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

Lead Chemistry Technologies: Tritium balance in the reactor, chemistry control and protective coating

IAEA National training course on Heavy Liquid Metal Cooled Fast Reactors: Benefits and Challenges

16° February 2026, RATEN (Romania)

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Nuclear Energy Systems Division (NUC)

Outline

- Lead Chemistry in FLRs
- Material compatibility in lead
- Oxygen control in LFRs
- Experimental facilities
- Tritium management in LFRs
- Protective coating

Introduction

- The investigation and qualification of materials to be used in the Generation-IV Lead Fast Reactor (LFR), in operational and accidental conditions, is a critical issue in the development of the Reactor.

- The chemistry control of Pb and LBE is a key topic to be addressed for the development of lead-cooled nuclear reactors for two main reasons: HLM oxidation and corrosion of structural steels. The activation of the coolant due to corrosion, irradiation, and fission products is also an important issue that requires specific control procedures to ensure the safe management of the operational and maintenance phases.

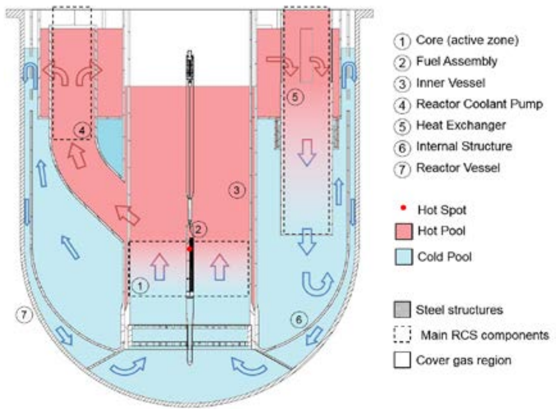
Introduction – LFR operative conditions

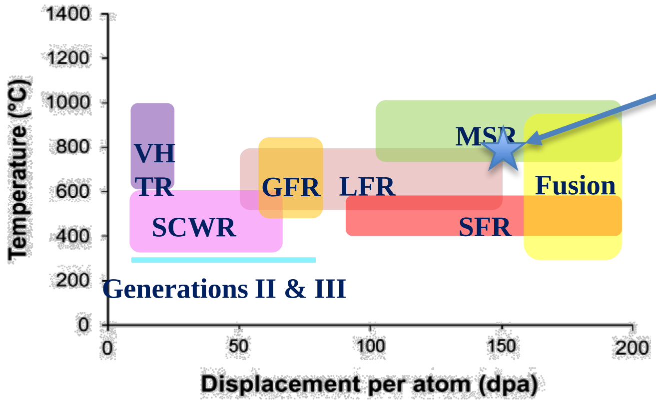
The operation of Lead Fast Reactor will be based on a stepwise approach:

- 1st stage: operation at **low power** in **low-temperature** range
  - Currently existing proven materials (bare steels) working in **O-containing Pb coolant**
- nst stage: operation at **full power** in **high-temperature** range
  - Advanced materials or protective measures fully qualified during earlier stages

Parameter	Stage 1	Stage 2	Stage 3
Core inlet T (°C)	380	400	400
Core outlet T (°C)	430	480	520
Hot Spot T (°C)	450	535	600
Core Power (MWth)	100	200	300

Temperature and C_o influences the corrosion resistance of materials as well as mechanical properties in Pb environment





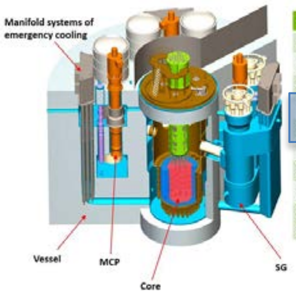
S.J. Zinkle and G.S. Was – Acta Materialia - 2013

Ultimate goal for LFRs:

- **700 °C**
- **150 dpa**

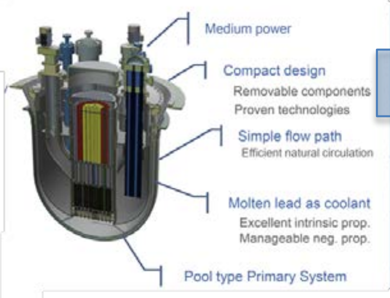
LFR in the world

BREST-OD-300: RUSSIAN LFR PROTOTYPE

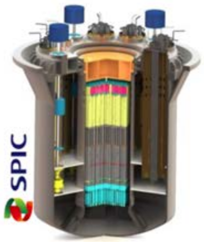


Coolant	Lead
Thermal Power	700 MW
Electric Power	300 MW
Number of loops	4
Inlet temperature	420°C
Outlet temperature	535°C
Fuel	U-Pu nitride
# of fuel assemblies	169 (no can)
Fuel charge	20.6t
Conversion efficiency	43.5%

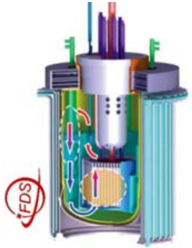
ALFRED LFR



Primary system	Pool-type, compact
Coolant circulation Normal operation Accident conditions	 Forced (8 pumps) Natural (pressure drop 0.15 MPa)
Pressure	< 0.1 Mpa
Temparature	400-480°C
Flowrate	26 000 kg/s
Reactor vessel	Austenitic SS, hung
Safety vessel	Anchored to the pit
Inner vessel (Removable)	Cylindrical, integral with the core support grid and the hot collectors
Steam generators	8, bayonet type with double walls,
Primary pumps	8, integrated with the SGs, in hot leg
Fuel assembly	Closed (with wrapper), Hexagonal, forced in position by springs
Control/Shutdown Systems	2 diverse and redundant systems concept derived from MYRRHA
Decay Heat Removal	2 separate and redundant systems of 4 Isolation Condensers connected to the Steam Generator (actively actuated, passively operated)
Refuelling System	No refuelling machine stored inside the Reactor Vessel



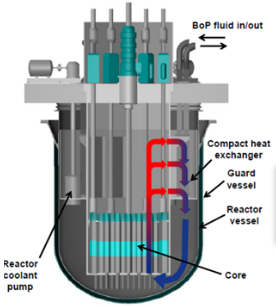
BLESS
100 MWe, China
Under design



CLEAR-1
10 MWth, China
Under design

Micro-Uranus
60 MWth, Korea
Under design

WESTINGHOUSE LFR

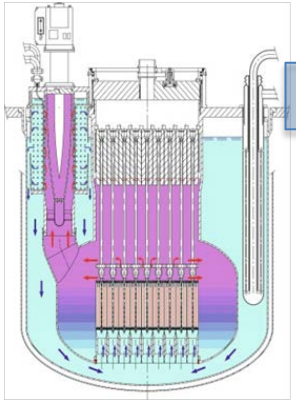


Plant characteristics	
Electric power, MWe	~450 (Fleet) ~300 (Prototype)
Safety philosophy	Passive plant
RCS layout	Pool type
Intermediate circuit	None
Number of HX/RCP	6 / 6
Plant's efficiency	Up to ~50% (Fleet) 41-43% (Prototype)
Core Tin, °C	~420
Core Tout, °C	Up to 650 (Fleet) 530 (Prototype)
Balance of plant	Supercritical CO_2
Fuel	UN (Fleet) UO_2 (Prototype)

Some innovation relative to more traditional LFRs:

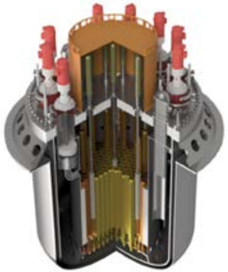
- Microchannel HX to compact the vessel and reduce likelihood and consequence of HX rupture
- High-performance materials pursued to increase operating temperature above 550°C
- Thermal energy storage for flexible operation

Newcleo LFR: AS-200

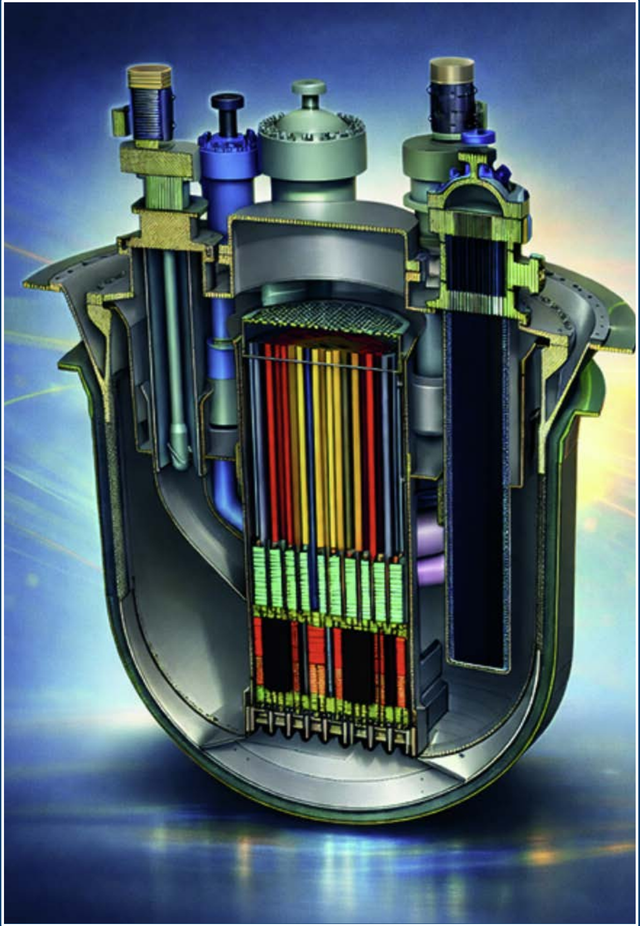


Power	480 MWth
Core coolant	Pure lead
Core coolant temperature	inlet 420°C, outlet 530°C
Layout	Pool-type
Circulation	Forced: 6 pumps
Spectrum	Fast
Fuel form	Extended-stem fuel assembly
Fuel	MOX
Secondary side fluid	Water
Steam generators	6 spiral-tube SG
Design life	60 years
Lifetime capacity factor	94%

SEALER-55 (Swedish Advanced Lead Reactor)



Item	Value
Power	140 MWth/55 MWe
Lead coolant mass flow	7400 kg/s
Lead inventory	800 tons
Core inlet/outlet temperature	420°C/550°C
Height	5.5 m
Diameter	4.8 m
Fuel	Uranium nitride (UN)
Fuel residence time	25 years



Lead Chemistry control

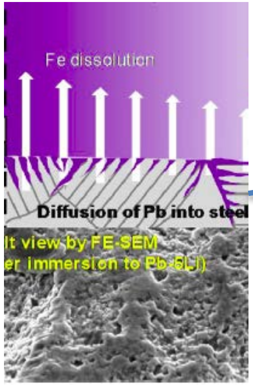
- Steel solubility in Lead alloys
- Pb/PbBi oxidation
- Oxygen monitoring in lead
- Oxygen control in Lead
- Test Guidelines and best practise
- Example: Pb chemistry - incidental scenario

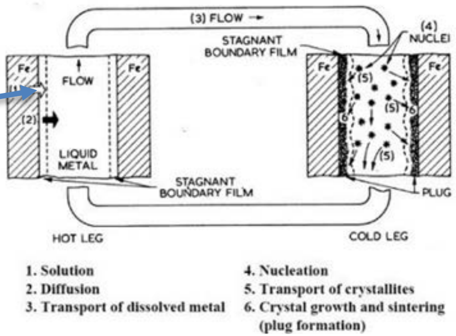
CHEMISTRY OF HLM (LEAD AND LBE)

Steel Corrosion - Pb and LBE have high capability to dissolve the alloy elements of conventional steels (Fe, Cr and Ni) damaging the structures, especially subjected to the highest temperature (e.g. core). Also, dissolved chemical elements contribute to the plugging since they tend to deposit in the cooling loop when they reach the solubility level.

Element	T (°C)	Pb		LBE	
		C_{sat} (% wt.)	C_{sat} (ppmw)	C_{sat} (% wt.)	C_{sat} (ppmw)
Fe	400	$2.2 \cdot 10^{-6}$	0.022	$2.9 \cdot 10^{-5}$	0.29
	450	$7.7 \cdot 10^{-6}$	0.077	$8.3 \cdot 10^{-5}$	0.83
	500	$2.2 \cdot 10^{-5}$	0.22	$2.0 \cdot 10^{-4}$	2.0
	550	$5.8 \cdot 10^{-5}$	0.58	$4.5 \cdot 10^{-4}$	4.5
Cr	400	$5.5 \cdot 10^{-7}$	0.0055	$3.8 \cdot 10^{-4}$	3.8
	450	$2.7 \cdot 10^{-6}$	0.027	$7.8 \cdot 10^{-4}$	7.8
	500	$1.1 \cdot 10^{-5}$	0.11	$1.4 \cdot 10^{-3}$	14
	550	$3.5 \cdot 10^{-5}$	0.35	$2.5 \cdot 10^{-3}$	25
Ni	400	$1.9 \cdot 10^{-1}$	1939	1.0	10013
	450	$2.7 \cdot 10^{-1}$	2697	2.0	20170
	500	$3.6 \cdot 10^{-1}$	3595	2.5	24828
	550	$4.6 \cdot 10^{-1}$	4627	3.0	29800

OECD/NEA, "Handbook on lead-bismuth eutectic alloy and lead properties, materials compatibility, thermal-hydraulics and technologies", (2015).





CHEMISTRY OF HLM (LEAD AND LBE)

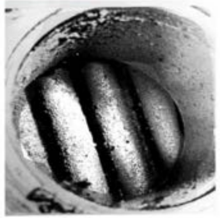
HLM oxidation - Pb and LBE solubilize significant amount of oxygen. When oxygen is dissolved up to the solubility level, coolant oxides formation (mainly PbO) and their consequent deposition may occur. Coolant oxides affect HLM thermal-hydraulics and cause the plugging of the structures, thus leading to potential safety risks.

T (°C)	Pb		LBE	
	$C_{O,sat}$ (% wt.)	$C_{O,sat}$ (ppmw)	$C_{O,sat}$ (% wt.)	$C_{O,sat}$ (ppmw)
400	$5.5 \cdot 10^{-5}$	0.5	$1.3 \cdot 10^{-4}$	1.3
450	$1.8 \cdot 10^{-4}$	1.8	$3.5 \cdot 10^{-4}$	3.5
500	$5.1 \cdot 10^{-4}$	5.1	$8.2 \cdot 10^{-4}$	8.2
550	$1.3 \cdot 10^{-3}$	13	$1.7 \cdot 10^{-3}$	17
600	$2.8 \cdot 10^{-3}$	28	$3.4 \cdot 10^{-3}$	34

OECD/NEA, "Handbook on lead-bismuth eutectic alloy and lead properties, materials compatibility, thermal-hydraulics and technologies", (2015).

