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Coolant quality control & Purification

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WHY IS IT NECESSARY TO CONTROL QUALITY AND TO PURIFY THE COOLANT IN LIQUID METALS

Primary coolant of XFR:

- [O] is a key parameter of corrosion → contamination→dosimetry → necessity to decontaminate (handling, repair, ISI,..): necessity to master [O]
- [O] well mastered can help to maintain oxide layer stable (protection against hard corrosion in heavy liquid metals HLM, enhancement of tribology)
- [O] can induce precipitation of coolant oxide (issue for HLM: PbO due to very low dissolution rate, no problem for Na), and modify composition of binary alloys, Pb-Bi...
- For Intermediate circuits of SFR (Na) :
 - [H] has to be maintained as low as achievable in order to detect as soon as possible a water ingresss in Na (Na-H₂O reaction generates H₂).
 - Moreover, Na purification allows to minimize tritium release. (Nota: Tritium release is a common issue for all nuclear systems, including FRs
- For all the circuits :
 - Control risks of plugging in narrow gaps, tubing, openings, seizing of the rotating parts, reduction of thermal transfer coefficient in IHX (Intermediate Heat Exchanger)...

→ to limit the plugging risk, necessity to maintain [O] < [O]* and [H] < [H]* at the coldest point of the circuits, for all operating conditions ; value recommended in SFRs: Tsat < Tcp - 30°C



SFR

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PRIMARY CIRCUIT OF SFR (POOL CONCEPT) 1/2



Heat Exchanger



PRIMARY CIRCUIT OF SFR (POOL CONCEPT) 2/2



Continuous

Diffusion of hydrogen through SGU walls Impurities in cover gas (Ar)

Discontinuous

Metallic oxides dissolution in Na

Air ingress after repair (air + moisture)

Water ingress in SGU

Oil ingress (pumps)

Metallic filling due to maintenance, etc...

Sodium pollution 1/2

→ The development of Sodium Fast Reactors (SFR) is possible thanks to the very attractive properties of Na.

→ Nevertheless, this coolant needs to be purified because of a potential accumulation of impurities such as oxygen and hydrogen and their deleterious consequences. These pollutants can be introduced during the operation of an SFR.

In the primary circuit:

- main discontinuous source of contamination due to O & H: adsorbed gas & metallic oxides less stable than Na₂O,
- contribution of O to steel corrosion in core,
- activated corrosion products transported towards the components: Intermediate Heat Exchangers (IHX)...
- contamination (⁶⁰Co, ⁵⁴Mn...) & dosimetry during handling and/or repair.



→ generally considered that an SFR must be operated with [O]< 3 ppm

in normal operation in order to control the generalized corrosion.

- → nuclear reactions in fuel and boron carbide : a very small continuous source of tritium in the primary vessel which permeates through the IHX towards the intermediate loops.
- → Some fission products if fuel cladding failure (¹³⁷Cs...)

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HE

QSE QSE Qualite Securite Environment Armon Commontes

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Sodium pollution 2/2

In the intermediate loops:

 main continuous source: hydrogen due to hydrogen diffusion in steam generators (SGU) through tube walls, due to aqueous corrosion on the water side and also to the thermal decomposition of hydrazine, used to control the oxygen content in the water.

- main potential discontinuous sources:

- sodium water reaction event: H₂, NaOH and potentially

Na₂O and NaH crystallized products.

→ strongly exothermic & extremely fast and may be inducing cracks in the neighboring pipes.

➔ [H] controlled at a low level (< 0.1 ppm) to detect asap a potential event in SGU producing.</p>

➔ Risk of deposits on the cold walls (Na2O & NaH), plugging of narrow sections, reduction of heat transfer coefficient in IHX

- contamination of the residual amount of Na by air and moisture, after draining, prior to handling and/or repair operation, inducing deleterious effects, mainly due to stress corrosion cracking induced by aqueous soda.

In all circuits:

- Potential oil ingress (pumps)
- Metallic filling due to maintenance, etc...





