Italian National Agency for New Technologies, Energy and Sustainable Economic Development

MATERIAL COMPATIBILITY WITH LIQUID METAL AND MITIGATION STRATEGIES: REMOVAL OF ACTIVATION CORROSION PRODUCT

Consultancy Meeting on Synergies in Technology Development between Nuclear Fission and Fusion for Energy Production

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Introduction

The compatibility of structural materials with liquid metals is of paramount importance towards the development of fission and fusion reactors systems.

Liquid metals generally present high solubility to common alloying elements of steels, such as nickel, iron, chromium, silver and copper.

The presence of corrosion products dissolved in the melt can generate:

- **Precipitation** in the coldest spots of the system where their solubility decreases and they can form plugs that can reduce the flow.
- **Activated corrosion product under neutron irradiation**, contributing to the Operational Radiation Exposure and increasing the radioactive inventory that can be mobilized in case of accident.

Introduction

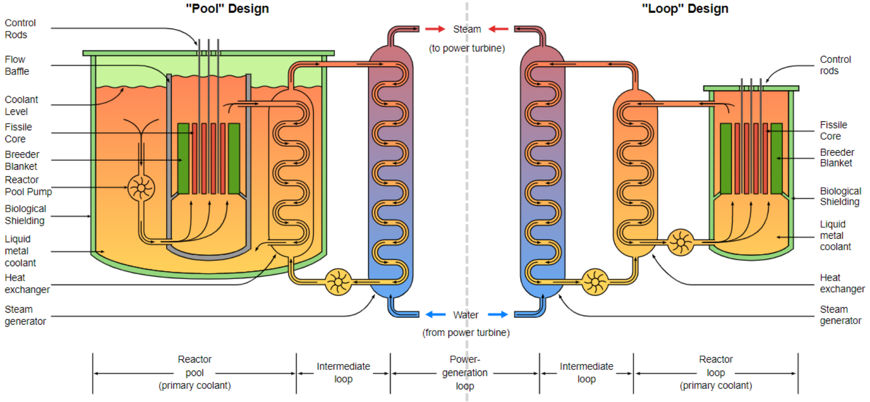
Strategies to mitigate corrosion and remove the corrosion product have to be conceived and put in practice. The common approach for fission and fusion systems is to use a combination of these techniques:

- using corrosion resistant materials and low activation materials;
- **minimizing the corrosion rates by controlling the liquid metal coolant chemistry;**
- reducing liquid metal velocity and temperature (when possible);
- **purifying the liquid metal;**
- depositing a protective coating on the exposed surfaces.

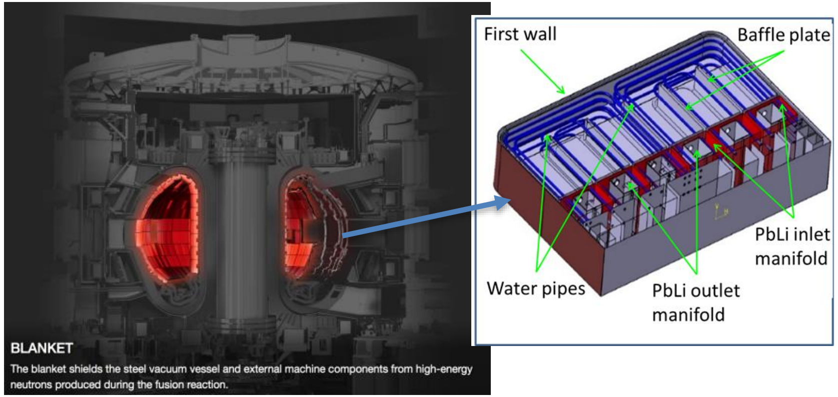
Liquid metal coolant

Pure **Lead** and **Lead-Bismuth Eutectic (LBE)** are candidate coolants for the so-called fourth generation of fission reactors, while **LiPb** is used as breeder materials in several concepts of Breeding Blankets for fusion reactors (e.g. the Water-Cooled Lithium Lead).