Slag in pipeline

Slag deposit in the circuit during circulation pump tests



Slag deposit in heat exchanger

$$Pb_{\,liq} + O_{\,diss} \leftrightarrow PbO_{\,diss}$$

$$\log C_{O,sat}^{Pb} = 3.23 - \frac{5043}{T}$$

$$\log C_{O,sat}^{LBE} = 2.25 - \frac{4125}{T}$$

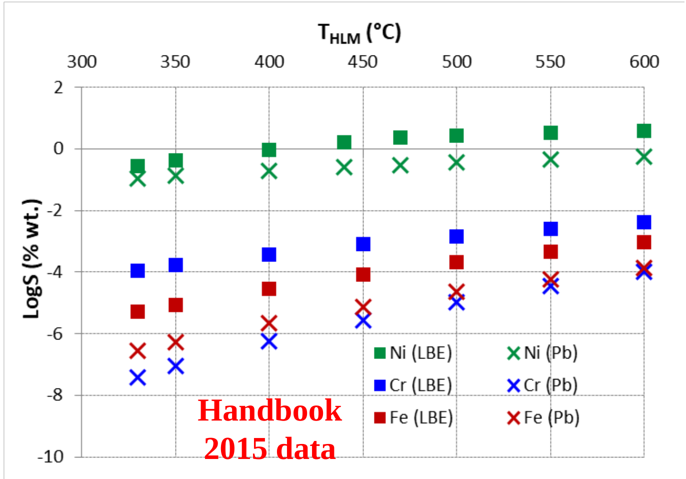
plugging in Pb-Bi cooled K-27 Russian Nuclear Submarine in 1960'

The first submarine "K-27" with Pb-Bi coolant
Startup - in 1963
Accident – in 1968
Cause of accident – absence of coolant technology systems

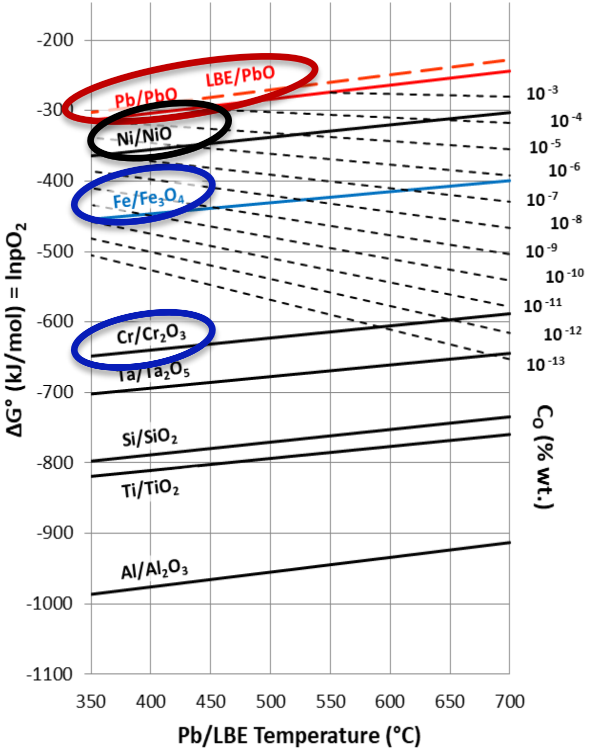
CHEMISTRY of Pb & LBE (Pb-55.5Bi) in F/M steel

Degradation mode of steels

- oxidation in oxygen-containing Pb alloy (thermodynamic stability of Fe/Cr oxides);
- dissolution of bulk material (higher solubility of elements in LBE);
- liquid metal embrittlement for F/M steels



Ellingham diagram (thermodynamics)

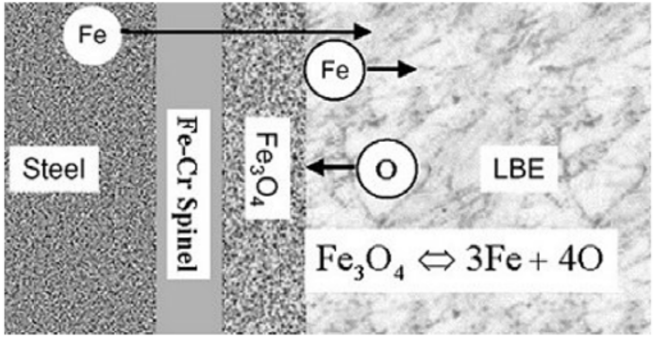


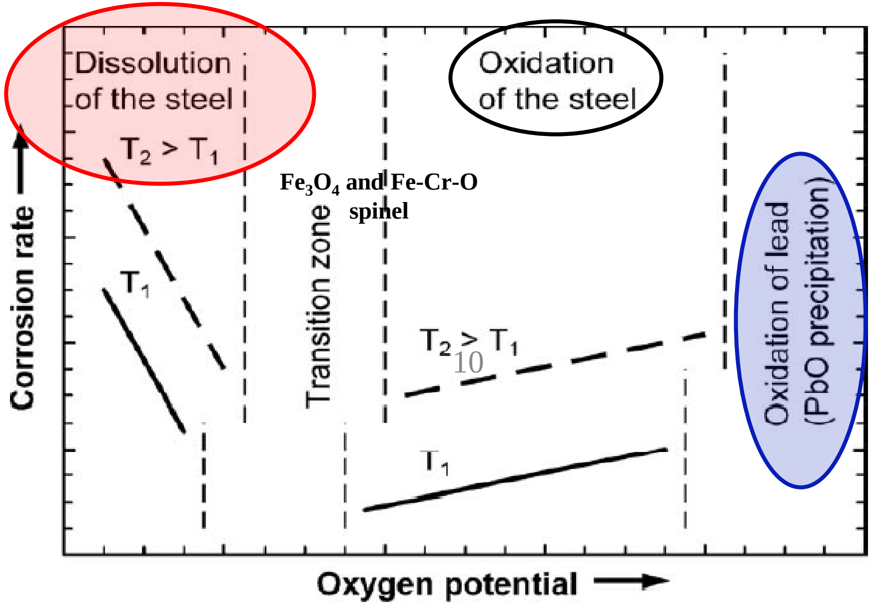
Oxygen control

The oxigen concentration required to reduce material corrosion is included in the range:

$$C_{O,magnetite} < C_O < C_{O,sat}$$

Where $C_{O,magnetite}$ is minimum oxygen concentration required for the formation of Fe_3O_4 above the steels.





CHEMISTRY OF HLM (LEAD AND LBE)

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Slag deposit in the circuit during circulation pump tests

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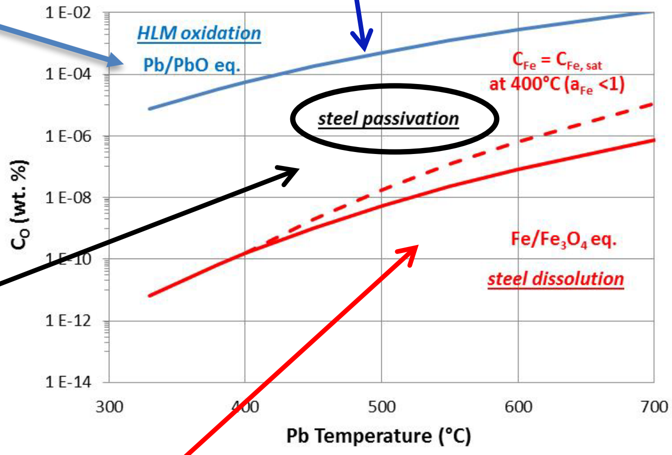
plugging in Pb-Bi cooled K-27 Russian Nuclear Submarine in 1960'

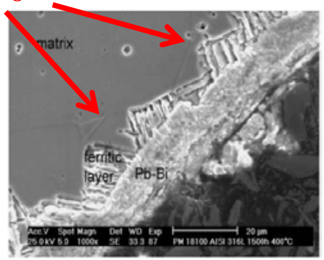
Oxygen saturation and PbO deposition



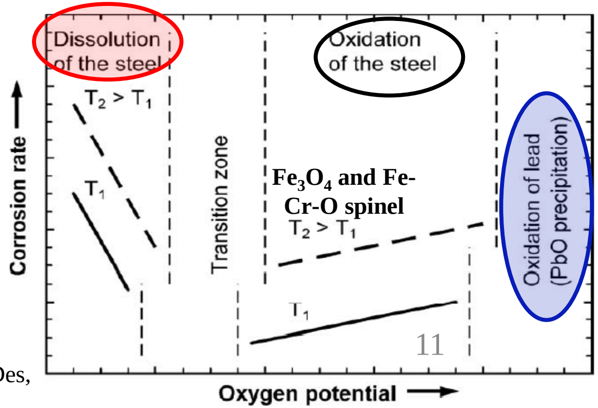
oxygen balancing for steel passivation and to avoid PbO formation (<u>oxygen sensors</u> +<u>oxygen control devices</u>)

Steel corrosion at low oxygen content

Ni and Cr dissolution in 316L steel. Flowing LBE, 400◦C , low C_O, 1500 h.

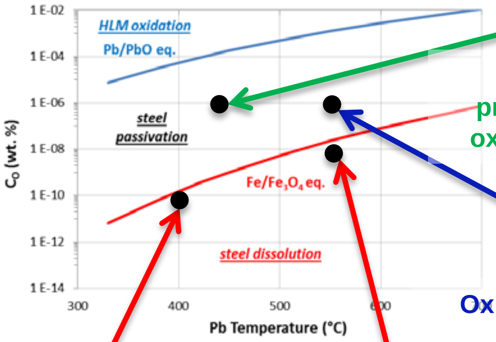


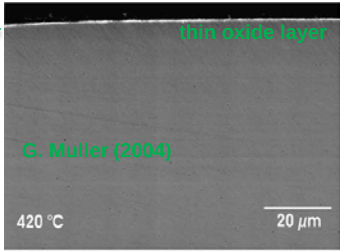
Benamati et al., J Nucl Mater 335 (2004) 169-173.



C. Schroer, Nucl Eng Des, 241 (2011) 4913-4923.

AUSTENITIC STEEL: CORROSION IN Pb and LBE





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

Thin protective oxide layer

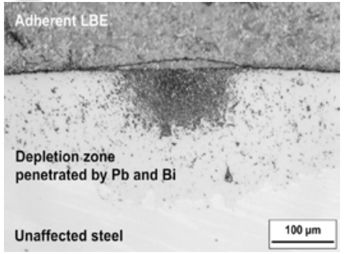
Corrosion in Pb/LBE is Oxygen & T dependent

- at low Co, dissolution at high and low T
- at high Co and T≤450°C, oxidation with formation of protective layer (few µm max);
- at high Co and high T≥450-480°C, oxidation + localized dissolution (ferritizzation up to 250µm + Pb penetration);

Ni/Cr dissolution (γ Fe → α Fe), Pb penetration, no oxidation

Oxidation + Ni/Cr dissolution (γ Fe → α Fe), Pb penetration

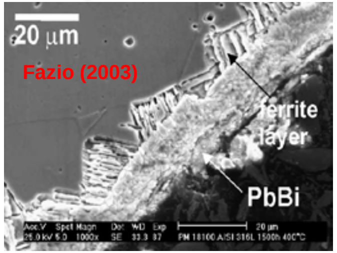
C. Schroer (2014)



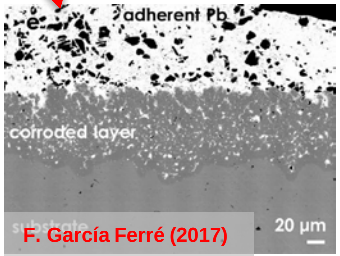
316L steel in flowing LBE, 550◦C, high C_O, 7500 h.

Other factors:

- LBE more aggressive than Pb (data available mostly related to LBE)
- erosion in flowing condition
- mass-transfer phenomena (dissolution hot zone + saturation & deposition in cold zone)



316L steel in flowing LBE, 400◦C, low C_O, 1500 h.



15-15Ti steel in static Pb, 550◦C, low C_O, 4000 h.

Oxygen monitoring

To control the oxygen concentration in Lead alloys the first task to be implemented is to measure the oxygen concentration at relevant operative conditions: temperature and pressure.

Potentiometric sensors based on **solid electrolytes** were developed in recent years to this purpose. Internal reference electrodes such as Pt-air and Bi/Bi2O3 liquid metal/metal-oxide are among the most used but they both have a weak point:

- Pt-air sensor has a high minimum reading temperature around 370-400°C
- Bi/Bi2O3 suffers from internal stresses induced by Bi volume variations with temperature, which may lead to the sensor failure in the long-term.

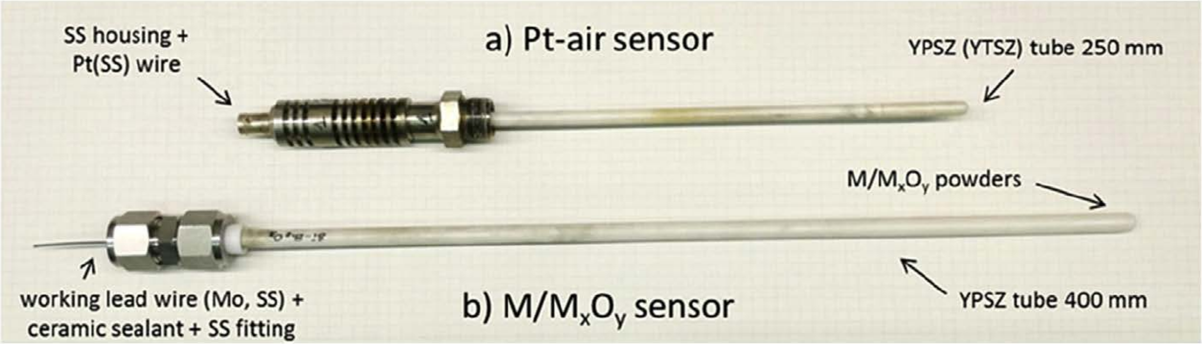
Property	Lead	Units
Melting point	327	°C
Boiling point	1748	°C
Density	10673	Kg/m3
Dynamic viscosity	2.698 E-03	Pa s
Kinematic viscosity	2.528 e-07	M2/s
Thermal conductivity	15.8	W/(mK)
Specific heat (Cp)	148.0	J/(kgK)

Oxygen monitoring

The **Potentiometric sensors** measure an electric potential at null current and they are usually composed of:

- a ceramic solid electrolyte with high oxygen ion conductivity
- a reference electrode with well-known oxygen activity located inside the ceramic element.