O & H solubilities in liquid Na



Main processes for Na purification



- Specific methods to obtain nuclear grade sodium
- Initial cleaning of loop, components and vessels
- Filtering
- Cold trapping
- Hot trapping
- And of course limiting ingress of pollution by appropriate operating rules



Crystallization methods

- Liquid evaporation (like salt)
- Reduction of the solubility by adding some additive impurity
- Cooling the liquid below saturation temperature



This last option is the most attractive : Convenient solubility laws for O and H (reach almost 0 near the Na melting point)

Easy implementation : cooling and solid retention































- If sodium is supersaturated, presence of agglomerates
- These agglomerates can turn into nuclei if free enthalpy of the system reaches a limit value (primary nucleation)
- Nevertheless some existing crystals can produce some small particles by attrition (secondary nucleation)
- The primary nucleation can be homogeneous (if it occurs in the sodium bulk) or heterogeneous if it occurs on metallic surfaces. Wetting characteristics have a large influence on heterogeneous nucleation





• Model of the kinematic wave (Franck-Vermilyea) : explain the formation of steps









Crystal growth (Na₂O)

Crystal growth (NaCl)



Growth phenomena

Two growth phenomena for Na₂O:

- low supersaturation : regular growth
- high supersaturation : dendritic growth



REGULAR GROWTH (X500)



DENDRITIC GROWTH (X20)



Growth phenomena



→ Kinetics of the overall phenomena = kinetics of the slowest step

Cold trap principle



Crystallization kinetics, given for one impurity O or H,]: in [kgNa2O/s] or [kgNaH/s]

$$r_{jX}(T,t) = k_{oX} \exp(-\frac{E_X}{RT}) A_{jX}(t) \left[\frac{(C-C^*)}{1.10^{-6} \rho_{Na}}\right]^{n_X} = Ko_X A_{jX}(t) [\Delta C]^{n_X}$$

In this equation:

Index X refers to Nucleation (N) or growth (G) Index j refers to the location on wire mesh packing (p) or cold walls (w). k0 is the rate constant (kg/(s.ppmnx.m²)), E is the activation energy (J/mol), R is the Boltzmann constant (J/(mol.K)). A is the crystallization surface of reference (m²) (wire or walls for nucleation, nuclei and crystals for growth). nX is the order of the crystallization process. C*(kg/m³) is the saturation concentration (from solubility law.) pNa is the sodium density in (kg/m³)

(C-C*) is the supersaturation at temperature T(K).





Phenomena	Nucleation (N)		Growth (G)	
Impurity	Na ₂ O	NaH	Na ₂ O	NaH
E (kg/mol)	-60	-450	-45	-43.6
n	5	10	1	2

Experiments carried out on Na₂O and NaH

For a cold trap designed with an upper packless cold zone:

→ Na₂O crystallization only on wire mesh packing

➔ NaH crystallization essentially on cold walls of the system, (if thermal flux is enough)

However, in case of a non-optimized packless cold zone, hydride might as well crystallize on wire mesh packing. Thus, cocrystallization occurs between sodium hydride and sodium oxide.

→ Hypothesis: kinetics parameters for NaH crystallization on cold walls identical to those on wire mesh packing.



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Transport Phenomena Coupling

C22





Main characteristics of the model:

Two types of crystallization behavior:

→ Two different modeling approaches (on cold walls or on mesh).

Crystallization	Wire mesh packing	Cold walls (packless zone)
Impurities	- Na ₂ O - NaH	- NaH
Models	- Porous medium densification	 Porous medium densification Interface tracking
Surface to crystallize	- Wire mesh - Oxide and/or hydride crystals	- Hydride crystals

→ For both approaches:

System : a porous media with a porosity ϕ referring to the void fraction of the liquid phase.

Porosity is initially:

- equal to 1 with deposit on walls (NaH),
- equal to the void fraction of the mesh packing if the deposit occurs on wire mesh (Na₂O).

Mixture of crystal and liquid sodium in which void fraction changes with time and space, as well as its physical parameters such as permeability, diffusion or thermal conductivity...

Fluid assumed to be incompressible and each infinitesimal volume assumed isothermal.

→ The model takes into account hydrodynamics in porous media, heat transfer, mass transfer, and nucleation and growth kinetics

→ Numerical model solved by finite element method in Comsol Multiphysics® software.





Cea Front propagation tracking for NaH crystallization

→ Density of NaH deposit experimentally estimated to be around 0.5
 → Crystal growth on cold walls can be seen as a phenomenon involving a moving interface, with propagation of a deposit front.
 → Tracking Moving Interface is a key element of the model





NaH deposits on cold wall (EPINAR experiment)

Interface tracking model for NaH crystallization on cold walls

C02



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Cea Purification system design methodology

- **Identification of the impurities to be removed** from the Na: mainly oxygen and moisture, potentially NaOH in case of very large sodium-water reaction.

- Assessment of their sources and their production rate (continuous & discontinuous)

i.e. Na-H2O reaction considered as instantaneous: necessity to define a Na leak scenario and a probability of occurrence. Then, it is possible to estimate the amount of water reacted and consequently the amount of products to be trapped.