Liquid Metal cooled Fast Breeder Reactors (LMFBR)



Water-Cooled Lithium Lead BB



Structural materials

Fusion Reactor

For fusion applications, the **reduced activation ferritic/martensitic (F/M)** steel EUROFER is considered the reference structural steel in the EUROPEAN DEMO. Its application requires a better **understanding of material compatibility** related to physical/chemical corrosion phenomena **in the 450-550°C** temperature range. The impact of corrosion includes deterioration of the mechanical integrity of the blanket structure. Furthermore, serious concerns are associated with the transport of activated corrosion products (**ACP**) by the LiPb coolant.

Fission Reactor

In fission, in parallel to the adoption of corrosion resistant materials (Ferritic/Martensitic Steels, also in the Oxide-Dispersion Strengthened version, vanadium alloys, refractory materials), the use of **stainless steels** is still under consideration by implementing a **strict control of the oxygen concentration** in the lead alloys. Indeed, a protective continuous oxide layer can form at certain oxygen concentration and temperature.

The research in both fusion and fission is investigating the removal of corrosion activated products with a purification system

DEMO – WCLL BB concept

The **Breeding Blanket (BB)** component of DEMO reactor serves several purposes:

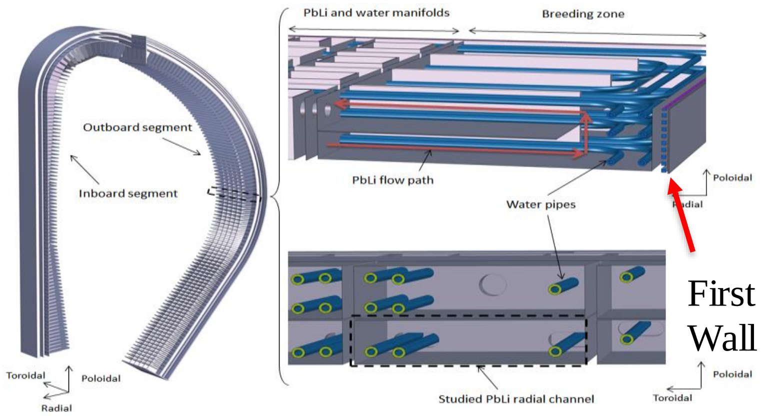
i) tritium generation
ii) remove heating power produced due to (n,Li)
iii) shielding

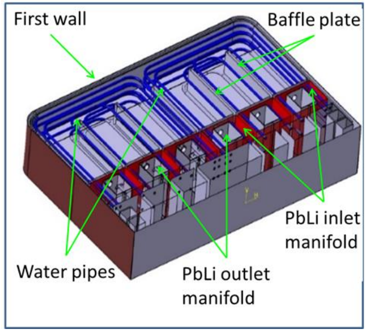
Presently in EU the conceptual design of 2 BBs have been selected as reference concepts:

- ❑ **Water Cooled Lithium Lead (WCLL)**
- ❑ **Helium Cooled Pebble bed (HCPB)**

In the **WCLL BB**, the heating power generated by nuclear reactions is removed by pressurized water and the **breeder and neutron multiplier** is constituted by the eutectic alloy **PbLi**.