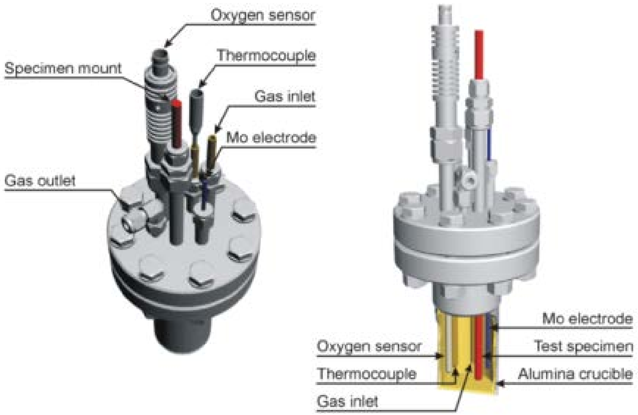
The conductive electrolyte is generally used in the form of a one-end closed tube or thimble and is often the Yttria Stabilized Zirconia (YSZ):



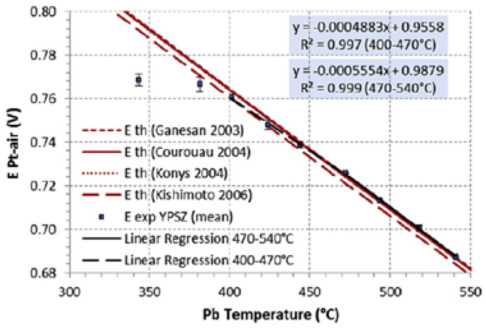
S. Bassini, Oxygen sensors for Heavy Liquid Metal coolants: Calibration and assessment of the minimum reading temperature, Journal of Nuclear Materials 486 (2017) 197e-205

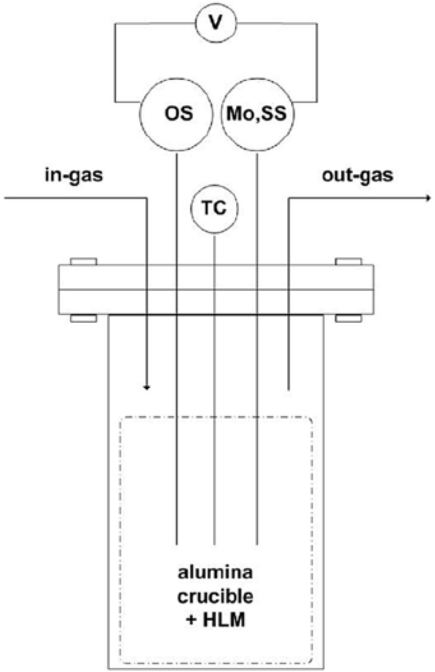
Oxygen monitoring

The set-up for oxygen sensors calibration and testing in liquid lead and LBE:



- OS: Oxygen Sensor
- TC: thermocouple,
- Mo,SS: electrode wire in liquid metal
- V: multi-meter



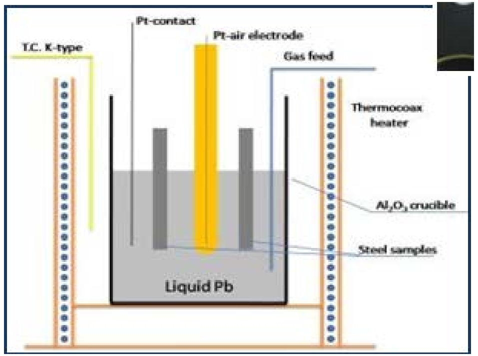


S. Bassini, Oxygen sensors for Heavy Liquid Metal coolants: Calibration and assessment of the minimum reading temperature, Journal of Nuclear Materials 486 (2017) 197e-205

Oxygen control

The main oxygen control methods are:

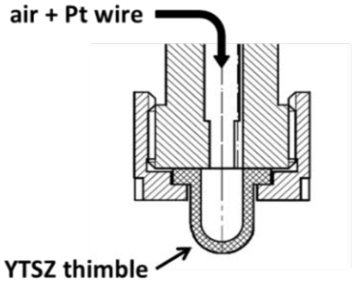
- gas-phase oxygen control
- solid-phase oxygen control



Type	Method	Advantages	Disadvantages
Gas-phase	Injection of O_2 and H_2 gases (oxygen supply and removal)	Simple operation; rapid adjustment of C_O	Potential PbO contamination during O_2 supply; precise control is difficult
	Injection of H_2/H_2O mixture	Set the desired oxygen concentration by controlling H_2/H_2O ratio in the gas	Long time to reach the equilibrium; difficulty in restoring large deviations
Solid-phase	PbO mass exchanger (oxygen supply)	Simple operation; efficiency due to solid/liquid contact; no PbO contamination of the coolant	Replenishment after the consume; poor experience in large scale experiments
	Oxygen getters addition (oxygen removal)	Simple operation; efficiency due to solid/liquid contact	HLM contamination with metal-oxides; replenishment after the consume; poor experience

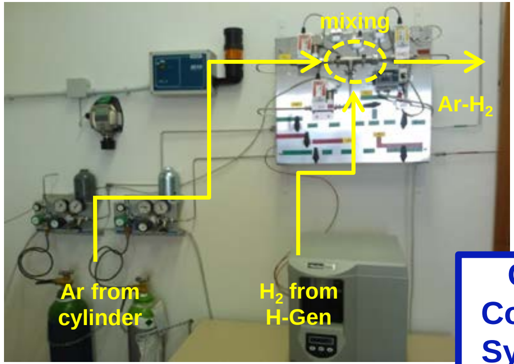
S- Bassini, PhD thesis, Coolant Chemistry Control in Heavy Liquid Metal cooled Nuclear Systems

OXYGEN CONTROL

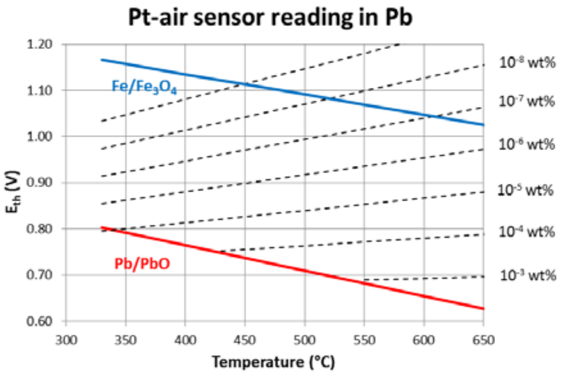


oxygen sensor for large HLM pool (Pt-air reference)

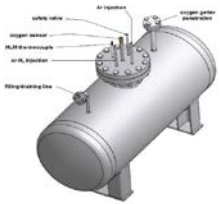
$$PbO_{diss.} + H_{2\,gas} \leftrightarrow H_2O_{gas} + Pb_{liquid}$$



Gas Control System



reading



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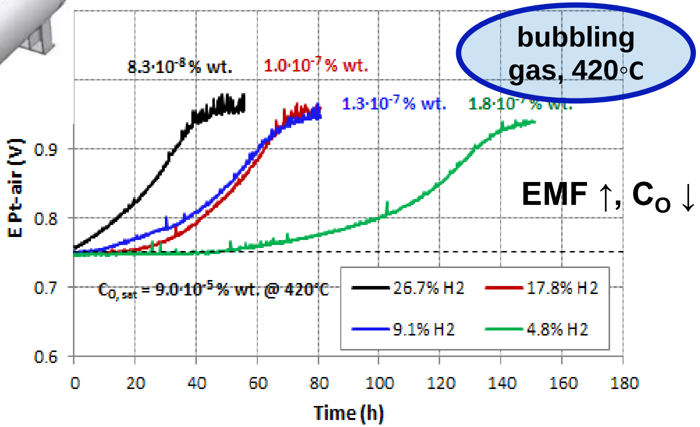
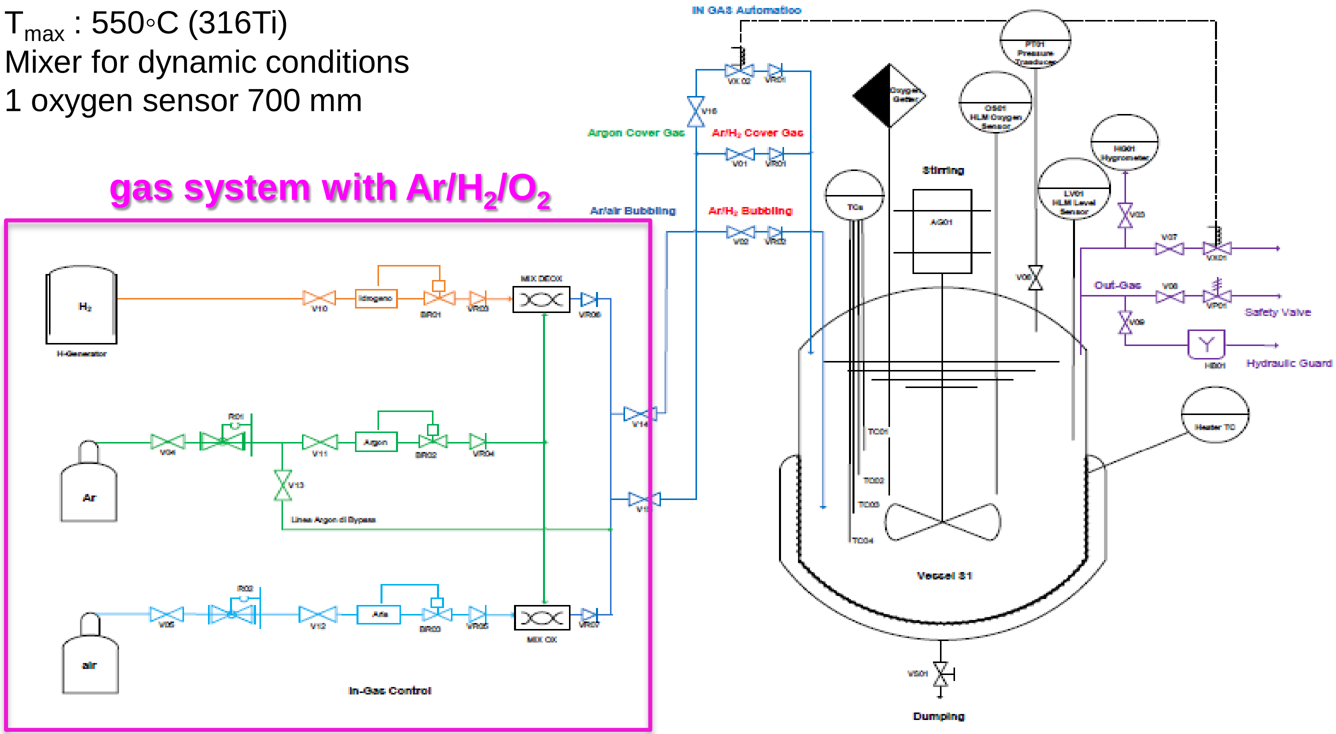


Dynamic tests in Pb (550°C - BID1 pool)

Isothermal small pool (Pb = 150 L) for testing OCS, used for exposure in dynamic conditions for GEMMA Project. The system has been equipped with a cold finger @ 420° C to simulate a cold point.

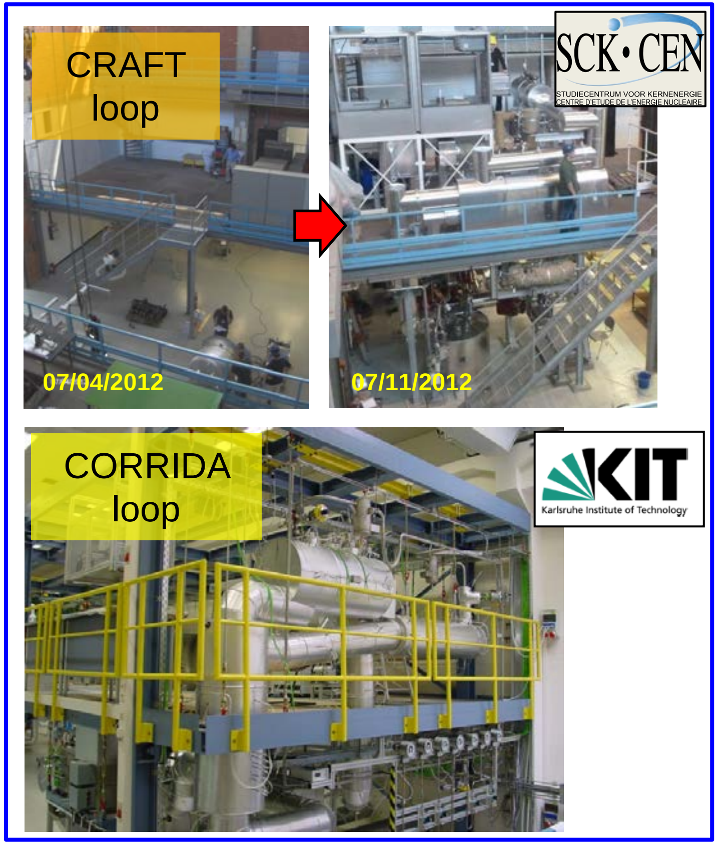
T_{max} : 550◦C (316Ti)
Mixer for dynamic conditions
1 oxygen sensor 700 mm

gas system with Ar/H_2/O_2



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

Corrosion Facilities



Corrosion Facilities

ENEA – *new*cleo

CAPSULES
operational since December 2023

Facility to test various kinds of steel, bare and coated, in stagnant lead under oxygen-controlled concentration, essentially between 10^{-8} - 10^{-6} wt %; temperatures span between 450 - 750 °C

CORE
operational in March 2024

Loop-type facility to test various kinds of steel, bare and coated, in fluent lead under oxygen-controlled concentration, essentially between 10^{-8} and 10^{-6} wt %; temperature in the corrosion test section 650 °C and velocity 1 m/s; in the erosion test section the temperature is 520 °C and the velocity 10 m/s. It will also be used to test the effectiveness of cold traps and mechanical filters

ENEA

Experimental Facilities

Facility used to investigate corrosion with chemistry control 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)
- CAPSULE newcleo lab at Brasimone(Italy)
- CORE1 and CORE 2 newcleo at Brasimone (Italy)

Modelling of Mass Transport and Activation of Corrosion Products

Liquid metal corrosion is a physical-chemical process involving species dissolution and transport, chemical reactions, and new phase formation:

- **OSCAR-Na** code, which is aimed to calculate the mass transfer of corrosion products and related contamination in the primary circuits of sodium fast reactors (SFR)
- **FISPACT-II** is an enhanced multiphysics, inventory and source-term code system utilized to calculate the neutron flux and energy spectra across each component of the blanket.

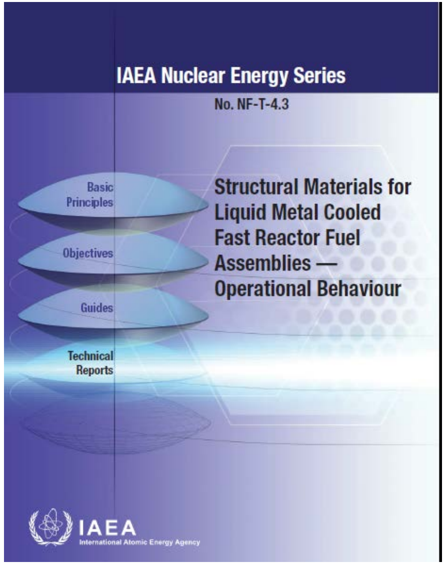
Corrosion Test Guidelines and best practise

Test guidelines and best practices for corrosion tests

- Identification of Structural material corrosion process in HLM
- Material characteristics (manufacturing, Roughness,…) and specimens size
- Identification of main operative conditions (oxygen concentration, T, velocity profile) and instrumentations used to measure the parameters in the test section
- Identification of chemical composition of the Liquid Metal used for the test
- Oxygen control system in the test section set-up
- Mounting, loading and unloading of specimens
- LMC test in static or flowing HLM
- Post tests analysis: gravimetric and microstructural analysis:
  - Pre-test measurements
  - Post-test measurements
  - Evaluation of measurements
- Record of the data

Conclusion

An important aspect to be considered is the compatibility between coolants and materials (in contact with coolants), which is one of the key elements characterizing the harsh operating conditions of a material in fusion power plants and fission advanced reactors.



