

GEN-IV COOLANTS QUALITY CONTROL

Dr. Christian Latge CEA, France 25 September, 2019



Meet the Presenter



Dr. Christian Latgé graduated with a degree in Chemical Engineering (1979) and earned his PhD from the Institute National Polytechnique in Toulouse (France). His PhD in CEA Cadarache was dedicated to Na chemistry and purification systems. He participated in the start-up and then operation of Superphenix and operational feedback analysis (Phenix, Superphenix and foreign reactors), in the field of chemistry, radiochemistry and technology. He was also involved in design activities in EFR & SMFR. As Head of Service, he coordinated activities dedicated to process studies for decontamination and nuclear waste conditioning in Cadarache. He carried out studies dedicated to tritium systems and hydrogen risk mitigation for the ITER project. As director of the international project "Megapie," Dr. Latgé led a team dedicated to the development of a lead-bismuth eutectic spallation target for nuclear waste transmutation. He served as the Head of Sodium School in Cadarache and now teaches at CEA-INSTN and several French universities. He has been involved in several educational sessions organized by the IAEA on Fast Reactors and he is the CEA representative on the GEN-IV International Forum Education & Training Task Force. He is currently involved in SFR and recently in the ASTRID project as an expert, and he is involved in several international collaborations related to the development of Fast Neutron Reactors.

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Coolant Functions for the Primary Circuit of XFR



- The coolant(s) must accomplish the following key tasks
 - Extract heat from the core: high specific heat and thermal conductivity ensure good extraction
 - Transfer heat to an energy conversion system (steam generator or exchanger + turbine) or to a system which directly uses the heat: heavy oil extraction (oil shales), thermochemical production of hydrogen, desalination of sea water
 - Assure safety by providing the system with a degree of thermal inertia
- In a Fast Neutron Reactor, the coolant must NOT
 - Significantly slow neutrons
 - Activate under flux, producing compounds which create unacceptable dosimetry
 - Change the behavior of structural materials
 - Induce unacceptable safety conditions
 - Induce insurmountable operating problems
 - Lead to wastes which can't be processed during operation or dismanting

Coolants Used in Nuclear Applications



Fission

Sodium for fast neutron reactors (many SFRs)

Sodium-Potassium (Na-K) for fast neutron reactors (DFR)

Lead for fast neutron reactors (FNR) cooled by lead (LFR)

Lead-bismuth eutectic for subcritical reactors (ADS: Accelerated Driven Systems), including their spallation targets and Russian submarine FNRs

Molten Salt for molten salt reactors (MSR)

Gas: He for Very High Temperature thermal Reactors (VHTR), for gas-cooled fast neutron reactors (GCR)

He-N₂ or Sc-CO₂ in innovative energy conversion systems (ECS) for SFRs

Water-steam as the primary coolant in pressurized water reactors (PWR), supercritical water in supercritical water-cooled fast reactors (SCWR), etc. and water-steam in the team generators of energy conversion systems (ECS) for sodium-cooled reactors, lead-cooled reactors, etc.

Fusion

Lead-lithium eutectic for blankets in thermonuclear fusion reactors

Lithium as a target neutron generator for the IFMIF project (International Fusion Materials Irradiation Facility) (Lithium investigated as a coolant for space applications, due to its very low density)

Note: In spallation targets, the lead-bismuth eutectic also serves to produce neutrons. In fusion, lithium acts as a generator of tritium.

Coolants: Sodium (Natrium)



The so-called « natron » was already known from Aegyptians, as « neter », from ancient Aegyptian langage ntr(ĵ), word which means that this product was extracted from dryed lake, located in the desert of « Nitrie » (Wadi El Natrun).





Na in the alkali metal family : Name coming from arabic : al kaja meaning : ashes coming from sea







Wadi El Natrun





Some explanations:

Green Tech =17,2%

-TPP triphenyl phosphine used for the synthesis of vitamin A -HPP High Performance Pigment

Coolants: Lead

- Relatively low cost,
- Two main production routes:
 - -primary production from mined lead ore
 - -secondary production, where it is recovered from recycled products (mainly batteries)



Used because of its malleability and resistance to corrosion
Figurine found in Egypt back to 4,000BC. Later, used by the Romans for water pipes, aqueducts, tank linings and cooking pots and then by ancient scientists in early cosmetics, paints and pigments....