Segment



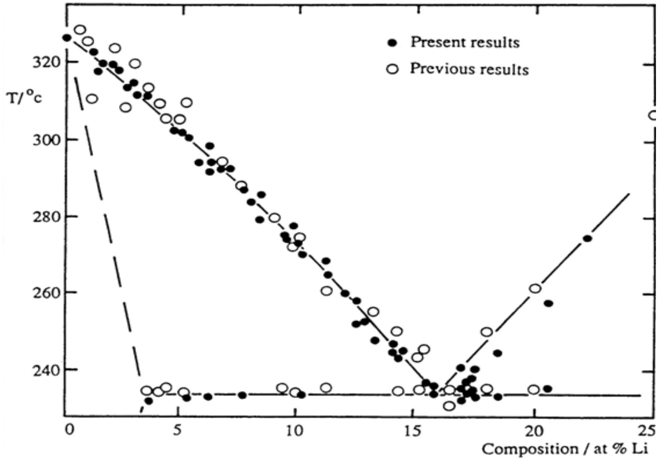


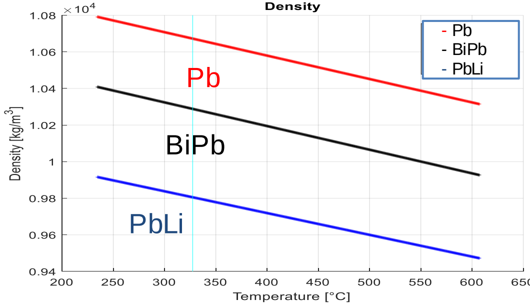
Liquid metal Breeder

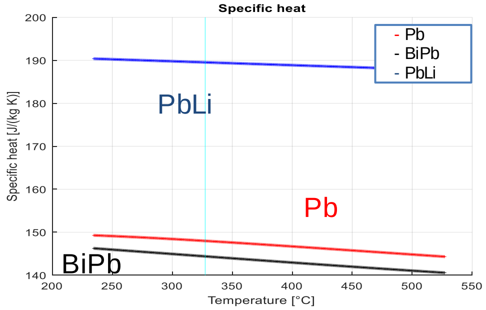
The Liquid metal used for WCLL BB is the eutectic alloy **Pb–15.7Li enriched at 90% in 6Li.**

PbLi present unique physical proprieties as:

- High density
- Opacity – optical methods not an option
- Corrosivity
- Typically high temperature (melting point 234°C)