Pb chemistry incidental scenario

To define the operation limits, plan Restart Limits and major accident limits of the structural materials used in the design of the LFR experimental analysis are investigated with the experimental facilities at **ENEA BRASIMONE**:

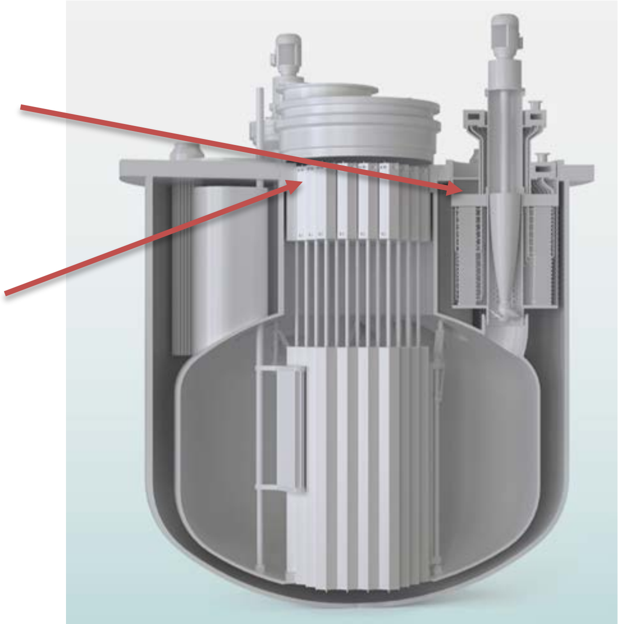
- **SOLEAD:** to investigate chemistry control in the lead in a big pool in standard operation and accidental scenario with interaction between liquid lead and water vapour/air
- **CAPSULE**: is used to investigate the corrosion behavior of materials in stagnant conditions with chemistry control in standard operation, transient and accidental conditions
- **CORE-1**: is dedicated to investigating the corrosion and erosion phenomena in flowing lead temperature range between 400° C and 650° C at 1-10m/s with chemistry control

Chemistry control in Lead in accidental scenario

1) Tests, consisting of water/steam injection inside the liquid lead, were carried out with the scope to support the **safety analysis** concerning the consequences of a leak-before-break in a tube of the **steam generator**.

2) A test, consisting of **water/steam injection inside the cover gas**, was carried out to support the safety analysis concerning the consequences of a steam inlet into the cover gas during the fuel handling.

3) A test, consisting of **injecting air into the cover gas**, was carried out, with the scope to study the kinetics of oxygen diffusion from the cover gas to the liquid lead.



Newcleo LFR AS:200

These tests had to provide information about the chemistry of lead and its control.

SOLEAD Experimental Facility

- **SOLEAD** (Solar tOwer LEAd Demo) experimental facility has used, in collaboration with newcleo, to carry out tests of interest for GEN-IV fast reactors, LFR type.

- The fields of SOLEAD application are: qualification of large size component, tests in natural circulation of the lead coolant, thermo-hydraulics tests in a big pool, material corrosion tests, lead conditioning and chemistry control tests.

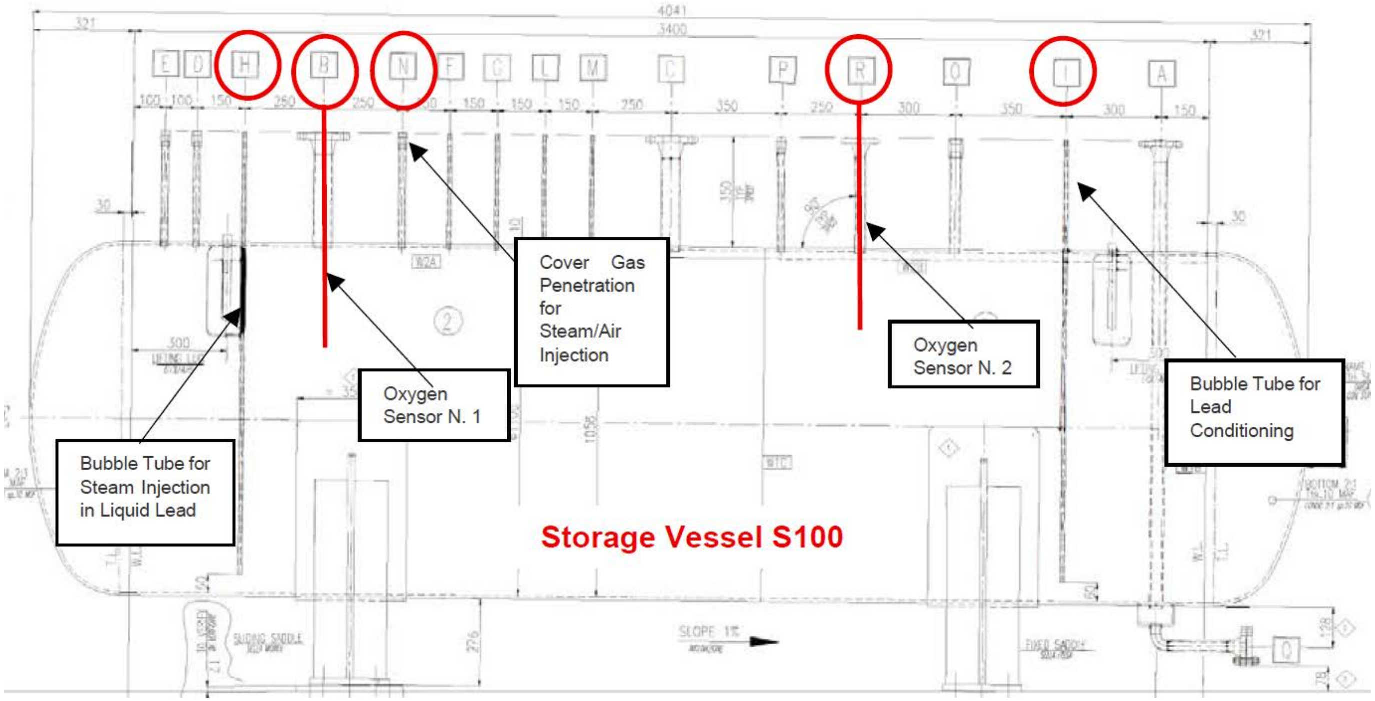
SOLEAD Application

Main Design parameters of SOLEAD facility

Data	Value
Lead quantity	37 t
Storage vessel capacity	3640 L
Main vessel capacity	3720 L
Maximum temperature of lead conditioning in storage vessel	500°C
Maximum temperature for tests in main vessel	800°C
Lead conditioning by gas mixture	$Ar/H_2/Air$
Oxygen concentration measurements by Electrochemical Oxygen Sensors	Max. 3 (in storage vessel)

SOLEAD Facility Description

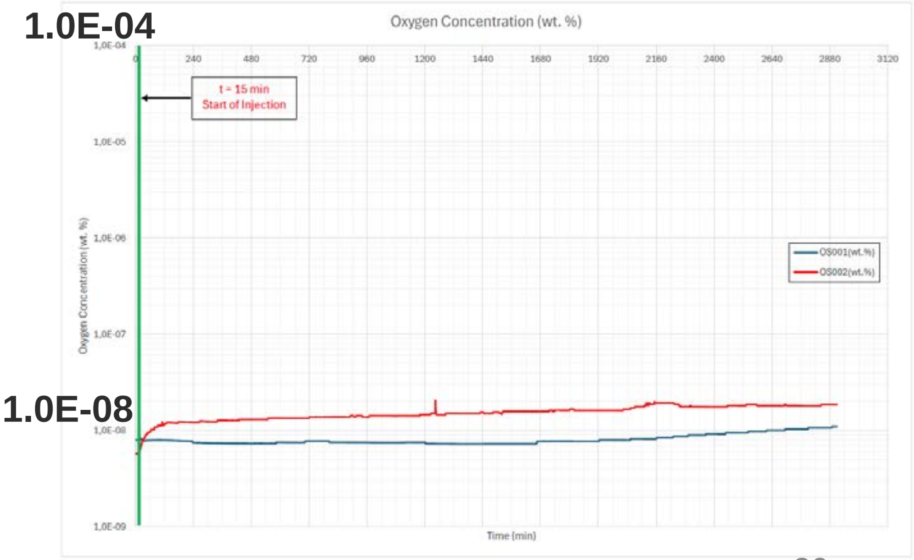
The facility is mainly composed of a main vessel S200, a storage vessel S100 and a gas panel, for the conditioning of the lead and the Ar supply to the cover gas of the vessels. For the tests described in the following, only the storage vessel was used.



Steam Injection in Liquid Lead

- The tests aimed to study if interactions occur when **steam is injected into liquid lead** and if these interactions, causing the dissociation of the water, can increase the oxygen dissolved in the liquid metal bath.
- Different quantities of steam have been injected inside the liquid lead: the minimum amount (**40 g**) of injected water has an oxygen content sufficient to increase its concentration inside the liquid lead from 10^{-8} wt% to 10^{-4} wt%.

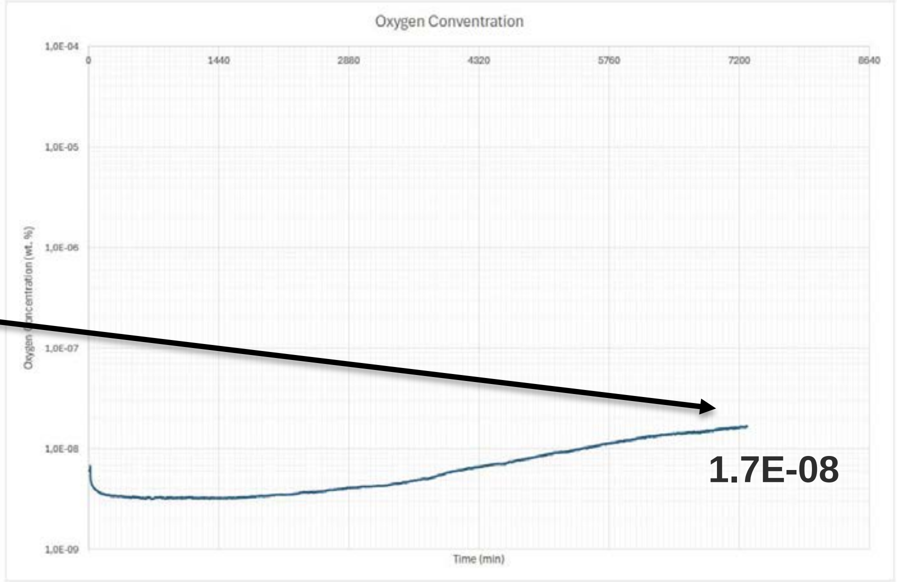
- The initial test conditions are the following:
  - Lead temperature: 480 ± 2 °C
  - Oxygen content in Pb: ~ 10^{-8}wt. %
- The Figure shows the oxygen concentration measured by the 2 Oxygen Sensors in Pb.
- The measured concentration is far from 10^{-4} wt%, value close to oxygen saturation in liquid lead at 480°C.



Steam Injection in Cover Gas

- The test aimed to study if interactions occur between **steam injected into the cover gas** and the lead free surface and **if these interactions can cause the dissociation of the water molecules**, with production of oxygen and hydrogen, and diffusion of oxygen into the lead bulk.
- The quantity of water that has been injected inside the cover gas is **100 g**. The initial test conditions are the same of the previous tests.

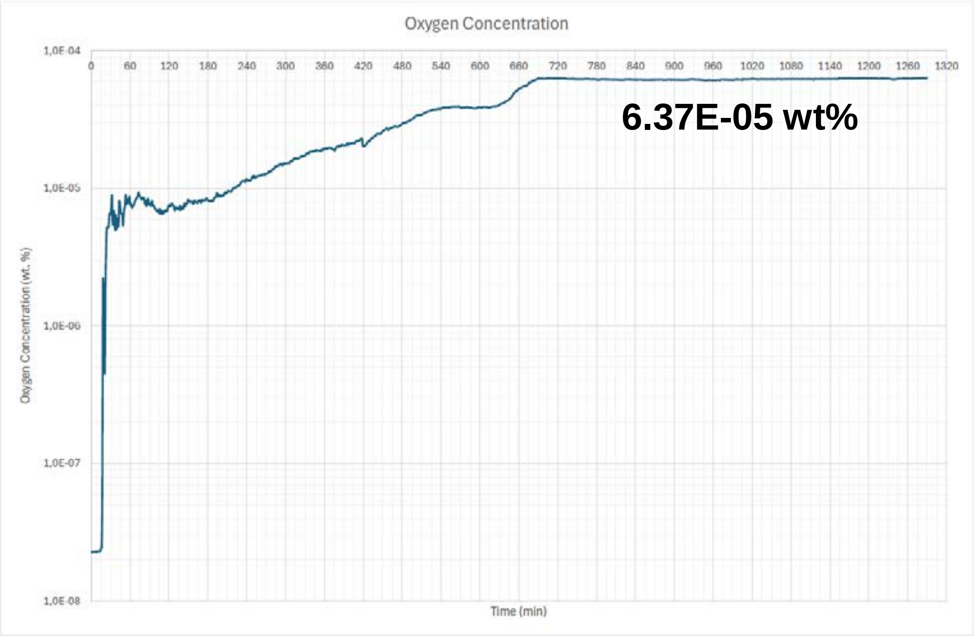
- The Figure shows the oxygen concentration measured by OS001, during the test.
- After the initial transient, the oxygen concentration measured remains approximately constant for a little over a day and then starts to increase, reaching the maximum value, at the end of the test, of approx. 1.7E-08 wt. %.



Air Injection in Cover Gas

- The aim of the test was to study if **interactions** occur between **air injected** into the **cover gas** and the lead **free surface** and the **kinetics of oxygen diffusion** inside the lead. The initial test conditions are the same of the previous tests. The quantity of air that has been injected inside the cover gas is **120 NL** (same atomic oxygen content of 40g of water).

- In this test, the oxygen concentration measured by OS001 shows a sharp increase. Then, the increase becomes less pronounced and, after approximately 675 min from the start of injection, the oxygen concentration remains approx. constant, reaching a maximum value of 6.37E-05 wt%, close to saturation. The arrest of the oxygen concentration growth is due to the decrease of the cover gas pressure and, as consequence, its lower oxygen content.



