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Liquid metal technologies

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CEA-DEN

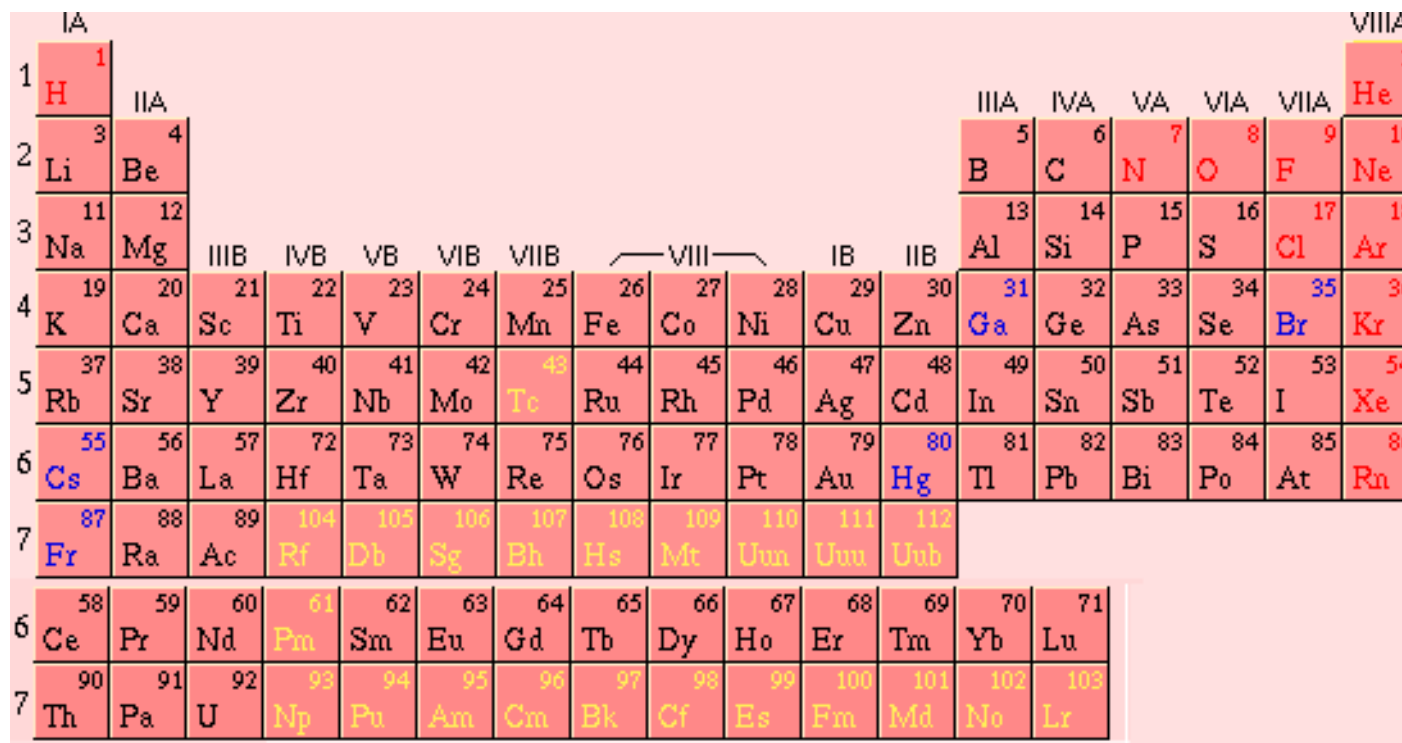
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afaq
QSE
Qualité Sécurité
Environnement
AFNOR CERTIFICATION
ISO 9001 - ISO 14001

فَقَلَّوْی



Na properties

Now let's review some properties and their consequences on technologies used for non-nuclear applications

Nota: Some properties have some specific consequences for nuclear applications but are not addressed here.

SODIUM PROPERTIES 1/4

→ a low melting point at 97.8° C:

- allowing shut-down for ie handling operations at T below 200° C, ie 180° C,
- limiting risk of freezing in heat exchangers, compared to some other coolants (ie lithium,...), but solid state appreciated for handling at room temperature
- favouring periodical inspection campaigns, at relatively low temperatures.