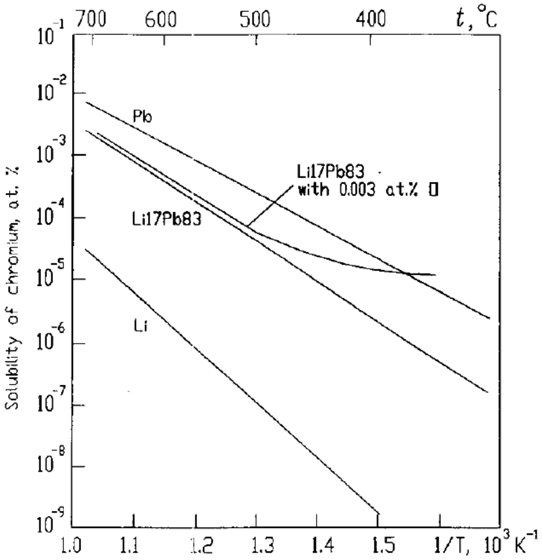


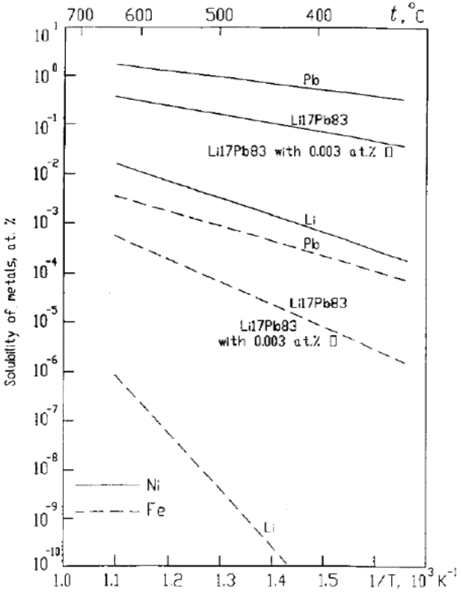


	Lead	LiPb	LBE
Melting temperature (°C)	327	234	124

Solubility in Liquid metal

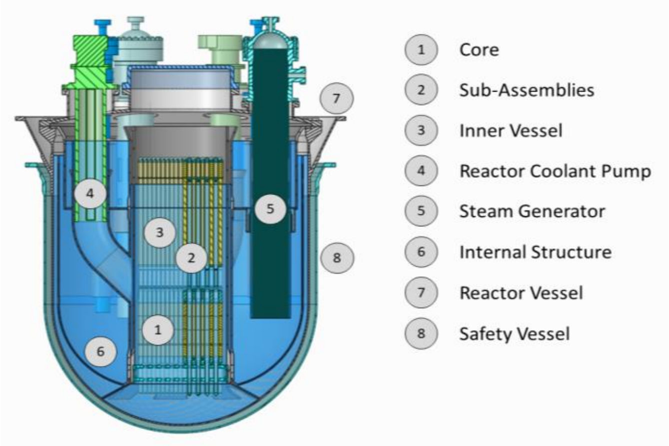
solubility of chromium, nickel and iron in lead, lithium and lead-lithium alloy

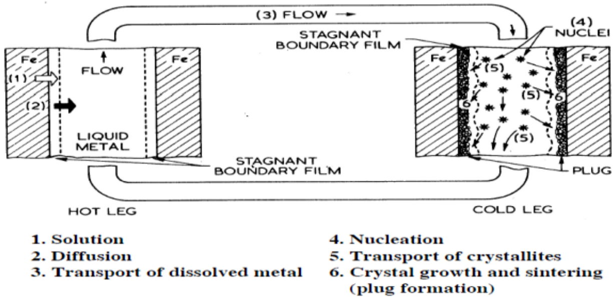


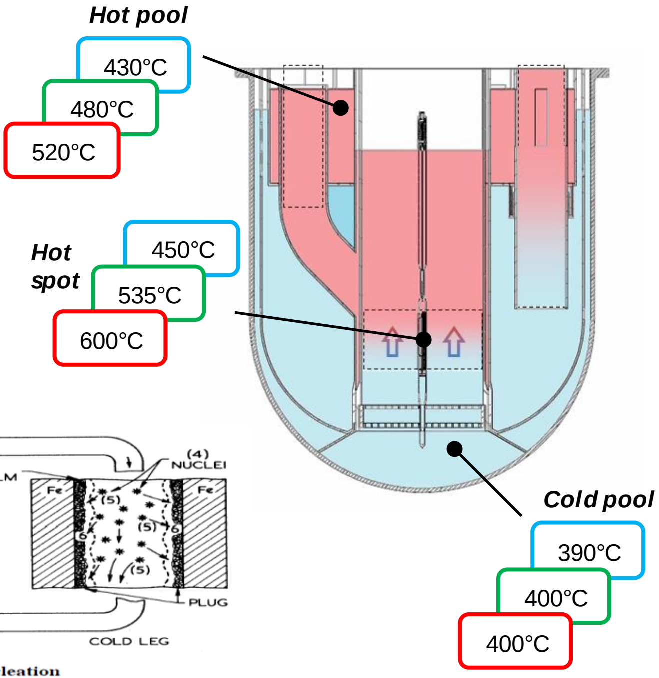


Pb/PbBi coolant chemistry

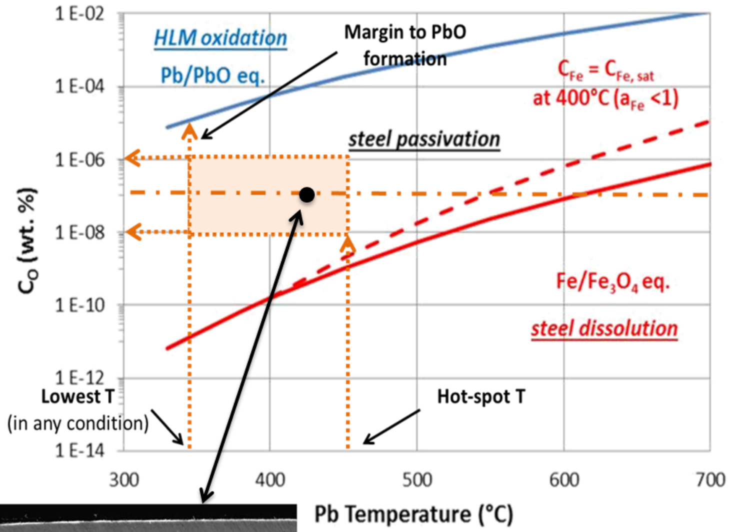
- In Gen-IV liquid metal reactors the corrosion of material is mitigated by the Pb/PbBi oxygen concentration control (up to 450-480°C); for higher temperature the use of protective coating is required
- Corrosion of structural material in the hot part of the reactor can precipitate in the cold part of the pool