Test Results – Chemistry control in lead

- The results showed that the **steam injection**, both in the lead and cover gas, has had a negligible impact on the coolant chemistry control.

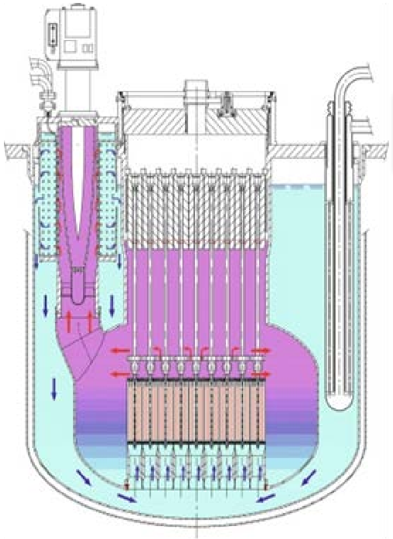
- The inlet of **air in the cover gas** has had a quick effect on the oxygen content inside the liquid lead; this fact leads to suppose that the operations of the facility could be compromised if countermeasures are not taken.

Materials Characterization in Lead

- Structural materials behaviour in lead are analysed at operational, accidental and transient conditions.
- Different product type of the alloy is investigated for each condition: forged bar, seamless pipe, laminated plate, and welded joint.

Component	Acc. Max Temp. (0) (°C)	Max. Rad. damage (dpa)	Material (early stages with C_O = 10^{-6}-10^{-8} w%)
Fuel cladding	530/750	100	15-15Ti 20% CW (AIM1)
FA Structures	500/750	100	15-15Ti 20% CW (AIM1)
Internal structures	500/700	<2	AISI 316LN (ASTM)
Steam Generator	500/700	0.01	AISI 316LN (ASTM)

Newcleo LFR: AS-200

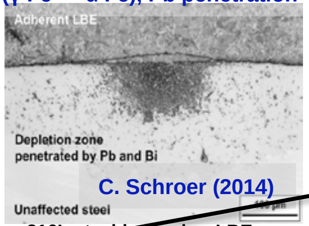


Power	480 MWth
Core coolant	Pure lead
Core coolant temperature	inlet 420°C, outlet 530°C
Layout	Pool-type
Circulation	Forced: 6 pumps
Spectrum	Fast
Fuel form	Extended-stem fuel assembly
Fuel	MOX
Secondary side fluid	Water
Steam generators	6 spiral-tube SG
Design life	60 years
Lifetime capacity factor	94%

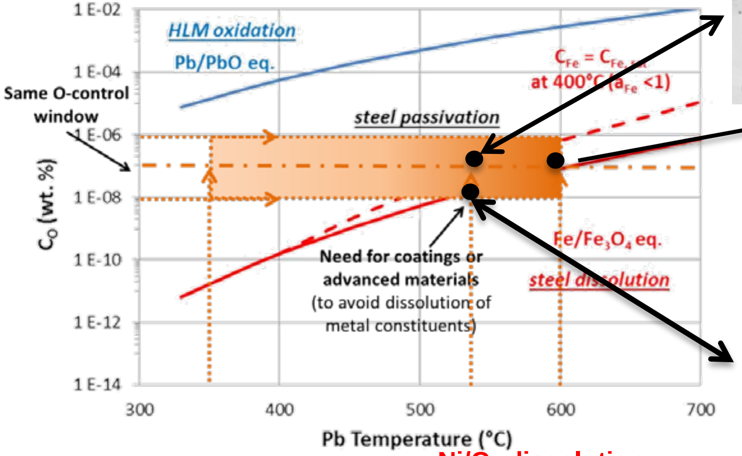
Material Characterization in Lead-accidental scenario

Screening tests on 316L (N) have been performed in CAPSULE at 500°C and 600°C with oxygen concentration slightly above the passivating one: 10-7wt.%. **Exceeding the operational limits** helps to see any difference in the materials' behaviour.

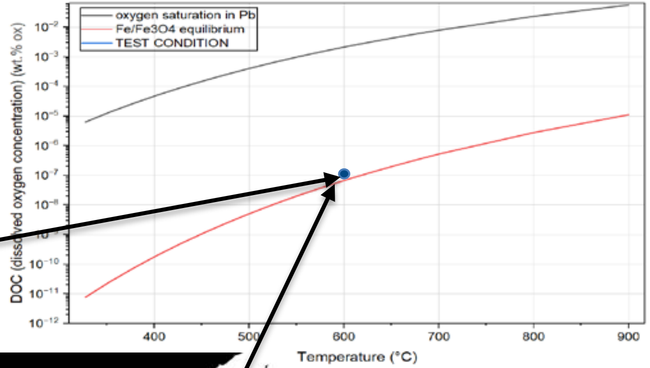
Oxidation + Ni/Cr dissolution (γ Fe → α Fe), Pb penetration

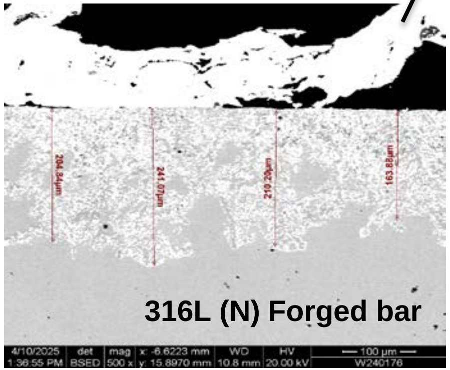


316L steel in flowing LBE, 550°C, high C_O, 7500 h.



Ni/Cr dissolution (γ Fe → α Fe), Pb penetration, no oxidation

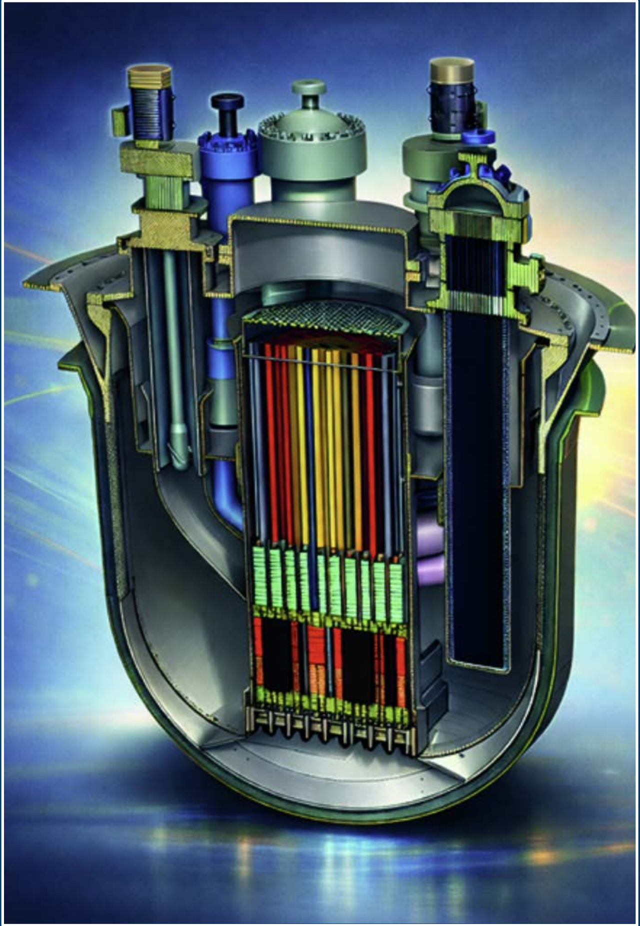




Material Characterization: accidental and accidental conditions

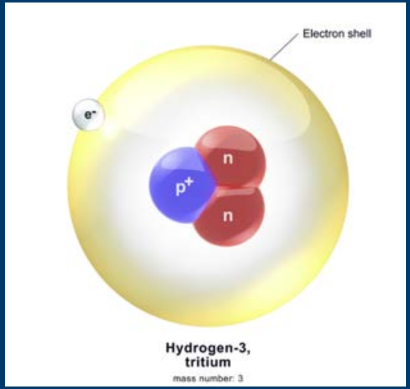
- **Accidental, transient and cumulative/integral durations of accidents, transients** and accidents throughout the anticipated lifetime of the relevant components and systems must be studied. Three different operative conditions can be identified as main area of interest:
  - **Operational limit** (Design Basic Condition (DBC)-1, 550°C, corrosion layer under 144 µm in 1,000 hours with an oxygen content of 10^{-7} wt.%)
  - **Plant Restart limit** (DBC-2 &3, 650°C, $10^{-2} > f > 10^{-4}$ y^{-1})
  - **Major Accident limit** (DBC-4 & DEC-A, 750°C, corrosion runaway threshold, $f > 10^{-4}$ y^{-1})

Subsequent tests under **normal operating conditions** should be conducted by varying temperature (440°C and 480°C), oxygen content (10^{-8} wt.% - 10^{-5} wt.%), and exposure time (ex. 500 - 8000 hours). A sensitivity analysis is performed to evaluate the effects of time, oxygen content, and temperature on corrosion and passivation layer development, using SEM and EDS analyses on cross-sections of the tested samples.



Tritium Management

- Tritium source
- Tritium transport in the reactor



Tritium sources

The main sources of tritium in a fission reactor are:

- ❑ fuel rods, via ternary fission of fissile nuclides
- ❑ reactions with boron in control and shielding rods
- ❑ reactions with impurities (mainly lithium)

$$^{10}_{5}B + ^{1}_{0}n \rightarrow 2\ ^{4}_{2}He + ^{3}_{1}H$$

$$^{10}_{5}B + ^{1}_{0}n \rightarrow ^{4}_{2}He + ^{7}_{3}Li$$

$$^{7}_{3}Li + ^{1}_{0}n \rightarrow ^{4}_{2}He + ^{1}_{0}n + ^{3}_{1}H$$

- ➢ **Ternary fission** is a rare type of nuclear fission in which three charged nuclides are produced instead of two. The specific amount of tritium produced by ternary fission depends on the fissile nuclide and the neutron flux spectrum
- ➢ => ranges between 0.8 and 20 x 10^{-4} atom/fission.

Tritium Yield by ternary fission from Fast Reactor with neutron energy 1-4 MeV

Reference	Tritium Atoms/Fission (x 10^{-4})				
	$^{232}_{90}Th$	$^{233}_{92}U$	$^{235}_{92}U$	$^{238}_{92}U$	$^{239}_{94}Pu$
Buzzelli at al. (1976) – Buzzelli and Langer (1977)	6	15	1.5	9	20

Tritium Yield from ternary fission

Reference	Tritium Atoms/Fission (x 10^{-4})				
	$^{233}_{92}U$	$^{235}_{92}U$	$^{238}_{92}U$	$^{239}_{94}Pu$	$^{241}_{94}Pu$
	Thermal Neutrons				
Fluss (1972)	1.1	0.85 ± 0.09			
Horrocks (1973)	0.88 ± 0.07	0.75 ± 0.08		1.51 ± 0.10	
Albenesius (1960)		0.95 ± 0.08			
Sloth (1962)		0.80 ± 0.01			
Ray (1966)		0.87			
Marshall (1966)				2.3	0.26
Albenesius (1959)		0.5 – 1.0			
Vorobiev (1969)		1.26			
Dakowsky (1967)		1.24			
	Fast Neutrons				
Fluss (1972) – Halpen (1971)		2.0 – 2.2			
Buzzelli (1976)		1.4 – 1.7	10 – 20.6		

J.E. Tanner – An overview of tritium fast fission yields – PNL-3563 UC-11 (1981)

Tritium sources - ternary fission

Knowing the number of tritium atoms produced per fission, it is possible to calculate the activity of tritium after a certain time t. The rate of tritium production by ternary fission can be calculated using the equation:

$$\frac{dN}{dt} = KWY - \lambda N$$

where:

N	= number of tritium atoms generated at time t;
K	= fission rate at unit power (3.121×10^{16} fissions/sec-MW);
W	= reactor power (MW);
t	= time (sec);
Y	= tritium atoms generated per fission;
λ	= decay constant of tritium (1.793×10^{-9} s^{-1}).

Integrating the equation it is possible to find the activity of tritium after a certain time t: $A = KWY\left(1 - e^{-\lambda t}\right)$

S_{tern}^{sp} = 2 - 4 x 10^4 [Ci/1000 MWe/y] = 2 - 4 x 10^4 [Ci/2500 MWth/y]

preliminary estimation of the tritium source for a reactor of 1000 MWe corresponds to 2500 MW

Tritium sources – control rod

A correct estimation of the ^{3}H yield from boron included in the control rods (B4C) requires to know the radial dependence of flux, the neutron spectrum and the amount of B involved in the neutron reactions.
For a preliminary estimation of the tritium generation rate from boron capture, it is possible to consider the same procedure already shown for the tritium source from ternary fission:

$$S_{B4C}^{sp} = 6.5 \times 10^{4} \text{ [Ci/1000 MWe/y]} = 6.5 \times 10^{4} \text{ [Ci/2500 MWth/y]}$$

To a preliminary evaluation of the total tritium source in the primary coolant of a LMFBR, one could suppose that all tritium generated by ternary fission is released in the coolant, while only 10 – 20 % of that generated by boron in control rods is released.

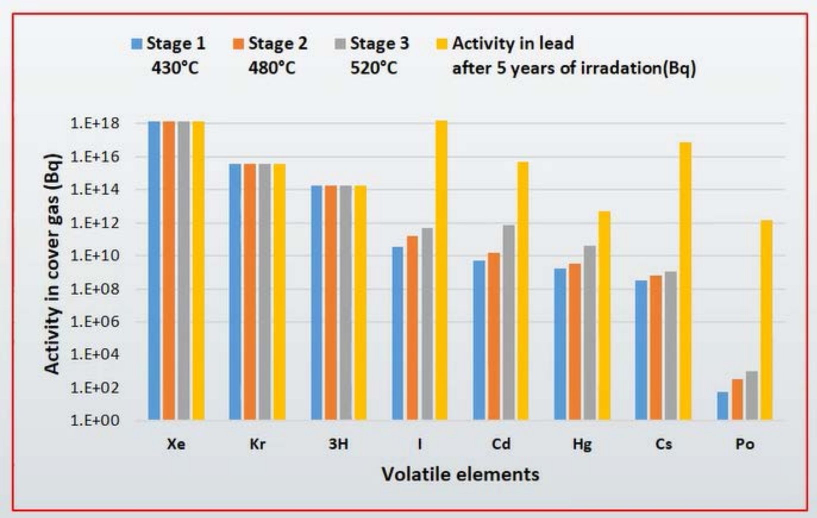
Tritium sources

Considering:

$$S_{tot}\left[\frac{Ci}{y}\right] = S_{tot}^{sp}\,\frac{P_{th}\,[MWth]}{2500}$$

Thermal Power (MWth)	Total Tritium Source in the Coolant (Ci/y)
300	3.18 ÷ 6.36 x 10^3
1500	1.59 ÷ 3.18 x 10^4

In the case that all the tritium generated is released in the cover gas the tritium inventory will be in the range 10^{+14} Bq.



