding of the faces of the samples).

# Conclusion

1. The results of the tests carried out show that the application of alkali-slag compounds of two tested types as a matrix material for the immobilization of the ash residue produced as a result of processing the spent IER of NPPs in a lead melt provides a high level of filling with RAW components and the improved quality of the compounds. These features enable us to recommend the developed recipes for further studies and tests of immobilization of the radioactive ash produced as a result of processing the IER.
2. The synthesized samples of the solidified compounds with the highest capacity for the ash residue (45.6%wt. and 46.4%wt.) comply with the main quality parameters, specified by regulations, of the compounds intended for long-term storage.
3. The developed recipes of the alkali-slag compounds dedicated for the ash residue immobilization make it possible to reduce considerably the volume of the end conditioned product. The total reduction by 13.5 times by volume and by 6.2 times by weight has been achieved as a result of the IER pulp processing and the ash residue immobilization into an alkali-slag compound.
4. It has been estimated that 0.97 tons of the ash residue produced as a result of the IER processing in a lead melt can be incorporated in 1 m$^3$ of the alkali-slag compound of the developed and tested composition based on the blast-furnace finely ground granulated slag.

# Thank you for attention!

РОСАТОМ

ГНЦ РФ-ФЭИ

HLMC - 2018

# THE PROSPECTS OF HEAVY LIQUID METAL COOLANTS USING IN HIGH-POWER INTENSE HEAT EXCHANGERS

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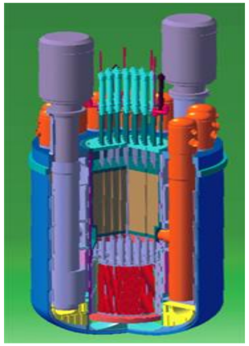
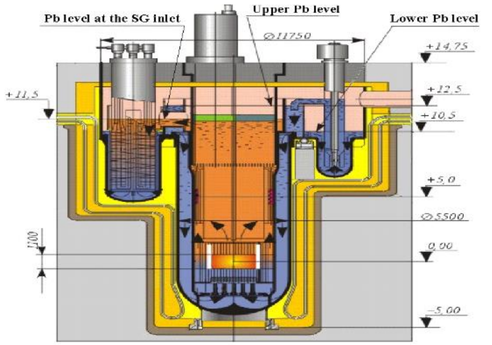
JSC "SSC RF – IPPE“
Obninsk, 2018

# Stages of HLMC technology development

History of heavy liquid metals using as coolants contains more than 60 years.



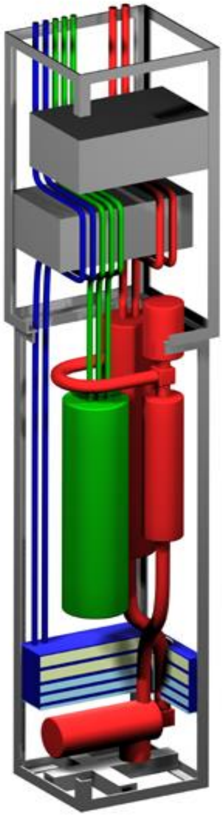


**Stage №1**
**(1951 – 1968)**

**Stage №2**
**(1968 – 1995)**

**Stage №3**
**(1995 – Present)**

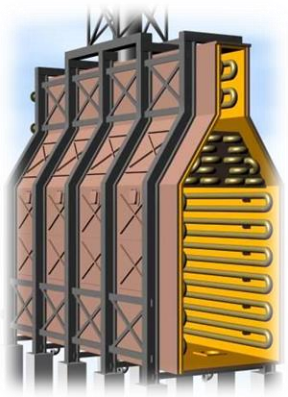
- **Hydrogen power engineering**
- **Perspective heatexchanger**
- **Desalination systems**
- **Utilization of LRW**
- **Processing of oil products**