- **Assessment of their potential sinks** i.e. corrosion of structural material, deposition in the coldest points of the circuits.

→ induces specifications on the removal rate to be obtained in order to prevent any deleterious effects, (exceptional corrosion due to large air ingress, stress corrosion cracking due to residual aqueous soda in remote locations...).

- Evaluation of the amount of impurities to be removed from the Na circuits, vessels, during the cold trap(s) operation over a given period depending on the strategy selected for the purification systems

→ induces specifications on the loading capacity

 Selection of several trapping zones (cold trap: generally a combination of 2 zones): Zone 1-A: Cooling zone, equipped with stainless steel mesh,
 Zone 1-B: Cooling zone, without mesh, with cooled walls, designed to trap or not NaH,
 Zone 2: Isothermal zone, located downstream from the cooling zone, after reaching the coldest point of the cold trap, equipped with stainless steel mesh.



Four main design criteria

Four main criteria generally considered for cold trap design:

Efficiency:

$$\varepsilon = \frac{C_i - C_o}{C_i - C_{\tau_{cp}} sat}$$

➔ recommended to get an efficiency of 1 for each trapping zone. (efficiency depends on the crystallization kinetics, residence time, local conditions....)

Purification rate: $Rp = \varepsilon \cdot D_{na} \cdot (Ci - C_{Tcp-sat})$

 duration of a purification campaign determined by the initial impurities content in Na and Rp

Capacity: total amount of impurities (mass or volume) accumulated in the cold trap over the entire time of operation, defined by the designer.

Compactness: ratio between the volume of impurities trapped in the cold trap and the overall internal volume of the cold trap.



Basic choice for purification system



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INTEGRATED PURIFICATION SYSTEM (SPX)





Instantaneous efficiency: E = (Ci-Co)/(Ci-C*) 0<E<1

Ci:concentration at the cold trap inletCo:concentration at the cold trap outletC*:concentration at equilibrium (solubility)

Purification rate: Vp = E.(Ci-C*).FNa

FNa: Na flow-rate

Capacity: Cap = $\Sigma \tau r$.Ed (in unit of volume)

where $\tau r = filling$ rate and Ed = deposited element concerned (area, volume)

Compactness: Comp = V1/V2

V1 = Maximum volume of the impurities retained in the trapV2 = Internal volume of the trap in which the deposit zones are located


Qualification strategy for SFR cold traps

In the eighties:

- **Definition of the main requirements**: pollution sources, purification rate, capacity, compactness)

- Design of the scale-one cold trap for the reactor, i.e. type of cold trap, cooling fluid, maximum allowable temperature, trapping zones to be implemented, ...

- Identification of similitude rules (heat transfer, residence time in each zone, mesh density, loading capacity...) and down-scaling of the mockup

- Manufacturing of the mockup and implementation of dedicated chemical instrumentation (O-meter, H-meter) on the facility used for qualification tests

- Loading of the ancillary cold trap, used as a polluting device, with Na2O or NaH or both

- Operating the cold trap in various conditions in order to assess the allocated performances (efficiency, purification rate and capacity) and to confirm the operating rules.

Today:

- Use of the new CEA code described here, validated using the previous experimental results, allows for a quite efficient design procedure, based on sequential calculations, avoiding long and very expensive experimental tests.



SuperPhenix Integrated plugging-meter (50 l/h)



H-meter for detection of Sodium-water reaction







Excellent operational feedback from Phenix & SPX (and also from international feedback)

- ; nevertheless tracks for improvement:
- **Reduction of Na transit time**
- Signal processing
- Other complementary solutions developped:
- (Acoustic detection, electrochemical H-meter,...)



Electro-chemical Hmeter (Courtesy of IGCAR)

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LFR

Hot and cold plenum







O Thermodynamic diagram



Thermodynamic diagram (from 400℃ to 530℃)

Hypothesis: T= 530°C Cladding temperature





CADXRACH 2: possibility to decrease depends on coating properties 2: if cladding are protected against dissolution (but not hot leg and SGU)

Diagram showing optimal working area

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? With margin?



Pb ways of pollution in Primary Vessel 2/2







Consequences of main potential events:



If air ingress, PbO is produced on Pb bulk surface, but very slow dissolution rate on surface, and risks of entrainment if vortices...