Tritium Inventory in LFR

Tritium sources

Drawbacks of tritium in Lead coolants:

- Tritium can permeate through the heat exchanger into the second coolant (water)
- Tritium can permeate through the vessel and be released into the environment
- Tritium will diffuse in the components (steels) and generate waste

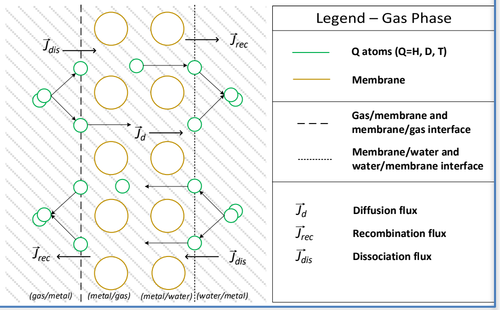
Tritium transport in the heat exchanger

$$H_2 + T_2 \rightleftarrows 2HT$$

$$HT + H_2O \rightleftarrows H_2 + HTO$$

$$T_2 + H_2O \rightleftarrows HTO + HT$$

$$HT + H_2O \rightleftarrows HTO + H_2$$

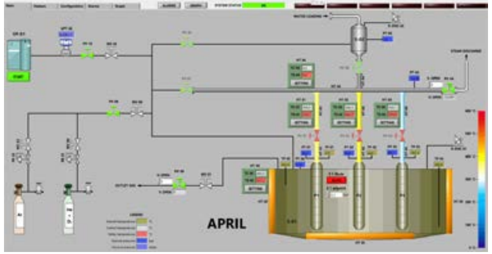


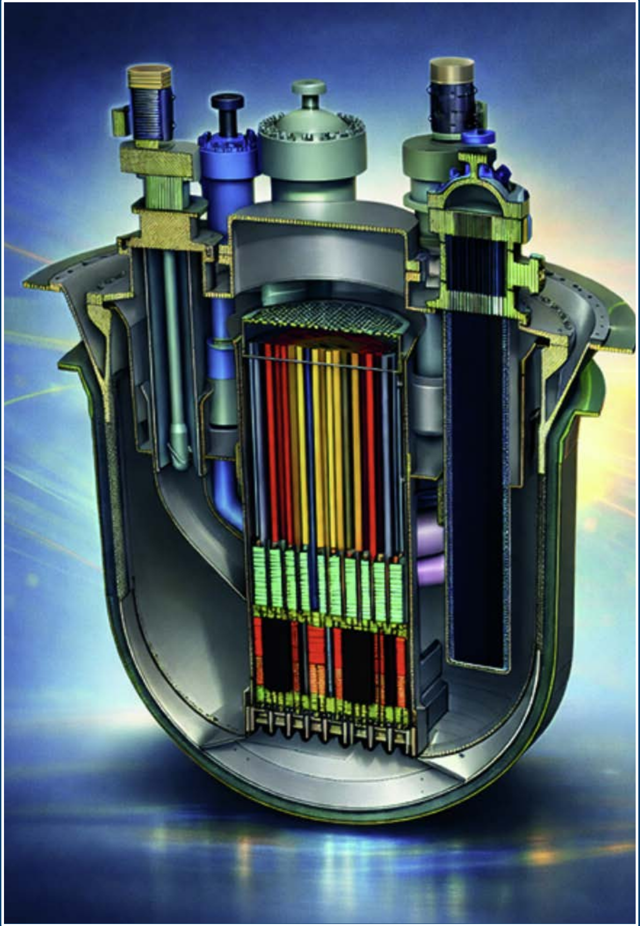
To be able to perform tritium balance in the reactor, it is mandatory to know Tritium solubility in Lead, and tritium permeation kinetics in the heat exchanger:

Investigator	Solubility (cc/100 g Pb) at 600°C	Sievert's Constant, K_S (appm H/torr$^{1/2}$) 600°C
Opie and Grant(3)	0.25	1.68
Hofmann and Maatsch(4)	< 0.01*	< 0.067*

E.M. Larsen UWFDM-415, https://fti.neep.wisc.edu, 1980

APRIL – facility to measure Tritium transport in the heat exchanger





Protective Coating

- TRL of the technology
- Coating Material
- Deposition Techniques
- Component to be coated

Identification of coating technologies

Coating function:

- ➢ Avoid material corrosion/erosion
- ➢ Reduce tritium permeation (cladding or heat exchanger)

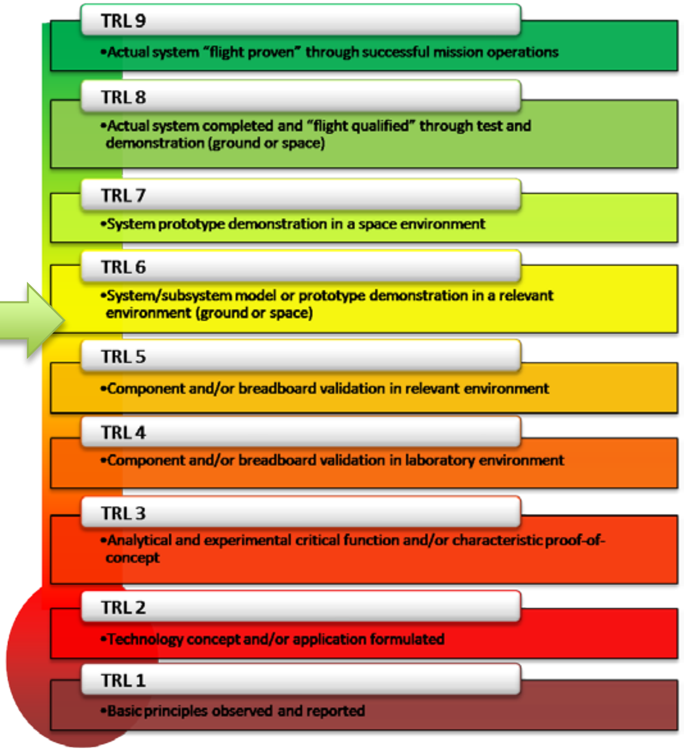
To select the reference coating technology for the short and long period for each components it is necessary to identify:

Material Selection

1. Assessment of the compatibility of proposed coating materials with the environment;
2. Assessment of the performance of such coatings taking into account the operating conditions.

Technology selection

1. Assessment of the compatibility of the manufacturing techniques with the application of the coating on the component
2. Status of the technique
3. Cost



Base Materials analysis (C_O= 10^{-6} - 10^{-8} wt. %)

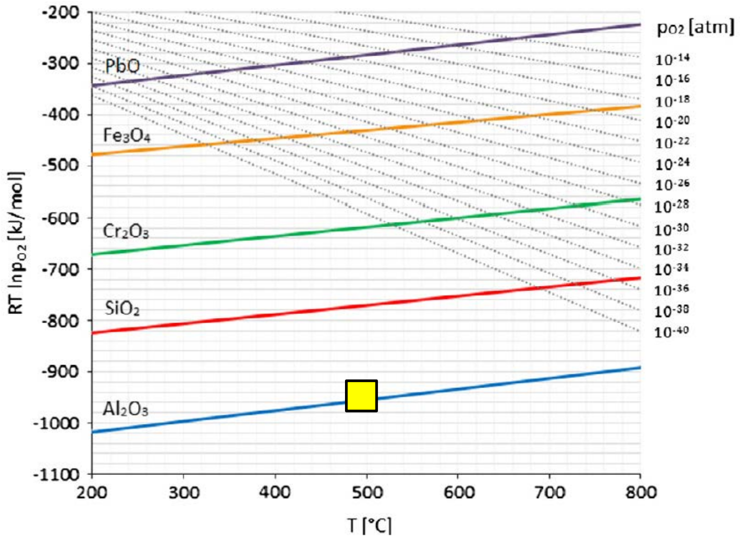
Component	N.O. Temp. (0) (°C)	Acc. Max Temp. (0) (°C)	Max. Lead vel. (m/s)	Max. Rad. damage (dpa)	Material (early stages with C_O = 10^{-6}-10^{-8} w%)	Material and/or Coating (later stages)
Fuel cladding	390-450/600	550/800	2	100	15-15Ti 20% CW (AIM1)	
FA Structures	390-430/540	500/700	2	100	15-15Ti 20% CW (AIM1)	
Internal structures	390-430/520	500/700	1.5	<2	AISI 316LN (ASTM)	
Steam Generator	390-430/520	500/700	0.9	0.01	AISI 316LN (ASTM)	
DHR Heat Exchanger	390-430/520	500/700	0.2	0.01	AISI 316L (ASTM) 15-15Ti (DIN 1.4970)	
Primary Pumps (impeller)	390-430/520	500/700	10÷20	0.01	AISI 300 series	
Reactor Vessel	390/400	420/430	0.1	<<2	AISI 316LN (ASTM)	

(0) Min. Temperature – Max. Temperature (early stages)/Max. Temperature (later stages)

Selection of coating Material

ALFA-Alumina (α-Al2O3)

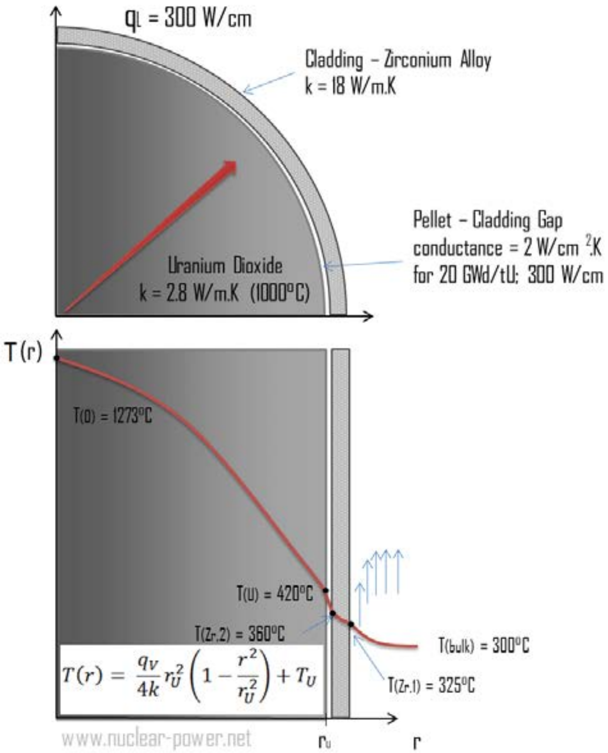
Al-based coatings are presently considered as reference base material for anti-corrosion/permeation barriers in lead. Years studies about Al-based coatings on various steels obtained with different techniques demonstrated that these layers have such anti-corrosion reduction behavior.



A large number of methods are available to deposit coating but previous results concerning fabrication and or qualification led to a selection of the following coating techniques:

- ✓ Pulsed Laser Deposition (PLD)
- ✓ Chemical Vapour Deposition (CVD)
- ✓ PVD
- ✓ D-Gun
- ✓ Thermal Spray
- ✓ Pack cementation
- ✓ Atomic Layer Deposition (ALD)

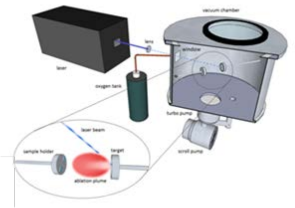
Coating for Fuel cladding



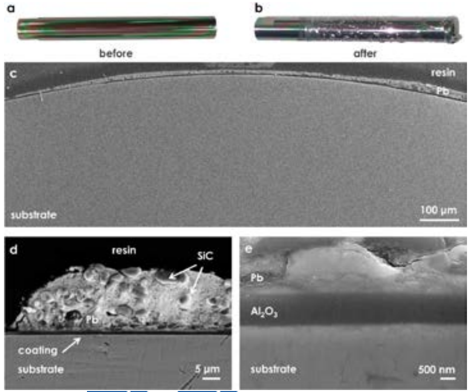
Main requirements:

- Thin film (cladding thickness ~ 0.5mm)
- High thermal conductivity
- Homogeneous
- Operation under high dpa
- High working Temperature
- Lifetime ~ 5years
- Applied on the external surface of tube

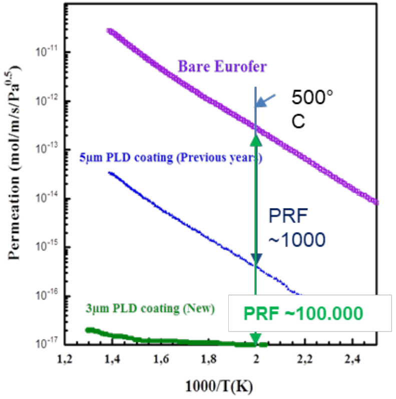
Pulsed Laser Deposition – Al_2O_3 coating

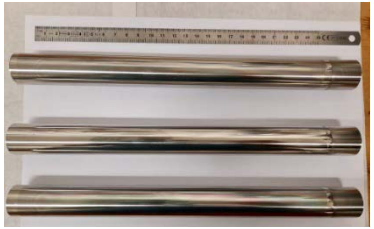


Property @RT	Sapphire	PLD Al_2O_3	AISI 316L
ν	0,24	0,295 ± 0,025	0,3
E [GPa]	345	193,8 ± 9,9	200
G [GPa]	175	75,5 ± 3,8	80
B [GPa]	240	159,2 ± 11,8	140
H [GPa]	27,8	10,3 ± 1	4
H/E	0,059	0,049 ± 0,007	0,025

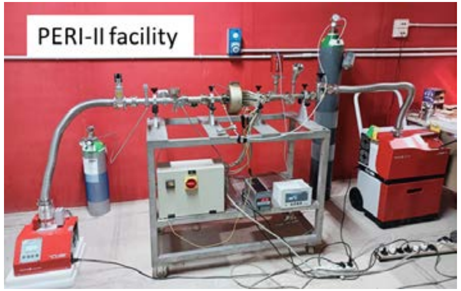


In the *PLD* a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material (EUROFER/AISI). Al is vaporized from the target and as result, a high homogeneous layer of alumina is deposited.