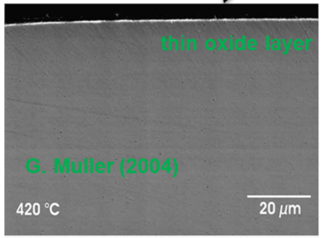






Pb/PbBi Coolant Chemistry Control





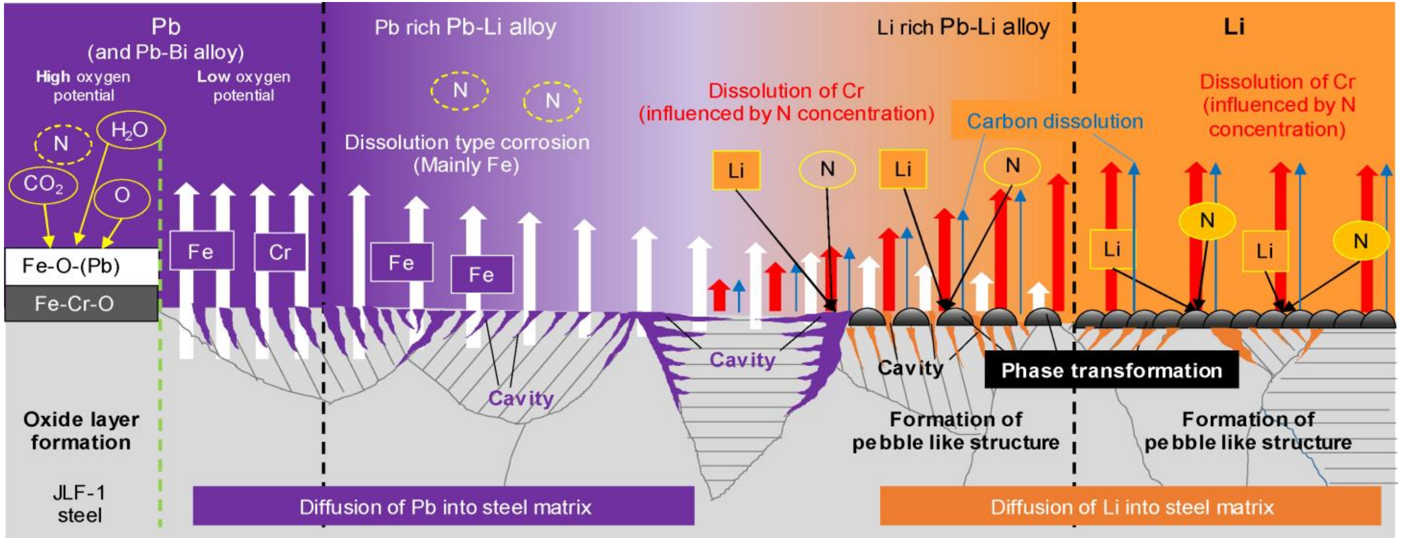
Thin protective oxide layer

316L steel in flowing LBE, 420◦C, high C_O, 2000 h.

- ✓ Data in LBE considered;
- ✓ Lack of corrosion data in Pb;
- ✓ Need for steels qualification in Pb at high and low T.

Formation of oxide film on steels via Oxygen Control
T range = 390-430°C
T Hot Spot = 450°C
$C_O = 10^{-6} – 10^{-8}$ % wt.