- Detection in cover gas (N₂ or O₂) by MS or gas chromatography
- Confirmation in Pb by O-meter
- If water ingress, very small amont of PbO produced continuously
 - Detection by O-meter and more probably by H-meter in gas plenum or water by SM or IR spectroscopy (to be investigated)
 - → Then, in both cases, purification by:
 - filtration,
 - H₂ reduction or
 - overflooding and collection in dedicated vessel.



[O] control strategy in hot and cold plenum



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O-meter

Possible O control strategy (OCS) (to be validated)





Table 1

Advantages and drawbacks of each method of oxygen control systems.



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Cea	Advantages	Same device for O ₂ control and purification by H ₂	No gas management
CADARACHE		No operation on the device in normal operation	No risks of plugging (oxide formation)
			Rather easy control by flow rate and temperature
	Drawbacks	Regulation rely on dissolved oxygen measurements in liquid phase by oxygen sensors if non equilibrium gases (Ar/H ₂) is needed	More complex design for mass-exchangers
		Need for a (very) efficient bubbling if equilibrium gases (H ₂ /H ₂ O) are used	More maintenance: pellets filling
		Risks of oxide formation (Ar/ O ₂)	Personal exposure (activated corrosion products as 54Mn or ⁶⁰ Co deposited on the cold part of the device)
		Large gas flow rates at the beginning of operation	Risks of oxide precipitation on pellets and sluggish kinetics for dissolution
		Need of a large dilution gas loop (Ar) with purification system (fission Products, activated Products, tritium, polonium)	
CADARACHI		Risk of contamination exposure for operators (gas leakage)	

PbO oxygen Control system (Russia)











Pb filtration



Several types of liquid filters tested (for Pb-Bi)

- Metallic mesh ; dynalloy, Poral (CEA)
- Filtration efficiency depends on :
 - Liquid metal properties (viscosity, density,..)
 - Particles : nature, form, size, concentration
 - Temperature
 - Hydrodynamics
 - Filters medium characteristics (geometry, porosity, pressure drop...)
 - Its location in system

Temperature max : 400℃

Flow velocity : ≈ 0.5 m/s, but filtration rate 0.2 cm/s (related to filter area, <2 cm/s recommended by manufacturers)

- Far from elbows...
- Need of a auxiliary « loop » or cartridge to have flow rate compatible with filters characteristics
- ➔ how to replace the filters (when loaded with impurities), in presence of high contamination and dosimetry ?
- Necessity to perform CFD calculations to confirm the best locations for implementation of the filters



Poral



Dynalloy



Pall cartridge

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Courtesy K Gladinek SCK_Mol ESNII+ Summer School

SOLID PARTICLE FORMATION IN LBE

- Plugging risk
 - By solids (particles, deposits) in HEX, core
 - Only by abundant elements
 - Mainly due to reactions with oxygen:
 - Pb (LBE) + O (LBE) \rightarrow PbO (s)
 - Corrosion products (Fe, Cr, Ni) (*e.g.* magnetite, Fe₃O₄)
- Corrosion products*
 - Largest contribution

	Duration	Ni (kg)	Cr (kg)	Fe (kg)	Mn (kg)	Total (kg)
EOL MYRRHA	40 years	460	320	230	90	1100

*A. Weisenburger (KIT), SEARCH deliverable 3.2 (2014) Courtesy of K. Gladinek SCK-CEN Mol ESNII+ Summer School PISA 2016



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MODEL (COURTESY K GLADINEK SCK-CEN U-GENT)

Modeling of nucleation and growth of oxides in LBE by CFD (K Kristof Gladinez PhD student U.Gent) :

→ Goal: define deposition and precipitation of oxides in LBE to identify a filtering strategy

→ Strategy:

- Develop kinetic model for particle formation & growth
- Couple with CFD calculations
 - Dissolved impurity concentration mapping
 - Particle formation dependent on local conditions:
 - T, concentrations and residence time
- Model the particle flow interaction
 - Particle accumulation, flotation,...



- Oxide particle distribution important to define the correct filtering method (non relevant for Na coolant)

→ Kinetic model: Classical (homogeneous) Nucleation Theory (including nucleation barrier)

Particles are extremely small: diameter~2E-9m \rightarrow Follow the flow perfectly

- Assumption of mass transfer limited growth and dissolution ((in Na: growth limited by mass transfer through boundary layer for Na₂O, or by integration to crystal lattice for NaH)

→Mass transfer to micro-particles in agitated systems (in Na: heterogeneous nucleation on mesh packing or cooled walls)

 $Sh = 2 + 0.52 Re^{0.52} Sc^{\frac{1}{3}} Re = (\frac{\varepsilon d^4}{\sigma^3})^{\frac{1}{3}}$, σ = kinematic viscosity

→ Necessity to perform experimental studies in MEXICO chemistry loop

Ref: Armenante, P. M. & Kirwan, D. J. Mass transfer to microparticles in agitated systems

Chemical Engineering Science, Elsevier, 1989, 44, 2781-2796)

Ref: Gladinez, K., Rosseel, K., Lim, J., Marino, A., Heynderickx, G., & Aerts, A. (2017). Nucleation and growth of lead oxide particles in liquid lead-bismuth eutectic. *Physical Chemistry Chemical Physics*, *19*(40), 27593-27602.