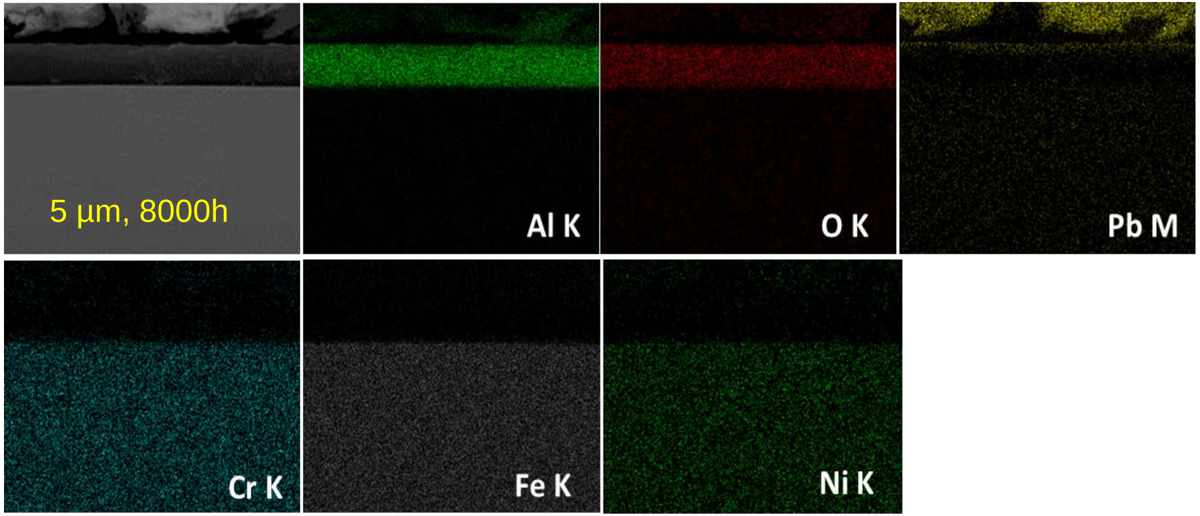
1" tube - 300 mm long AISI 316L coated with α - AL2O3 - 3 µm

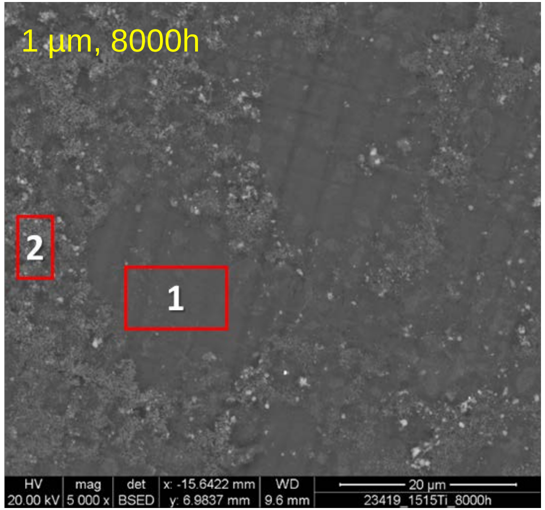


PLD coating was investigated in the frame of Fission and Fusion program (**FP8-BB EUROFUSION**) in terms of:

- Corrosion tests in the Temperature range 350-650°C in Pb, LiPb
- Permeation test in the Temperature range: 300-550°C in gas and H_2O
- Ion irradiation up to 100dpa and neutron irradiation at 3 10^{14} n cm^{-2} s^{-1}

Alumina by PLD – 8000h





- Coating produced by X-nano
- No cracks, no coating degradation due to Pb interaction, steel substrate well protected both with coating thickness 1 and 5 µm.
- The surface is compact, no discontinuities are observed.

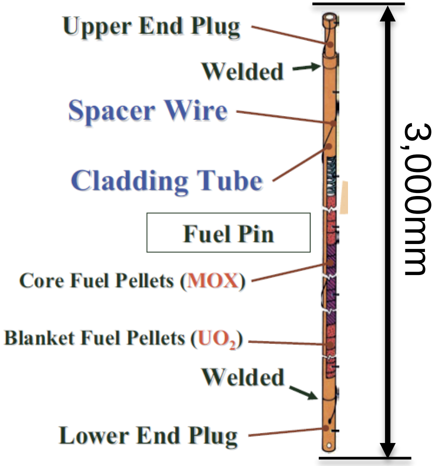
	Element	OK	AlK	PbM
Area 1	Wt%	47.6	50.6	1.8
	At%	61.2	38.6	0.2
Area 2	Wt%	44.2	52.2	3.5
	At%	58.6	41.0	0.4

Pulsed Laser Deposition (PLD)

Main Characteristic:

- ✓ capacity to coat only on open surface
- ✓ room T process: possibility to coat cold-worked steels, i.e. AIM-1;
- ✓ anti-diffusion and anti-permeation capability against several gases (e.g. H_2 and D_2): particularly relevant for tritium confinement, for either fission- or fusion-based systems;
- ✓ high radiation tolerance: Al_2O_3 films have been irradiated with heavy ions up to 150 dpa, showing neither cracking, nor delamination.
- ✓ quasi-metal mechanical behaviour: properties similar to that of steel substrate;
- ✓ Corrosion resistance with Pb up to 550°C

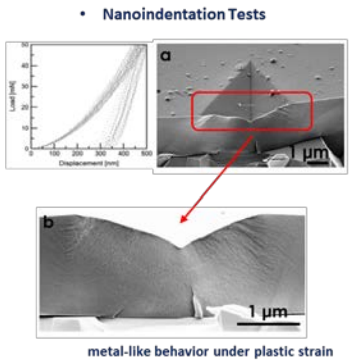
Pulsed Laser Deposition (PLD)



- ❑ 1:1 scale PLD facility was designed and will be installed in 2026-2027 in **ENEA Brasimone** to validate the process at an industrial scale.

The facility will be able to:

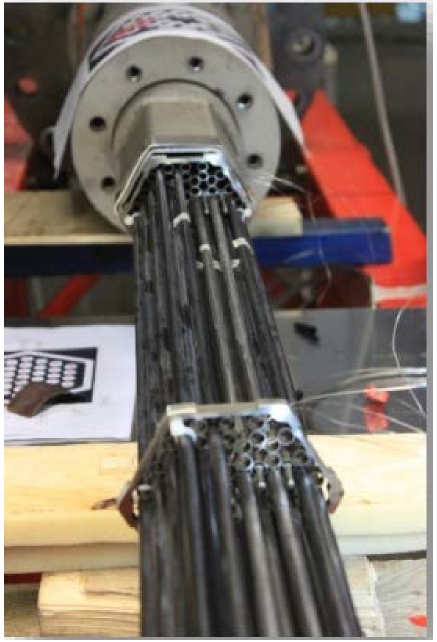
- ❑ Manufacture the coating on pipes characterised by a length of 3,000mm, and a diameter in the range between 6 and 13mm
- ❑ Manufacture the coating on 1000 pipes per year.



Heat Exchanger and DHR

Main technical issues to be considered:

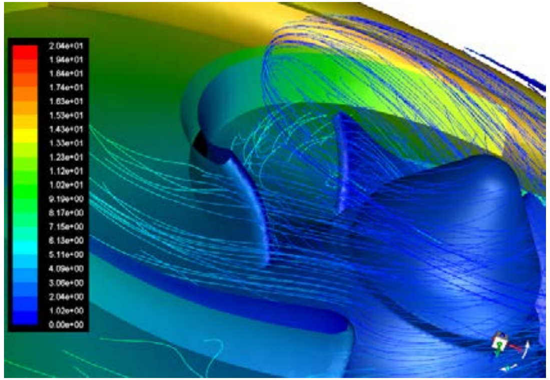
- Large size component with welds
- Tubes should be welded
- High Thermal conductivity is required
- Thermal Gradient
- Pressurised tubes => mechanical stress

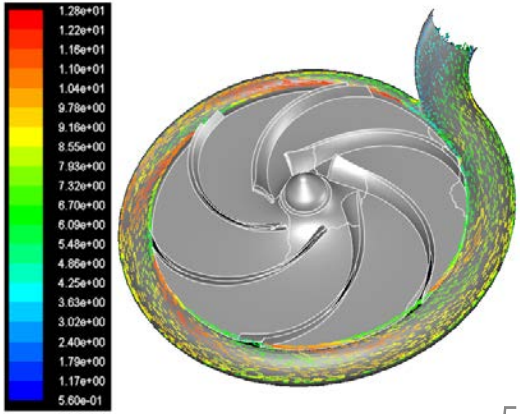


Pump Impeller

Main requirements:

- ❑ Resistant to erosion (Pb velocity profile in the range 20m/s)
- ❑ Resistant to corrosion in Pb
- ❑ Protection for wear resistant and hardness
- ❑ Complex geometry





Diffusion Coating

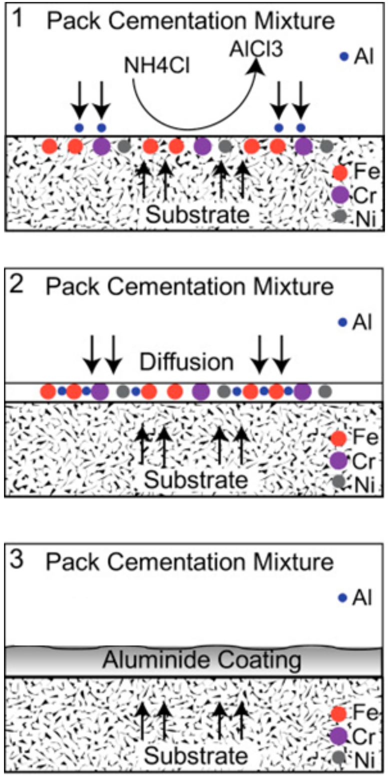
Diffusion coatings consist of a "*[surface enrichment of the substrate material with elements able to form a protective scale of oxide]*", i.e. Al, Cr and Si or combinations of them, with depths from 10 up to several hundreds microns.
In the diffusive process, these elements combine with the constituents of the substrate alloy.

Diffusion coatings can be produced by different processes:

1. **Pack cementation process**, slurry technology,
2. **Chemical Vapor Deposition (CVD**) process

The different processes share the same main steps, which are:

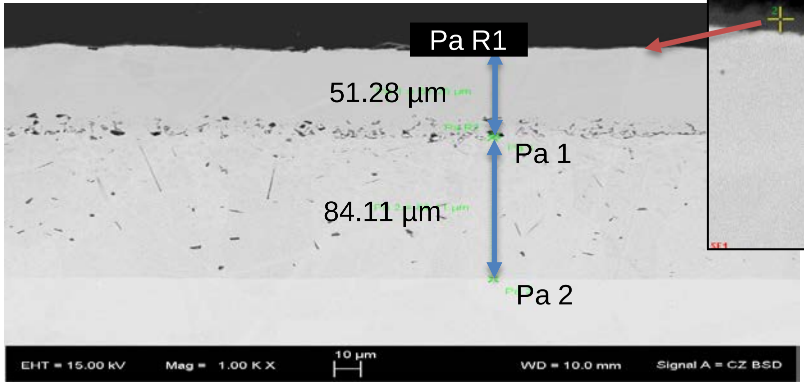
1. generation of vapors containing Al, Cr or Si;
2. transport of the vapors to the surface of the component to be coated;
3. reaction of the vapors with the alloy of **the substrate and diffusion process** within the substrate.

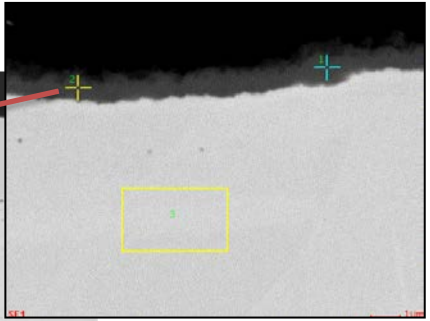


Packed cementation process on industrial comp.

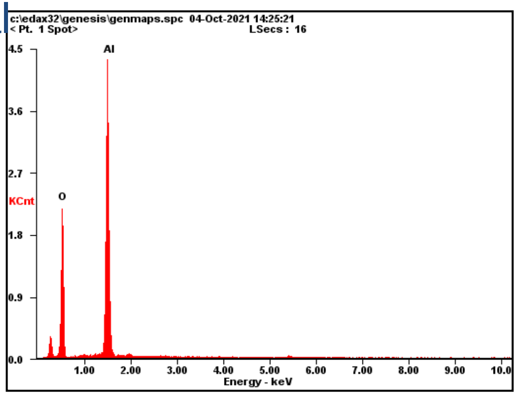
The coating results composed by three distinct layers:

- internal layer consists **of α-Fe(Al)** phase where the Al content goes from **18% wt. to 0** close to the substrate.
- Intermediate internal layer, composed of **Fe-Al** phase with an Al content of about **20% wt**.
- external layer, composed of $\mathbf{Al_2O_3}$ - $FeAl_2$ phase => required heat treatment



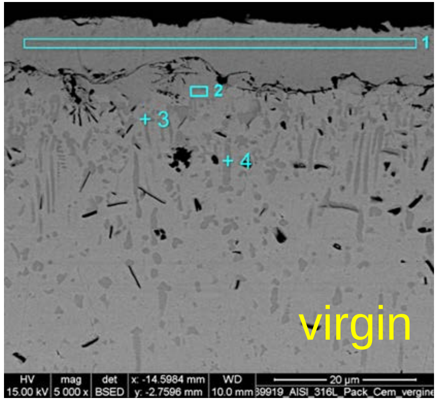


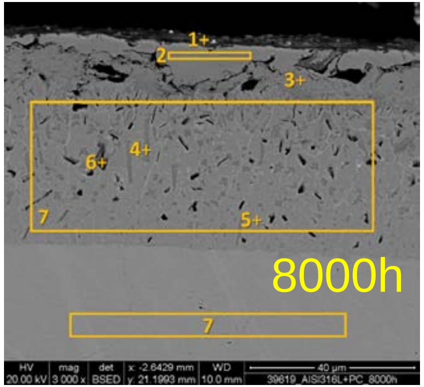
External Layer

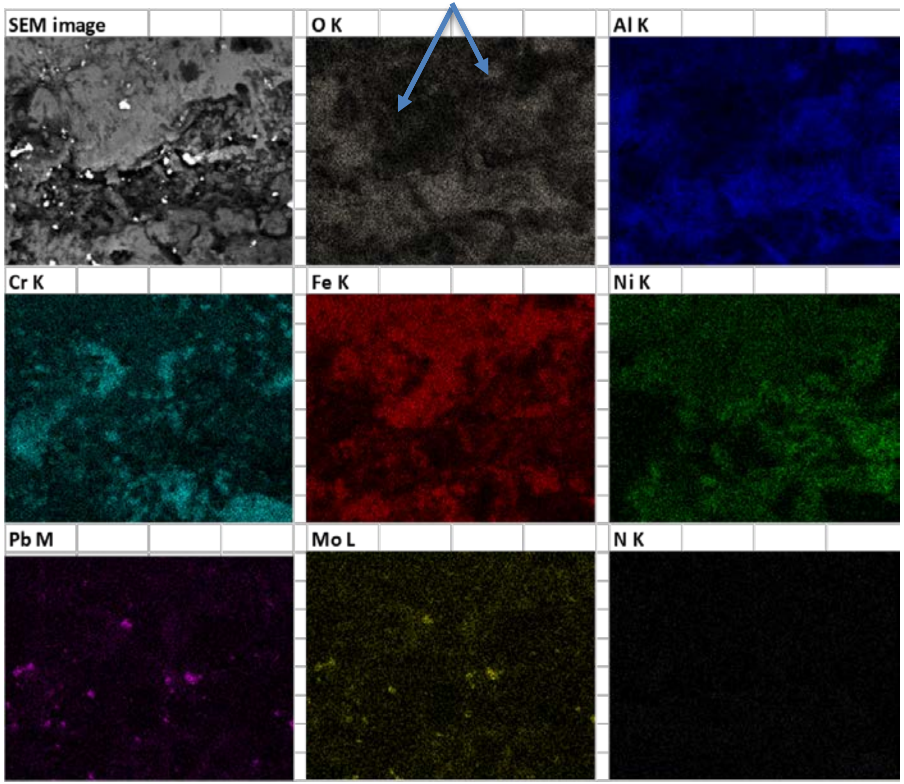


Element	Wt%	At%
OK	43.16	56.15
AlK	56.84	43.85

Pack Cementation modification – 8000h







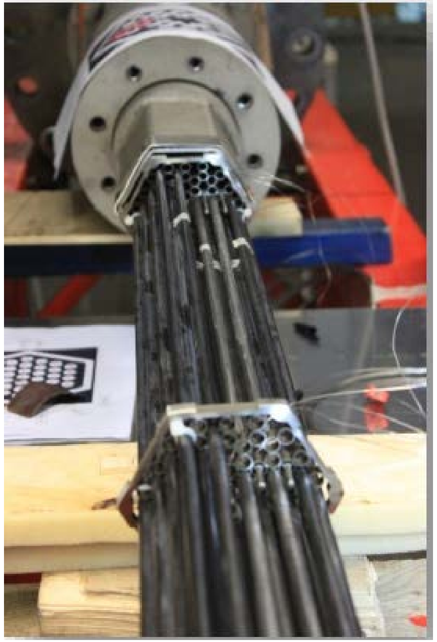
Lincotek pack cem. coating on 316L
External layer rich in Al ~ 8 µm
Diffusion layer ~ 40 µm
NiAl precipitates (B2-NiAl, grey)
Also Al-O precipitates (black spots)