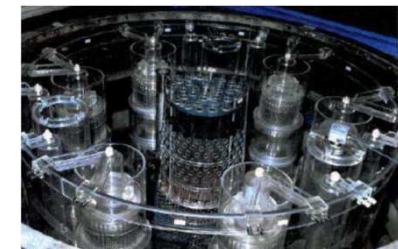


→ a large range of temperature in liquid phase (97.8°C- 881.5°C):

- Flexibility for Na uses as a cooling media

→ a low density and low viscosity

- due to the similitude between sodium and water density and viscosity, possibility to carry out some experimental thermo hydraulic studies and code validation with water.
- low density favours Ultra Sound transmission in structures, due to the large difference of density between steels and Na.



Example of mock-up
for a SFR

→ a very high thermal conductivity of sodium and very attractive heat capacity:

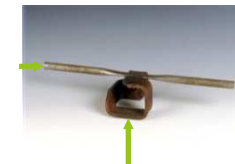
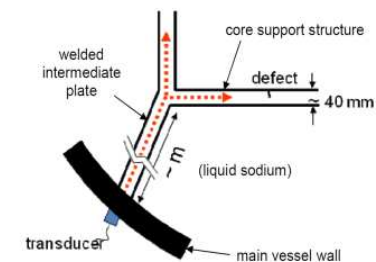
- very efficient heat exchangers (small size)
- significant inertia if loss of heating

→ an excellent electrical conductivity:

- allowing to use Electro-magnetic pumps, Electro-magnetic flow-meters...

→ a low saturation vapour pressure:

- a very limited Na transfer in the cover gas plenum, inducing few deposits in the upper structures,
- in case of fire, very short sodium flames and heat produced by the fire rather low, allowing to extinguish the Na fire by spreading a powder



NUCLEAR GRADE SODIUM (MSSA): SPECIFICATIONS

Silver	< 5	Activation
Barium	< 5	Clogging
Boron	< 5	Nuclear reactions
Calcium	5	Clogging
Carbon (total)	10	Mechanical properties
Chlorine + bromine	15	Corrosion
Lithium	< 5	Tritium
Sulphur	20	Corrosion
Uranium	< 0,1	Nuclear reactions
Aluminium	< 5	
Chromium	< 3	
Copper	< 3	
Tin	< 2	
Magnesium	< 2	
Manganese	< 2	
Molybdenum	< 5	
Nickel	1	
Lead	< 2	
Potassium	~ 300	Gas blanket activity
Titanium	< 5	
Vanadium	< 3	
Zinc	< 2	

➔ Consequences for both nuclear & non-nuclear applications

→ no specific toxicity (like lead) but irritation and local corrosivity

Biological utility: essential

Daily recommended consumption: 2 to 15g:

MNa in human body (70kg): 100g

- Bones: 10 000 ppm
- Blood: 1970 mg/l

➔ large availability and cheapness

Earth's crust: 23 000 ppm

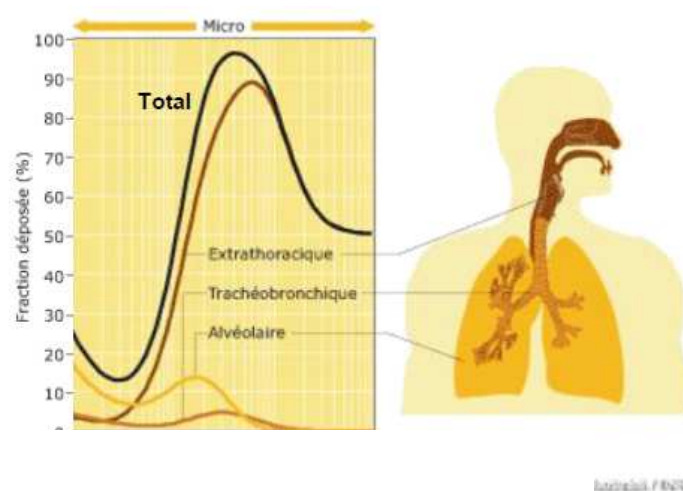
Sea water: 10 500 ppm

Main resources:

Halite (“NaCl” Mines)

Trona: $\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$

Yearly output: c. 200 000 ton.year⁻¹



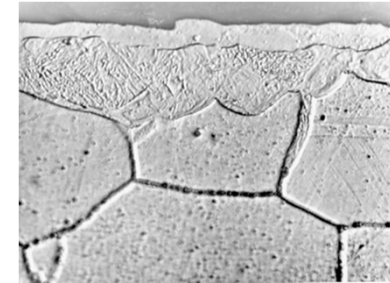
Dépôt total et régional chez l'homme, en fonction du diamètre des particules inhalées (d'après INRS, 2009).