Pb-16Li/RAMF Corrosion

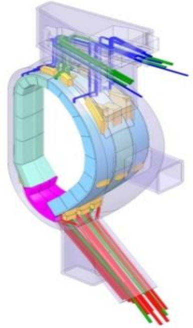


Masatoshi Kondo, Fusion Engineering and Design 125 (2017) 316–325

- The solubility of Fe in the liquid Pb-Li alloys must be larger when the Pb concentration was higher in the alloy
- In the Pb-16Li alloy the corrosion is due to dissolution
- Pb-16Li preferential attack along grain boundaries

Pb-16Li/RAMF Corrosion

Pb-16Li corrosion



- The corrosion phenology is due to **dissolution** of alloying elements in PbLi, where the driving force is the chemical potential.
- Separation of atoms from the solid matrix into the liquid **occurs due to the difference between the chemical activity** (chemical potential) **of a particular steel component in the solid and in the liquid**.
- An associated mass flux from the solid wall ***I*** (kg/m^2 s) at the solid/liquid interface can be written as:

$$I = k(C^S - C_W)$$

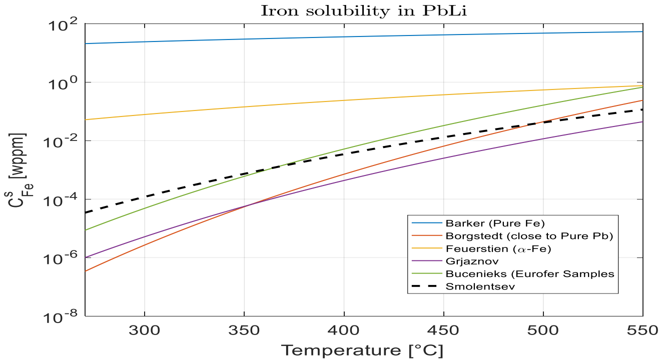
$C^S \rightarrow$ Saturation Concentration $\left[\mathrm{kg/m^3}\right]$

$C_W \rightarrow$ Concentration in the LM at the interface

$k \rightarrow$ Dissolution rate constant $[m/s]$

$$C^S_{Fe} = e^{\left(a - \frac{b}{T}\right)}$$

Correlation	***a***	***b***
Smolentsev	13.604	12975
Barker (pure Iron)	5.811172	1508.35
Borgstedt (close to pure lead)	24.7136	21517.7
Feuerstien (α-Iron)	4.94	4292
Grjaznov	17.6562	17099
Bucenieks (EUROFER Samples)	21.47	18000



Difference between the lowest and highest predicted values **about one order of magnitude**

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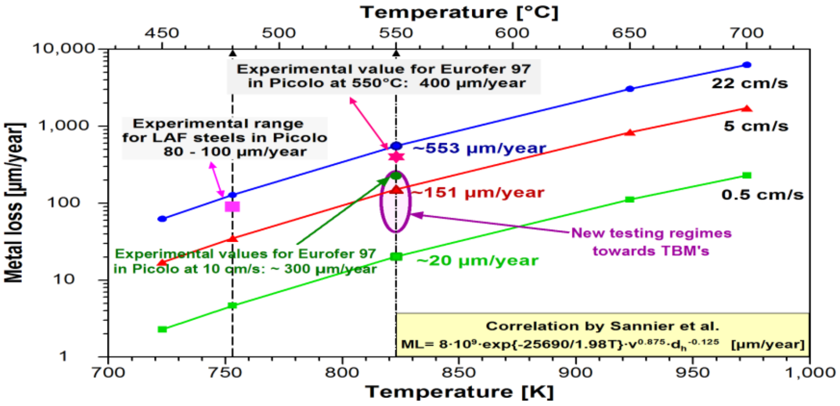
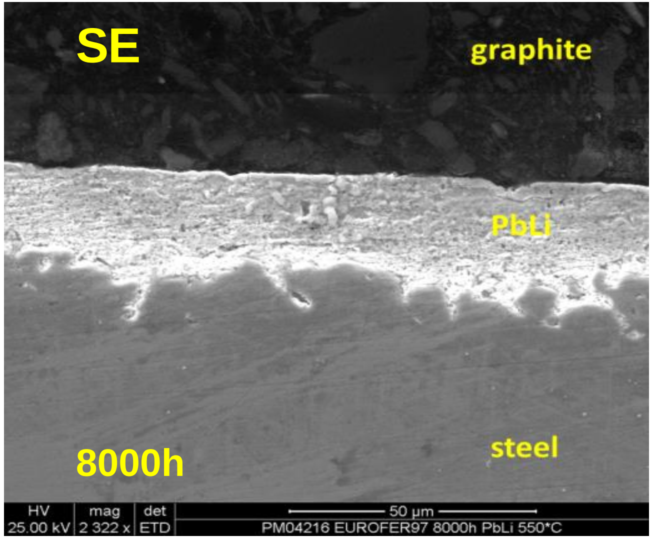
Pb-16Li/RAMF Corrosion