No thickness variation after 8000h. External oxidation on the outer layer, not homogeneously dispersed over the surface (point 1 and EDX maps)

Heat Exchanger and DHR

Main technical issues to be considered:

- Large size component with welds
- Tubes should be welded
- High Thermal conductivity is required
- Thermal Gradient
- Pressurised tubes => mechanical stress



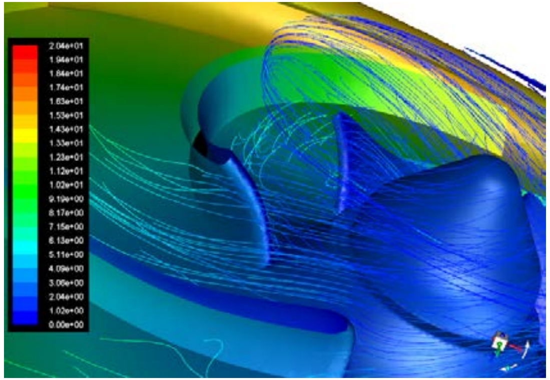
Proposed coating processes:

➢ Pack cementation process

Pump Impeller

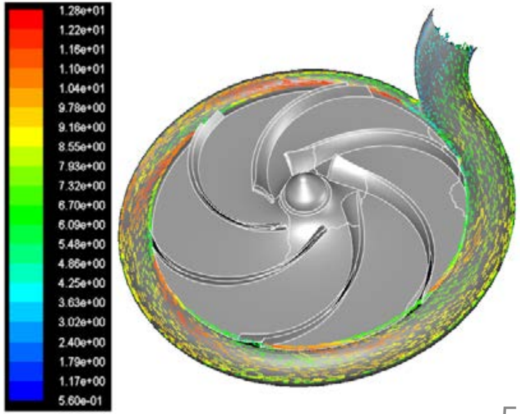
Main requirements:

- ❑ Resistant to erosion (Pb velocity profile in the range 20m/s)
- ❑ Resistant to corrosion in Pb
- ❑ Protection for wear resistant and hardness
- ❑ Complex geometry



Proposed coating processes:

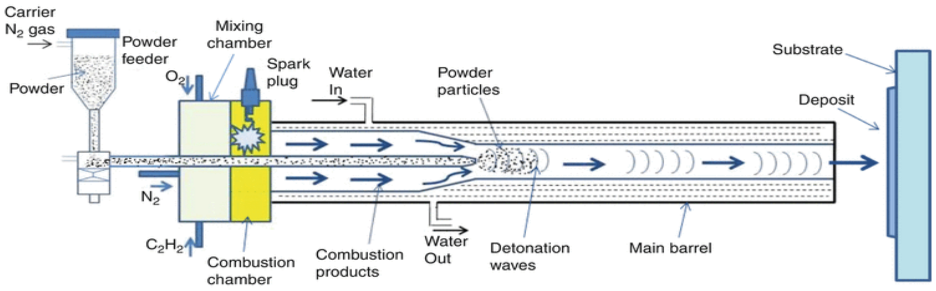
- ➢ Pack cementation process
- ➢ Chemical Vapour Deposition(CVD)
- ➢ PVD



Detonation Gun

Al_2O_3 coating by D-Gun

D-gun spray process is a thermal spray coating process, which gives an extremely good adhesive strength, low porosity and coating surface with compressive residual stresses.
A precisely measured quantity of the combustion mixture, consisting of oxygen, Nitrogen, acetylene are fed through a tubular barrel closed at one end. Simultaneously, a predetermined quantity of the coating powder is fed into the combustion chamber

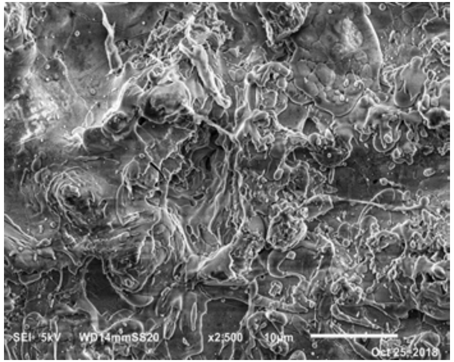


The gas mixture inside the chamber is ignited by a simple spark plug. The combustion of the gas mixture generates high pressure shock waves (detonation wave), which then propagate through the gas stream.

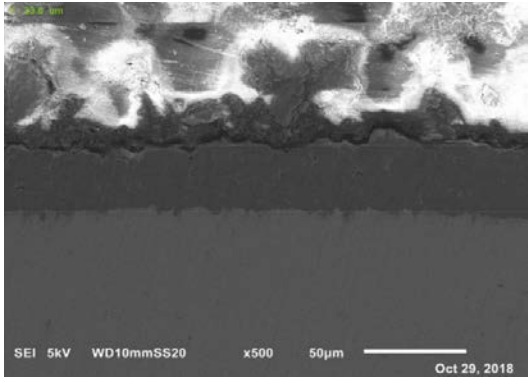
Detonation Gun

- Microstructural analysis 04514

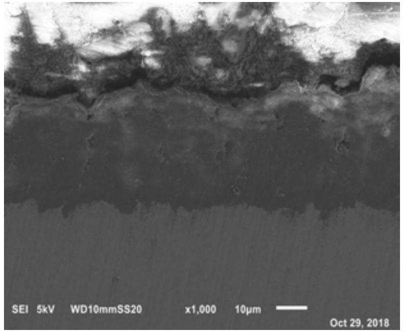
Spec. N	Programme	Substrate preparation, N. sandblasting	N. Layer	Substrate
04414	1	15	3	15-15Ti
04514	1	10	4	15-15Ti
04004	1	30	5	15-15Ti
04014	2	5	5	15-15Ti
04114	2	15	3	15-15Ti



- no open pores can be observed on the surface



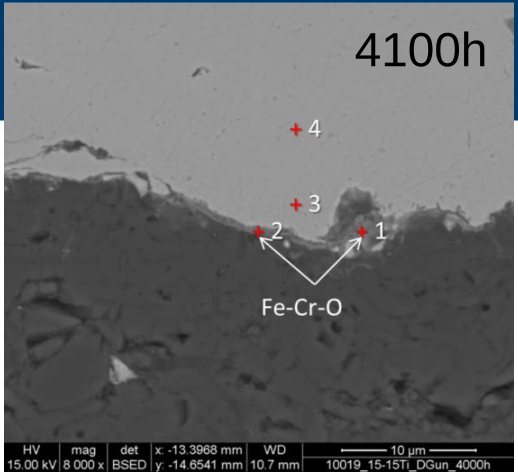
- average coating thickness of **about 34 μm**
- Increasing the number of layer from 3 to 4 the thickness of the coating doesn't increase
- porosity on the surface of the coating is reduced
- The coating had many closed pores but it is compact
- uniform composition and adhesion on the coating to the substrate

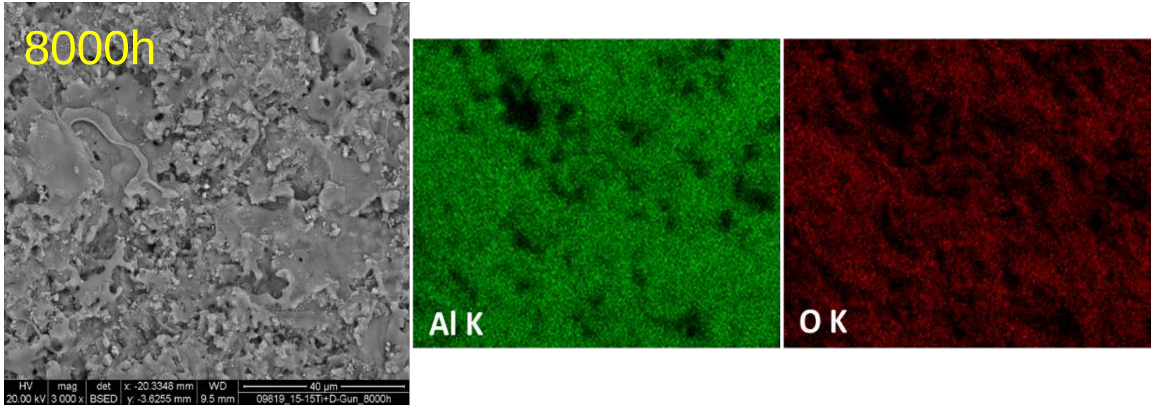


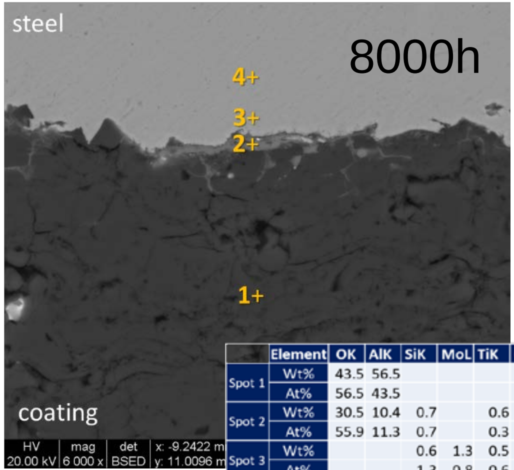
- good adhesion of the coating and no cracks with substrate can be observed

Alumina by D-Gun – 8000h

- Coating produced by ENEA
- Adhesion. No significant cracks. No variations of the thickness (30-40 µm) up to 8000h.
- Presence of porosity → oxidation on the steel substrate under the alumina coating: thin Cr or Fe-Cr oxide (thickness < 5-6 µm).







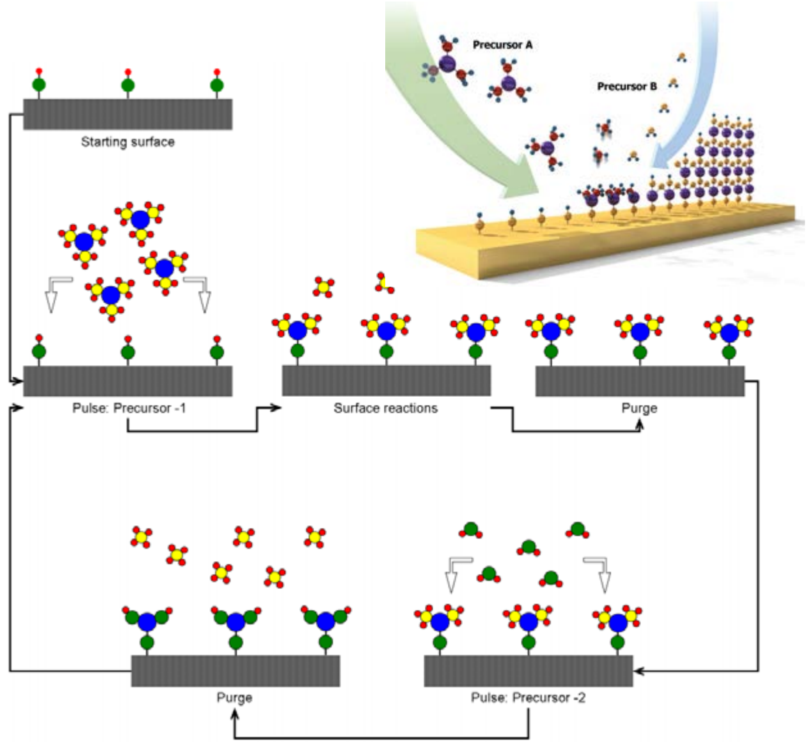
	Element	OK	AlK	SiK	MoL	TiK	CrK	MnK	FeK	NiK
Spot 1	Wt%	43.5	56.5							
	At%	56.5	43.5							
Spot 2	Wt%	30.5	10.4	0.7		0.6	36.0	5.6	14.7	1.6
	At%	55.9	11.3	0.7		0.3	20.3	3.0	7.7	0.8
Spot 3	Wt%			0.6	1.3	0.5	10.4	1.3	68.7	17.0
	At%			1.3	0.8	0.6	11.2	1.4	68.7	16.2
Spot 4	Wt%			1.0	1.9	0.6	14.9	1.7	64.6	15.3
	At%			2.1	1.1	0.7	15.9	1.7	64.2	14.5

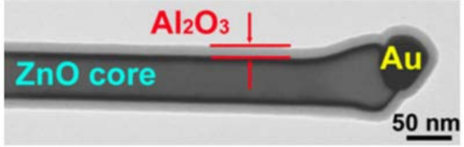
ENEA

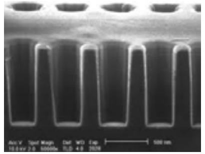
GEMMA project

Atomic Laser Deposition

Atomic Laser Deposition







a) *trimethylaluminum (TMA), i.e. the first precursor, enters the chamber and reacts with the substrate, producing gaseous by products and leaving a functionalized surface;*

b) *Nitrogen is used as carrier gas to purge the system;*

c) *water, i.e. the second precursor, enters the chamber and reacts with the surface of the substrate, producing a thin layer of Aluminium Oxide and gaseous by products;*

d) *Nitrogen is again injected in the reaction chamber to purge the system. These four steps are then repeated cyclically.*

Status:

- ✓ Can be performed at 150-300°C
- ✓ Can be deposited inside and external to the tubes
- ✓ Max size of the components that can be coated 30x30x30cm

Thank you for the attention!

Marco Utili
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