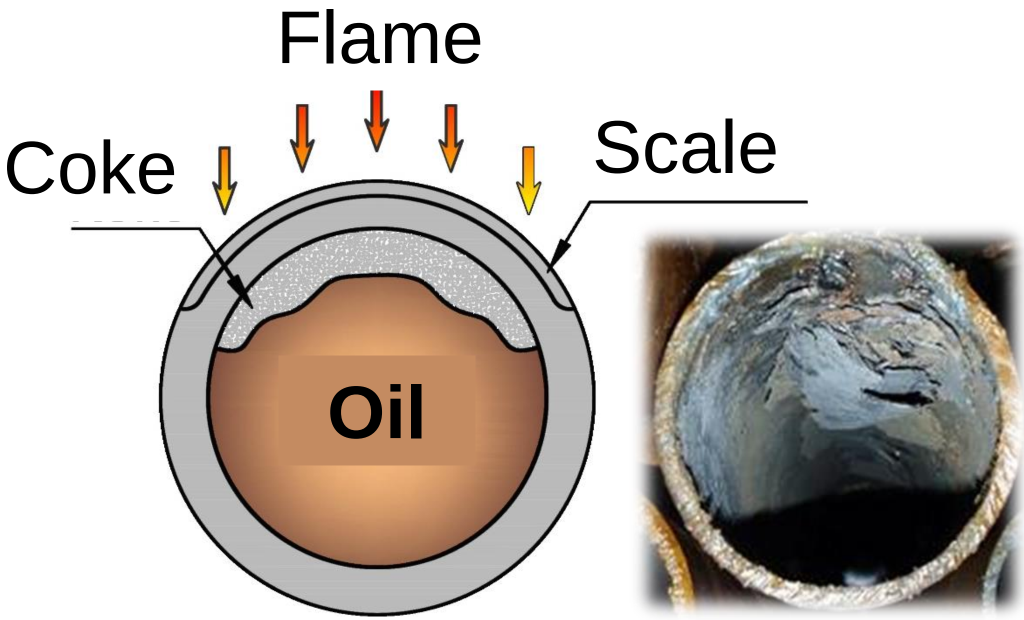


# Tubular furnaces of oil fire heating

The tubular furnace is used in oil-processing industry and is intended for heating of hydrocarbons raw materials (up to the temperatures of 350÷500℃), by open fire heating of a tubular coil by gases in the furnace camera from combustion of liquid or gaseous fuel.

There is a problem at their operation – uneven heating of a heat exchange pipe. As a result there are sites of local overheating. Temperature gradient on an internal surface – to 12℃

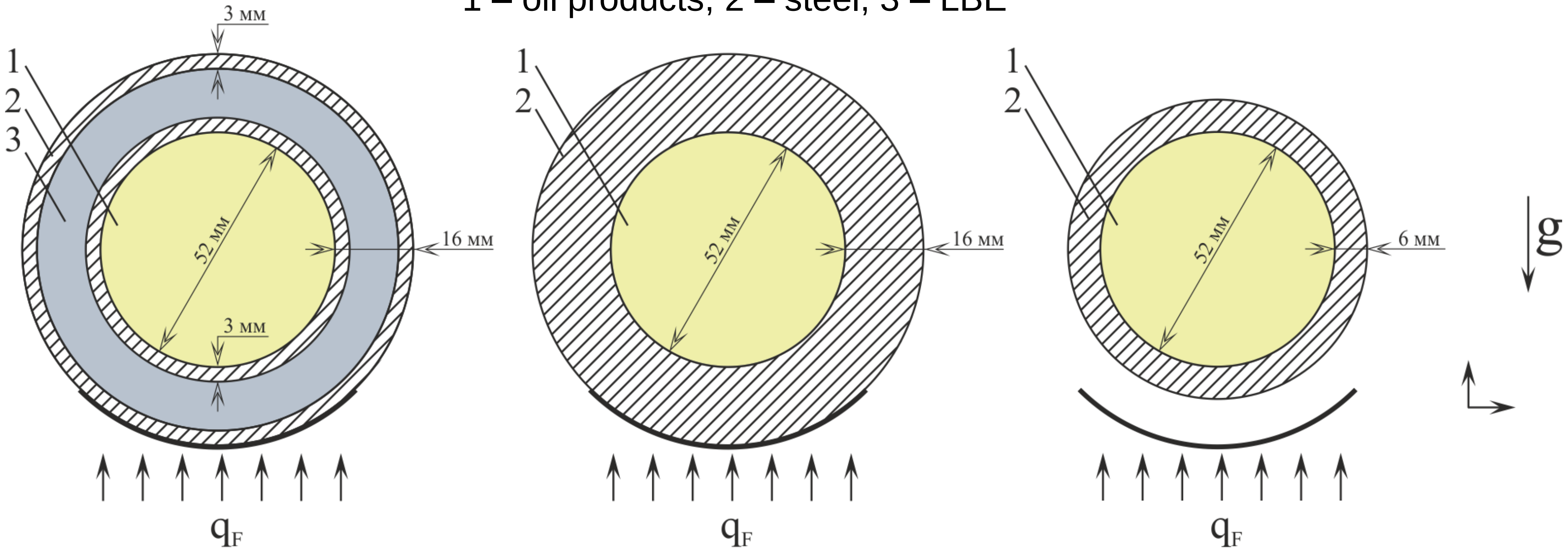




**Problems of fire heating**
**(The Heatexchange pipe of the furnace of fire heating in a section)**

# The calculation conditions

1 – oil products; 2 – steel; 3 – LBE



а) б) в)