Courtesy of ILA



Water ducts from roman city Arles (France)

Lead Properties

Symbol: Pb Atomic Number: 82

Atomic Mass: 207.2 amu Melting Point: 327.5°C (600.65 K) Boiling Point: 1740.0°C (2013.15 K)

Number of Protons/Electrons: 82 Number of Neutrons: 125 Crystal Structure: Cubic Density & 293 K 11.36 g/cm³ Colour: bluish





at 500°C		
	sodium	lead
Melting point (°C)	98	327
Boiling point (°C)	882	1737
Density (kg/m3)	832	10390
Dynamic viscosity (Pa.s)	2.3 10-4	18.9 10-4
Specific heat (J/kg/K)	1262	149
Thermal conductivity (W/m.K)	67	15
capture cross section (barn)	2.8 10-3	4.7 10-3
Activation	22Na 2.6 ans	207Pb 52h
	24Na 15h	



Nom: Plomb Symbol: Pb N° Atomique: 82

Coolant for FBRs alternative options: BREST-300, ALFRED, CLEAR

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Coolants: Lead-Bismuth Eutectic

- Bismuth: By-product of Lead ore
- Low melting point (125°C), compared to lead
- Lead can be oxidized with significant precipitation of PbO particles
- No chemical reaction with water but water may violently vaporize depending on local conditions (ie ΔT between the 2 phases, dispersion...)
- Significant corrosion → protective coating required:
 - Al, Si.... coatings, or
 - [O] controlled to maintain a protective oxide film at the surface
 - → introduction of steam+H2 and
 - → Introduction of O by an "equilibration", method using PbO pellets)
- Very large operating feedback available on this coolant:
 - USSR submarines and dedicated research,
 - ADS studies (MYRRHA, CLEAR, MEGAPIE, EU projects...)
- Note: LBE has been investigated as an alternative coolant for intermediate circuits of SFR

→ if LBE ingress in primary vessel, interaction with primary Na $(BiNa_3 - \Delta H = 137 \text{ kJ/mol LBE})$







Main Impurities

Primary circuit



- Initial impurities in « nuclear grade » coolant, prior to reactor operation, can induce deleterious effects: coolant (Li) and cover gas contamination (K), corrosion (Cl, F...), clogging (Ca in Na), mechanical effects (C), nuclear reactions (U, B..),....
- Main impurities introduced during operation:
 - Oxygen and moisture from fresh metalic surfaces, during handling operations
 - Metallic oxides dissolved in coolant
 - Activated corrosion products (⁵⁸Ni, ⁶⁰Co, ⁵⁴Mn...) dissolved or particles
 - Fuel particles and Fission products (¹³⁷Cs...) (pin rupture)
 - Tritium from Pu ternary fissions, B₄C
- Intermediate circuits of SFR (Na) :
 - Na-water products (H_2 , NaOH converted into O and H dissolved in Na)
 - H₂ produced by aqueous corrosion in SGU, migrating towards Intermediate circuit (driven by Richardson law)
- Energy Conversion System (Based on Brayton or Rankine thermodynamic cycle)
 - Tritium from primary circuit (and diffusing though SGU walls in the water (Energy Conversion System)
- All circuits: Potential oil ingress (pumps), metallic filling due to maintenance, etc...

Why is it necessary to control quality and to purify the coolant?