The corrosion rate in PbLi depends strongly on:

- Components concentration in PbLi (e.g. Cr and Fe)
- The kinetics governing the corrosion phenomena:
  - PbLi Temperature
  - PbLi velocity profile



J. Novotny and A. Skrypnik, Journal of Nuclear Materials, vol. 417, no. 1-3, pp. 1191-1194, 201]



Pb-15.7Li Chemistry

Pb-15.7Li chemistry

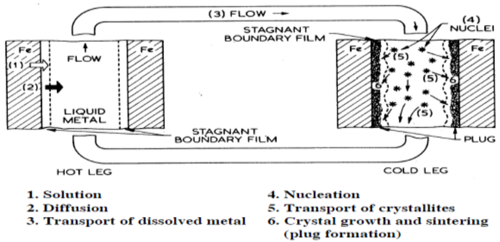
Corrosion products

Helium

Activation products

Dissolution of P22/EUROFER →
- Temperature
- Pb-15.7Li velocity
- Impurities

Transport of CPs →
- Formation of plugs
- Corrosion increases



$$(n,\alpha)T: \quad n + {}^{6}Li \rightarrow T + {}^{4}He + 4.8MeV$$

$$(n,n,\alpha)T: \quad n + {}^{7}Li \rightarrow T + {}^{4}He + n - 2.47MeV$$

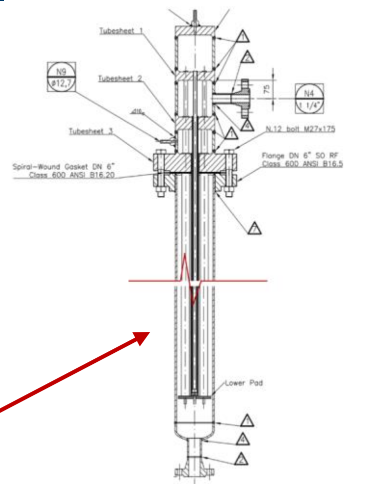
$$x_{\mathrm{He}}[\mathrm{at.\,fraction}] = k_H \cdot p_{He}[\mathrm{Pa}]$$

Helium solubility in PbLi is unknown, semi empirical correlation is used but should be validated by:
- Dynamic molecular analysis
- Experimental R&D

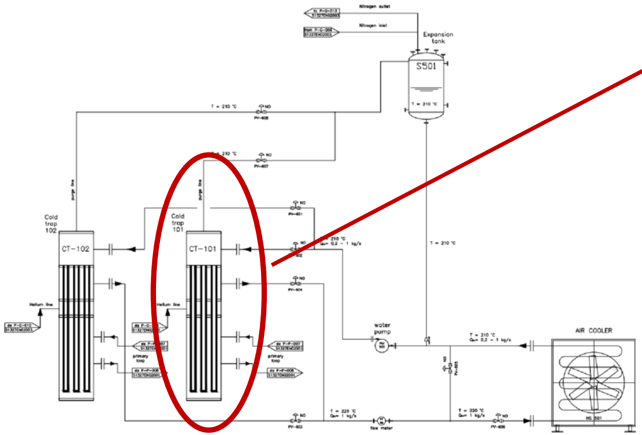
Species	Half time	Specific activity after irradiation [Bq/kg]
^{3}H	**12.32 y**	**$8.89\ 10^{12}$**
^{203}Hg	**46.6 d**	**$2.41\ 10^{10}$**
^{204}Tl	3.78 y	$6.91\ 10^{9}$
^{202}Tl	122.2 d	$1.16\ 10^{9}$
^{210}Po	**138 d**	**$5.49\ 10^{8}$**
^{203}Pb	51.9 h	$2.37\ 10^{7}$
^{210}Bi	5.01 d	$5.86\ 10^{6}$
^{205}Pb	$1.5\ 10^{7}$ y	$4.61\ 10^{6}$
^{207}Bi	32.2 y	$6.95\ 10^{5}$
^{208}Bi	$3.7\ 10^{5}$ y	$3.79\ 10^{4}$
^{210}Pb	22.3 y	$6.92\ 10^{3}$
^{209}Po	**102 y**	**$5.14\ 10^{3}$**
^{206}Bi	6.24 d	$1.53\ 10^{3}$