*Heat exchange pipe with the ring gap filled lead-bismuth (a), and without ring gap (б, в) in the field of gravity*

Calculation conditions:

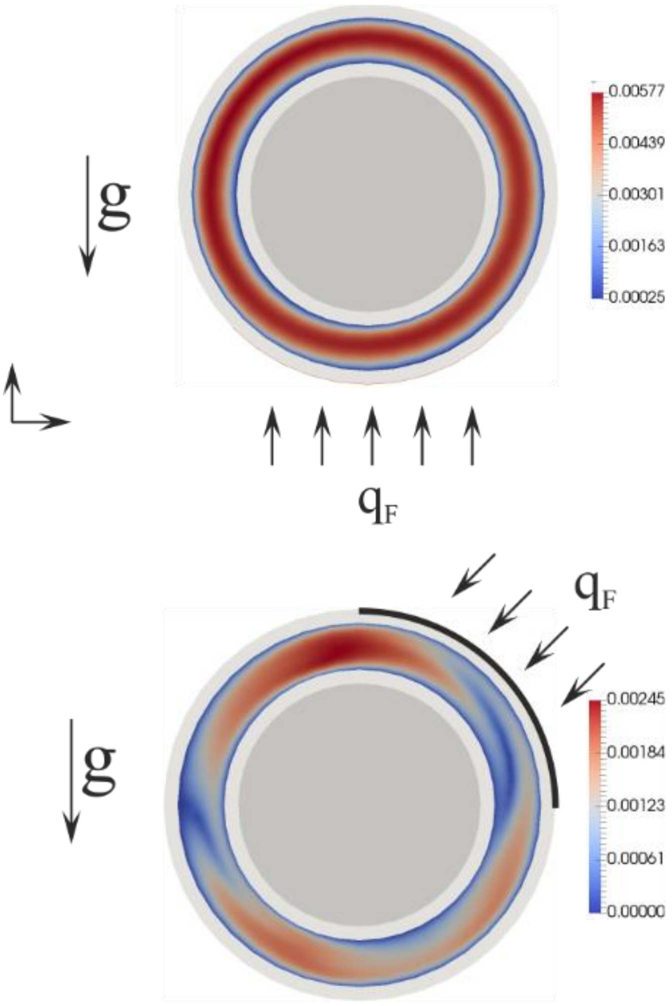
Oil speed on an entrance – 0,1 m/s

Temperature on an entrance – 423 K

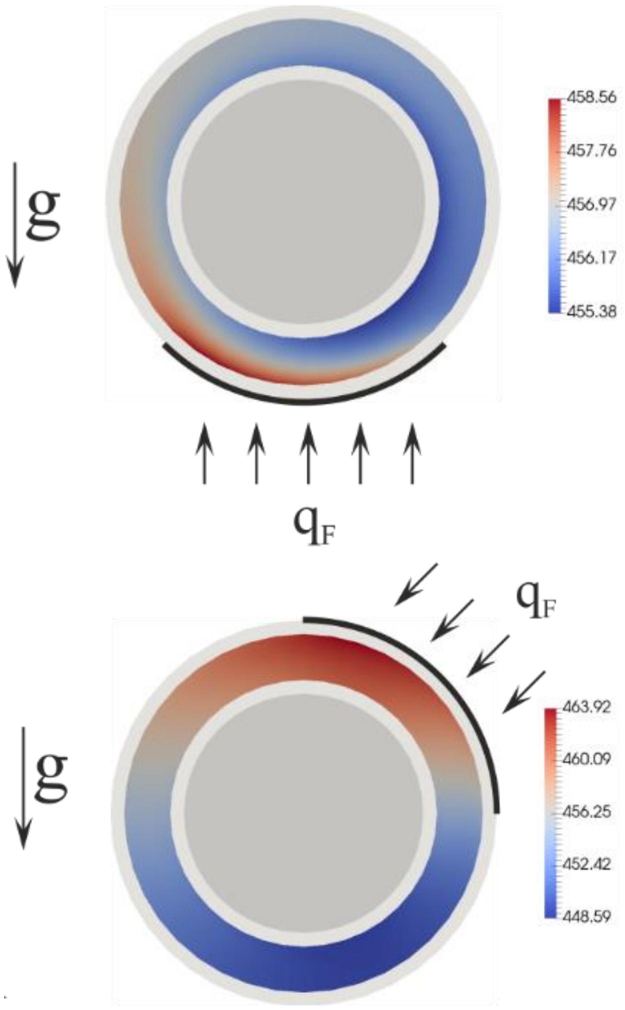
Density of a thermal stream – 4,4 kW/m$^2$