- Primary coolant of XFR:
 - [O] is a key parameter of corrosion
 - -For SFR \rightarrow contamination \rightarrow dosimetry \rightarrow necessity to decontaminate (handling, repair, ISI,..): [O]<3ppm
 - For HLM-FR (or ADS) → necessity to master dosimetry and to eliminate corrosion particles (filtering)
 - [O] well mastered can help to maintain oxide layer stable (protection against hard corrosion in heavy liquid metals HLM). It also allows enhancement of tribology.
 - [O] can induce precipitation of coolant oxide : issue for HLM: PbO particles due to very low dissolution rate; in case of very large O ingress, it can modify the composition of binary alloys ie Pb-Bi... (it is not a problem for Na),
- 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 ingress in Na (Na-H₂O reaction generates H₂): [H] <0.1 ppm
 - In steady-state operation, aqueous corrosion in SGU produces Fe₃O₄ and H: H diffuses towards intermediate Na.
 - Moreover, Na purification allows to minimize tritium release. (Nota: Tritium release is a common issue for all nuclear systems, including HLM cooled FRs
- For all the circuits :
 - Control plugging hazards in narrow gaps, tubing, openings, seizing of the rotating parts, reduction of heat transfer coefficient in IHX (Intermediate Heat Exchanger)...
 - → to limit the plugging hazard, 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</p>

Various Processes to Purify LM



- **Cold trap** (O & H: impuritie's crystallization)
- Hot trap (O or H: gettering effect)
- "RVC Trap (Cs: adsorption on carbon solid foam, followed by absorption)
- Mechanical Filter (sintered filter, mesh... for particles)
- **Skimmer** (for floating oxide layer)
- Chemical reduction of metallic oxides,

••••



Sodium



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→ O control: no necessity to keep a minimum value to protect structures (coating) No risk of Na₂O precipitation in Na bulk)

 \rightarrow Ternary oxydes (Na_xM_yO_z limited amount, thermodynamic stability depends on T, [O])

Cold Trap Principle



C. Latgé

« Sodium quality control; French developments from Rapsodie to EFR". Conférence FR09 Kyoto Décembre 2009 GEN International Forum

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 Na₂O NaH Na₂O NaH E (kg/mol) -60 -450 -45 -43.65 10 2 1 n



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

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 nonoptimized 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.



Simulation Tool

Two types of crystallization behavior:

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

➔ 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 (Na $_2$ O).

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. (Validated / experiments)

Ref: N. Khatcheressian, C. Latgé, X. Joulia, T. Gilardi, X. Meyer, "Development of a coupled transfer model for Sodium purification system in a Fast Breeder Reactor," IAEA International Conference on Fast Reactors and Related Fuel Cycles – FR13 Paris (France) Mars 2013



Interface tracking model for NaH crystallization on cold walls



Na₂O crystallization modelling (in mesh): see next slide

Na₂O Crystallization Modeling





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: Cooling zone, equipped with or without stainless steel mesh, cooling zone, 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

Many concepts developed in various countries

Performance Criteria for Cold Traps



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

- Ci: concentration at the cold trap inlet
- Co: concentration at the cold trap outlet
- C*: 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 trap V2 = Internal volume of the trap in which the deposit zones are located

Basic Choices for Cold Trap





Alternative option: Cold trap equipped with a cartridge (ie Primary integrated purification system) (SPX, of interest for BN1200, FBR1&2)

Primary Integrated Purification Units of SPX (IPU)









Nominal flow-rate: 10 m³/h (each IPU)

Superphenix



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SPX Secondary Purification System (Loop Concept)







Some Developments in CEA





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. 28

Chemical Instrumentation

Na continuous monitoring:

- Plugging meter: allow to estimate [O] and/or [H]
- O-meter, electrochemical device with reference electrode,
- H-meter, (diffusion +MS or electrochemical H-Meter)
- **C-meter,** electrochemical device with reference electrode,

Periodical measurement: sampling (ie crucible) + analysis in Laboratory for radioactive species (activated corrosion products, tritium...)

Electrochemical cell (Courtesy UKAEA): Thoria doped with Yttria, Reference electrode : air, In/In₂O₃



Two O-meters currently being developed in CEA (DTN-Cad & DPC Saclay)



Na-CO₂ Interaction and Consequences

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- Low temperature, < 500° C

Na/CO₂ reaction Complex intermediates: Na₂C₂O₄, Na₂CO₃, Na₂O, C, etc.