**Total & local Na deposit in human body
versus of particles diameter (from INRS 2009)**

SODIUM PROPERTIES 3/4

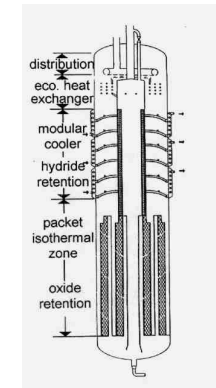
→ a **very good compatibility with steels**:

- no significant liquid metal embrittlement and
- very low corrosion kinetics,
- limited mass transfer and consequently very limited effect on heat transfer through heat exchangers.



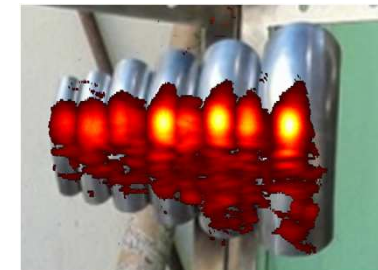
→ a **very limited amount of particles in sodium**, due to the instability of ternary oxides (except NaCrO_2) and high dissolution rates in Na, due to its reducing properties.

→ **low oxygen and hydrogen solubilities in Na, almost nil near the melting point**, allowing its purification thanks to cooling and retention system, called “cold trap”.



→ a **very good wetting**, due to the reduction of metallic oxides with Na over about 300.C.

- This property improves the quality of periodical inspections, carried out with ultra-sonic systems, necessary because of the opacity of the liquid metal.



SODIUM PROPERTIES 4/4

→ a very important reactivity with water:

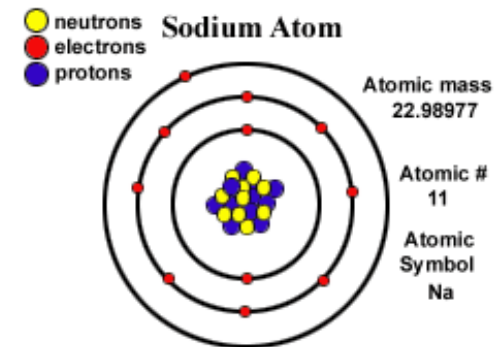
- possible deleterious effects in Na-water heat exchangers (Steam Generator Units (SGU) in SFR), in case of pipe rupture,
- but this reactivity allows efficient components cleaning, prior to repair or Na treatment during decommissioning phase (conversion into sodium hydroxide then sodium salt, without any inherent toxicity).

→ In these applications, in order to mitigate H₂ explosion hazards, it will be necessary to detect (or monitor) production of H₂, (Ni membrane + mass spectrometer, electro-chemical H-meter) without rupture of the confinement (inertization).

→ Use of recombiners and appropriate design of buildings has to be considered.

→ an important chemical reactivity with air, which can induce Na fire (T depends on dispersion conditions).

→ This event can be avoided by inertization or mitigated by early detection or confinement or dedicated powder extinguishers.