# The calculation results of the pipe with a ring gap

Distribution of the coolant speed (m/s) in a ring gap



Distribution of the coolant temperature (K) in a ring gap



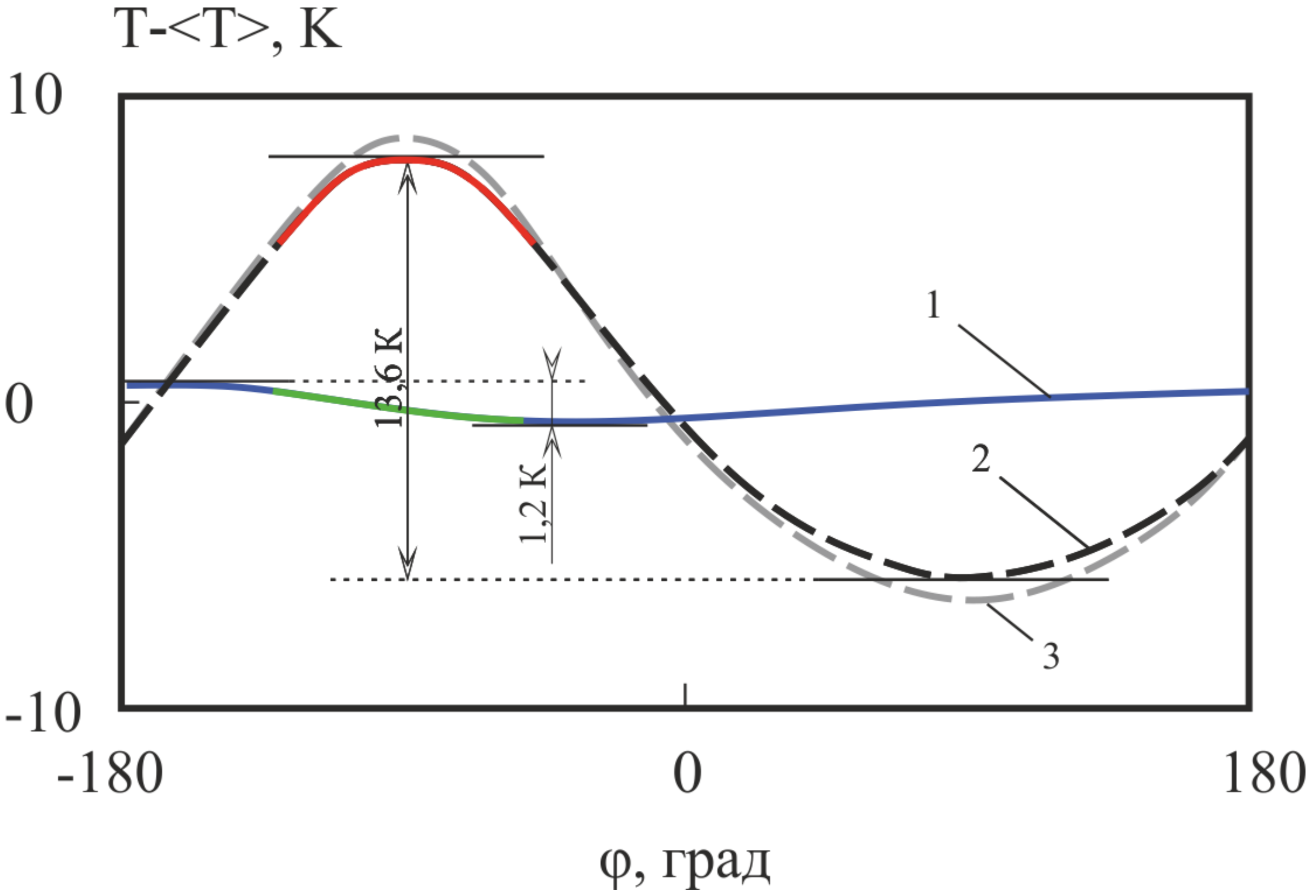
# The calculation results of various heat exchange pipes

Distribution of temperatures on angular coordinate on the surface of contact of oil with steel:

1 – heat exchange pipe with the LBE ring gap

2 – 16 mm steel heat exchange pipe

3 – 6 mm steel heat exchange pipe



# Conclusion

**The conducted researches have shown:**

- The offered design of a heat exchange pipe, is able to afford to reduce coke production in furnaces of fire heating of oil products due to alignment of temperature fields on the section of a heat exchange pipe.
- Important factor of alignment of temperature on the section of a heat exchange pipe is implementation of steady natural circulation in a ring gap.
- The design brings additional thermal resistance in heat transfer coefficient size from flame to oil products, comparable with a thermal resistance ~ 10 mm steel.
- Implementation of certain design decisions requires continuation of researches regarding experimental tests on small-sized models.

# Thank you for your attention