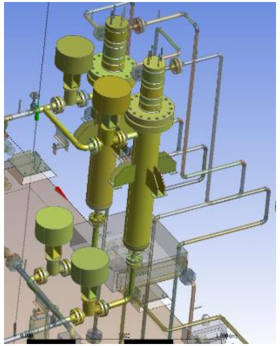
Cold Trap

A system devoted to remove the corrosion product was developed in the frame of WCLL -BB. The Cold Trap system consists of a heat and mass transfer device, where a supersaturated solution of impurities is generated as the result of the primary fluid cooling, causing the crystallization of the impurities both on the immovable surfaces and in suspension.



This system is essentially composed by a cold trap (CT) consisting in a heat and mass transfer device, where a supersaturated solution of impurities is generated as the result of LM cooling, causing the crystallization of the impurities both on the immovable surfaces and in suspension.

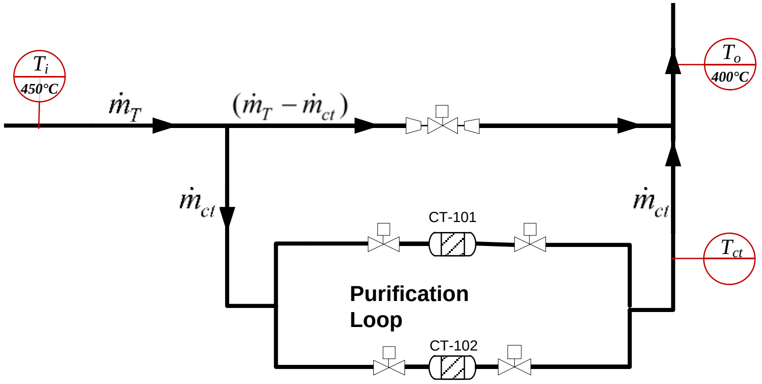




Cold Trap

The principle of the CT is to maintain the impurity equilibrium concentration in the loop below the LiPb solubility at lowest temperature (Tlow) foreseen in the plant **(Tct < Tlow)**. Such an apparatus has the purpose of collecting the impurities generated during the operation, avoiding therefore, the corrosion products precipitating in the loop.

Cold trap is installed in a bypass of the loop



$$\dot{m}_{ct} = \dot{m}_T \frac{(T_i - T_o)}{(T_i - T_{ct})}$$

Experimental Facilities

Facility used to investigate corrosion in static or flowing lead or LBE

- COSTA at KIT (Germany)
- CORRIDA at KIT (Germany)
- CRAFT at SCK-CEN (Belgium)
- OLLOCHI at JAEA (Japan)
- BID1 at ENEA Brasimone (Italy)
- LECOR at ENEA Brasimone (Italy)
- HELENA at ENEA Brasimone (Italy)
- RACHEL Lab at ENEA Brasimone (Italy)

Facility used to investigate corrosion in static or flowing PbLi

- PICOLO loop at KIT (Germany)
- MELILOO loop at Cv Rez (CezhRepublic)
- IELLLO at ENEA Brasimone (Italy)
- RACHEL Lab at ENEA Brasimone (Italy)

Moreover, numerical codes, such as OSCAR and PACTITER, are under development and validation to predict the amount of Activation Corrosion Products and their transport in the loops.

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