Sensors (O-meters) for large HLM facilities and industrial-scale reactors (DEMETRA Project)





Characteristics

- □ Electrolyte thimble
 - Seal between electrolyte and housing immersed in the liquid metal
 - Glass ceramic sealant developed for compatibility with YSZ and steel (thermal), and with liquid Pb alloys (chemical)
- □ Reference electrodes:
 - Bi/Bi₂O₃
- □ 3-YSZ with optimized mechanical properties
- Prototype for oxygen measurement in a depth of ~5 m below the surface of a liquid-metal pool

(based on R&D by IPPE)

Hydrogen & tritium transfer from SGU in LFR



Kutim code - Distribution of hydrogen and tritium in the different media of the reactor :

governs tritium activities in liquid and gaseous releases, as well as tritium activities build-up in units such as the purification units.

Main objectives of the code :

Assess tritium releases to the environment (gaseous and aqueous)

- at the design stage
- at the operating stage

guarantee that they are below the authorised thresholds

Assess tritium activities in the different media (Na, steel,...) and Tritium build-up



in purification units



GFR



Purpose of Helium chemistry control

- Ensure <u>safety</u> during operation and in case of accident : limit the inventory of particles, fission products and activated species,
- Increase <u>service life</u> : minimize the interactions between gas and structures <u>Specification for Primary Coolant Chemistry</u>



Source of impurities in primary coolant





Background on He Purification

- Chemical Impurities: H₂O,CO,N₂,H₂, CH₄, CO₂, O₂ (tritiated species will behave as H₂, H₂O and CH₄)
- Helium chemistry specifications depend on operating conditions

	Partial Pressure (µbar or ratio)	Temperature < 950°C	Temperature < 1000°C	
Possible	H ₂ O/H ₂	> 10 ⁻³	> 10-2	
Recommendations	H ₂ O	< 10 µbar	< 10 µbar	
(for VHTR; to be up dated for GFR)	СО	> [130 – 450] µbar	> [500 – 1570] µbar	
	CH ₄ /H ₂ O	<< 100	<< 100	
	N ₂	< 5 µbar	< 5 µbar	

• Continuous process with operating conditions:

- Pressure = Primary circuit pressure
- Flowrate = [5%-10%] of primary circuit flowrate or 5% of He inventory per hour

• Purification system principles:

- Filtration
- Oxydation of hydrogen into water
- Adsorption of impurities on one or several fixed beds





Reference process for Helium purification





Alternative purification systems

- Membranes,
 - Getters,
- He Cryogenic traps

Studies on Helium purification and control at CEA

1.Improve the knowledge for Helium purification using standard processes through the development of a loop dedicated to Helium chemistry control and monitoring (HPC)

- •Operating on a stand-alone basis
- •Connected to a loop representative of Helium Primary Circuit

2.Evaluate new materials (alternative metal oxide, molecular sieve, activated carbons)





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DE LA RECHERCHE À L'I Cea **CIGNE** – the facility Reactor V Pure helium Mixing chamber **Analysis Exhaust Pre-heater** ं \sim Impurities Clamp ///// Reactor wall Frit CuO Line cord resistor Operating conditions: Cleading — Thermocouple ✓ 50-1200 NL/h Atmospheric pressure T < 400 °C 333333 3

CADARACHE





HPC – Main characteristics

	Flow rate (g/s)	Pressure (bars abs.)	Temperature (℃)	Volume (L)
Oxidation (CuO)	5 - 20	25 - 80	300 Regeneration: 350℃	10
Molecular sieve	5 – 20	25 – 80	25 Regeneration: 250℃	50 (x 2)
Activated carbon	5 – 20	25 – 80	-180 Regeneration: 150℃	20

For inlet impurities concentration of 40ppmV, regeneration frequency

- Oxidation column :
- Molecular sieve column :
- Activated carbon column:
- 5 days 12 hours









Thank you for your kind attention

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