CO formation

Na-CO reaction: induction period

- High temperature, 500-600° C

Na/CO₂ reaction is more rapid and global

Na + CO₂ \rightarrow Na₂CO₃ + C







Na₂CO₃: - particles; - Very low dissolution rates **→** Filtration



Sodium Decontamination – Cesium Trapping



Reticulated vitreous carbonaceous (RVC) traps : Cs adsorption on RVC

Efficient process ; operation at T around 200°C

(possibility to reduce contamination by a factor 10 for each transfer through the trap)

Applied to EBR2, BOR60, RAPSODIE, CABRI...(and in future PHENIX)

<u>Note</u> : necessity to take into account delay before Na treatment and decay ¹³⁷Cs/ ²²Na (Feedback from RAPSODIE)

3 cartridges adsorbed about 0.49 TBq ¹³⁷Cs

Will be applied soon for primary sodium of PHENIX, prior its treatment (conversion into NaOH)

Ref: Redon B., *Etude et modélisation du piégeage sur matériaux carbonés du césium 137 lors de la purification du sodium primaire des réacteurs à neutrons rapides*, Thèse de doctorat de l'INPG, 11.09.**1998**



RVC

Activated Corrosion Products Trapping GEN International

Operational feedback in Germany: Ex : ⁵⁴Mn, ⁶⁵Zn 50h in Na at 360°C 1mmNi : 83kBq/cm²

Operational feedback in France : loop TPL SILOE, and in Belgium : BR2

Nickel foil for ⁵⁴ Mn (tested in EBR2) (mounted in Fuel Assembly above pins. Less efficient for ⁶⁰Co



Up to now, not mandatory for SFRs To be investigated for longer operation, i.e. 60 years?

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Heavy Liquid Metal Systems (Pb, Pb-Bi)





Diagram [O]-T (Courtesy SCK PhD K Gladinez SCK-Mol Univ Gent (19-09-2019)

Main results:

- Metastable field: possibility to nucleate, then to favour crystal Growth (Fig 1)
- Nucleation in LBE bulk (particles) or on metallic cooled surfaces (Fig 2), then growth (Fig1).
- Very limited dissolution rate of PbO particles (compared to Na due to its reducing properties): necessity to perform CFD calculations to follow particles then to find the best location for a « cold trap ».
- Possibility to foresee the use of a cold trap which includes cooling to increase supersaturation and promote homogeneous nucleation then filtering area (packing).
- Possibility to favour heterogeneous nucleation on cold walls (Fig 3):
 - \rightarrow to be investigated deeply.
 - → For Na: cold trap includes cooling to increase the supersaturation then packing implemented to provide heteregeneous sites for nucleation then to act as « seeded » surfaces for growth.







These data will allow SCK to design efficient purifications devices.

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. Ref: Gladinez, K., Rosseel, K., Lim, J., Marino, A., Heynderickx, G., & Aerts, A. (2017). Determination of PbO fouling mechanisms (to be published in Nuclear Engineering and Design)

Previous R&D

- Filtering: metallic mesh, dynalloy, sintered filter
- Filtration efficiency depends on :
 - Liquid metal properties (viscosity, density,..)
 - Particles : nature, form, size, concentration
 - Temperature
 - Flow velocity
 - Filters medium characteristics (geometry, porosity, pressure drop...)
 - Its location in system
- Best results obtained with Dynalloy filter (100μm mesh, metallic textile)



Figure 6: Dynalloy filter N°9 characterization









Sintered filter « Poral »



Dynalloy



Pall cartridge



Thank You for Your Kind Attention



Upcoming Webinars

23 October 2019 Passive Decay Heat Removal System

Dr. Mitchel Farmer, ANL, USA

13 November 2019 Czech Experimental Program on MSR Technology Development

18 December 2019 TRISO Fuels

Dr. Jan Uhlir, Research Center Řež, Czech Republic

Dr. Madeline Feltus, DOE, USA