SODIUM PRODUCTION

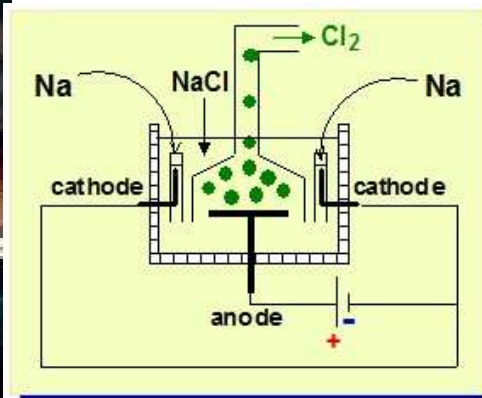


Mine in Varangéville France

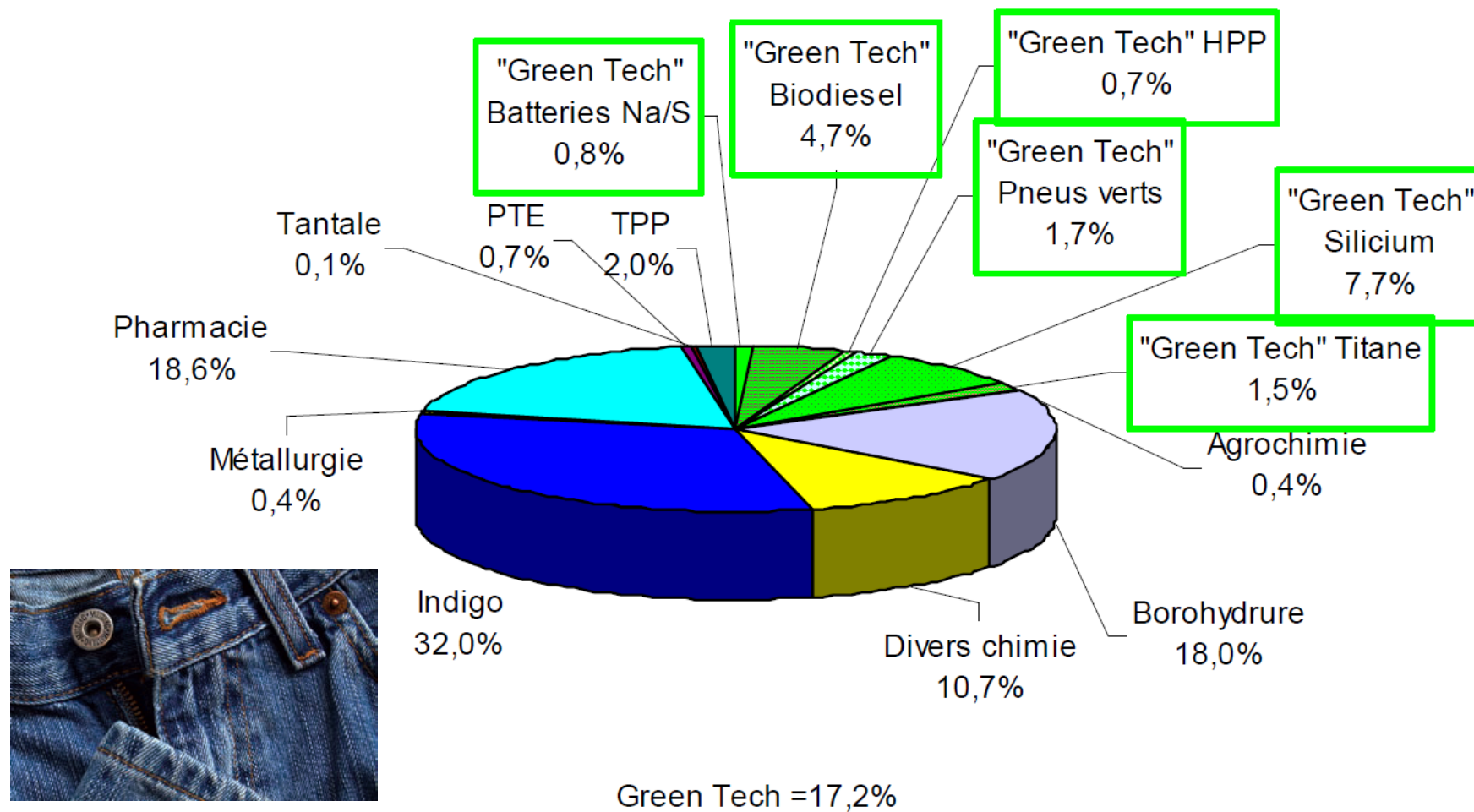
***Produced by electrolysis of the
eutectic NaCl/CaCl₂***



***Electrolysers at M SSA plant
Métaux Spéciaux (Moutiers France)***



SODIUM USES (COURTESY OF MSSA)



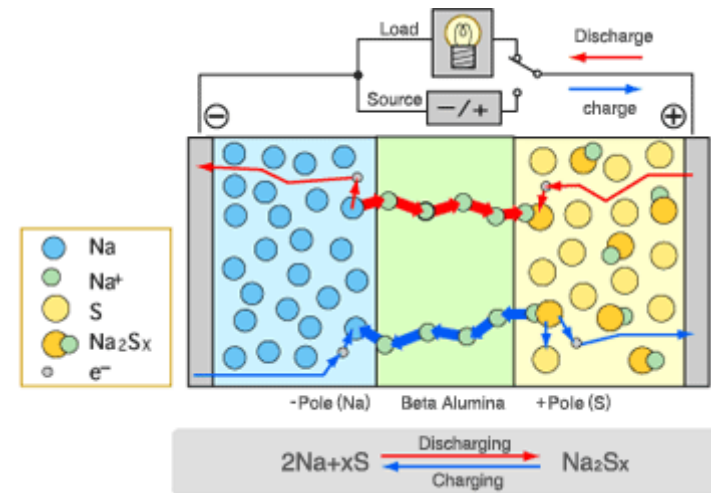
Some explanations:

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

NA-S BATTERY

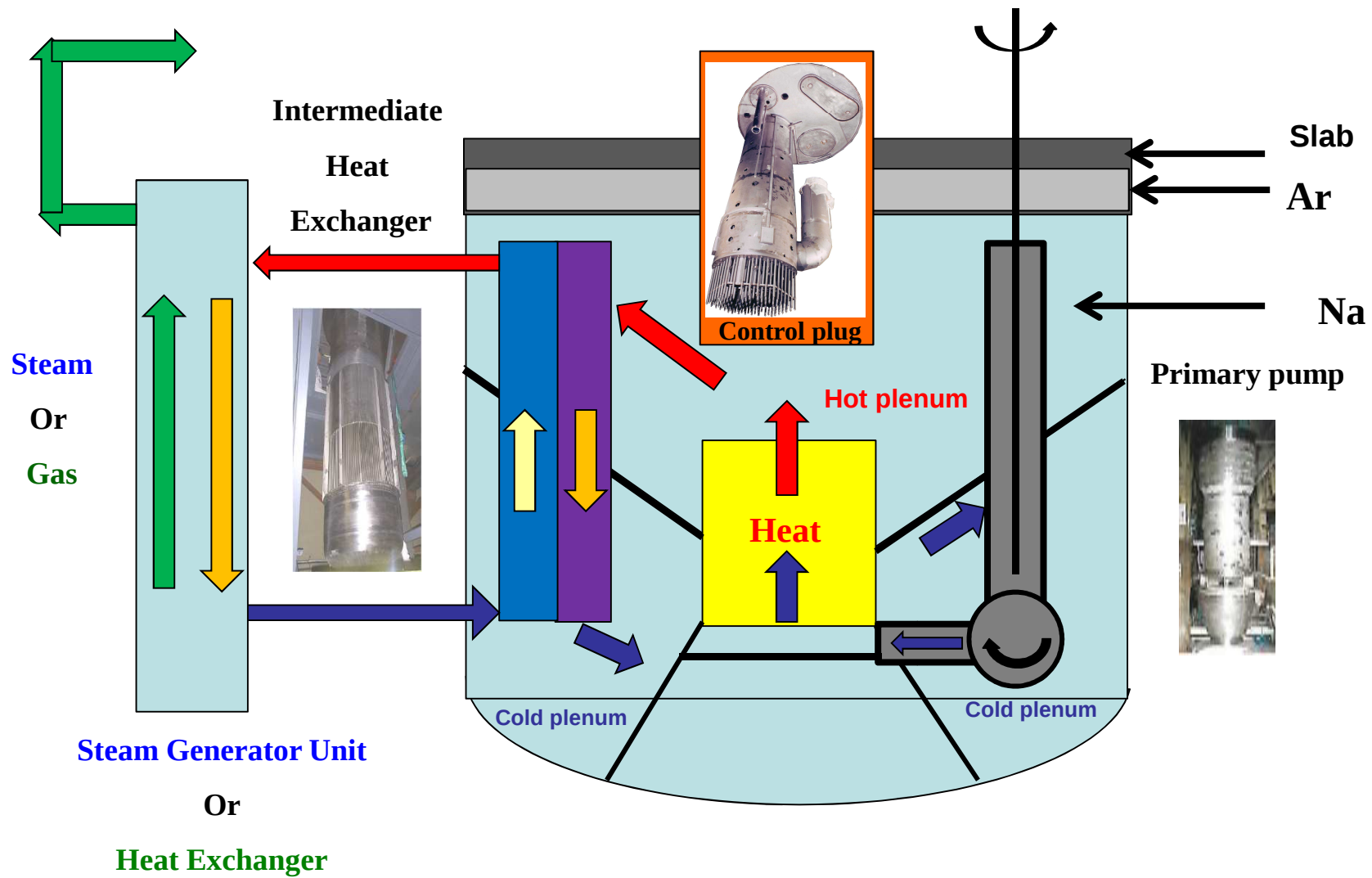
→ During the discharge phase, molten sodium at the core serves as the anode (Na gives electrons to the external circuit).

→ Na separated by a beta-alumina solid electrolyte (BASE) cylinder (good conductor of Na ions) from the cathode (container containing molten sulfur adsorbed on a carbon sponge). When Na gives off an electron, Na^+ ion migrates to the sulfur container. The electron drives an electric current through the molten sodium to the contact, through the electrical load and back to the sulfur container. Here, another electron reacts with sulfur to form S_n^{2-} (Na polysulfide)



Exemple: 34 MW NAS alongside 51 MW Wind Farm Courtesy of NGK Insulators – Japan)

PRIMARY CIRCUIT OF SFR (POOL CONCEPT) 1/2



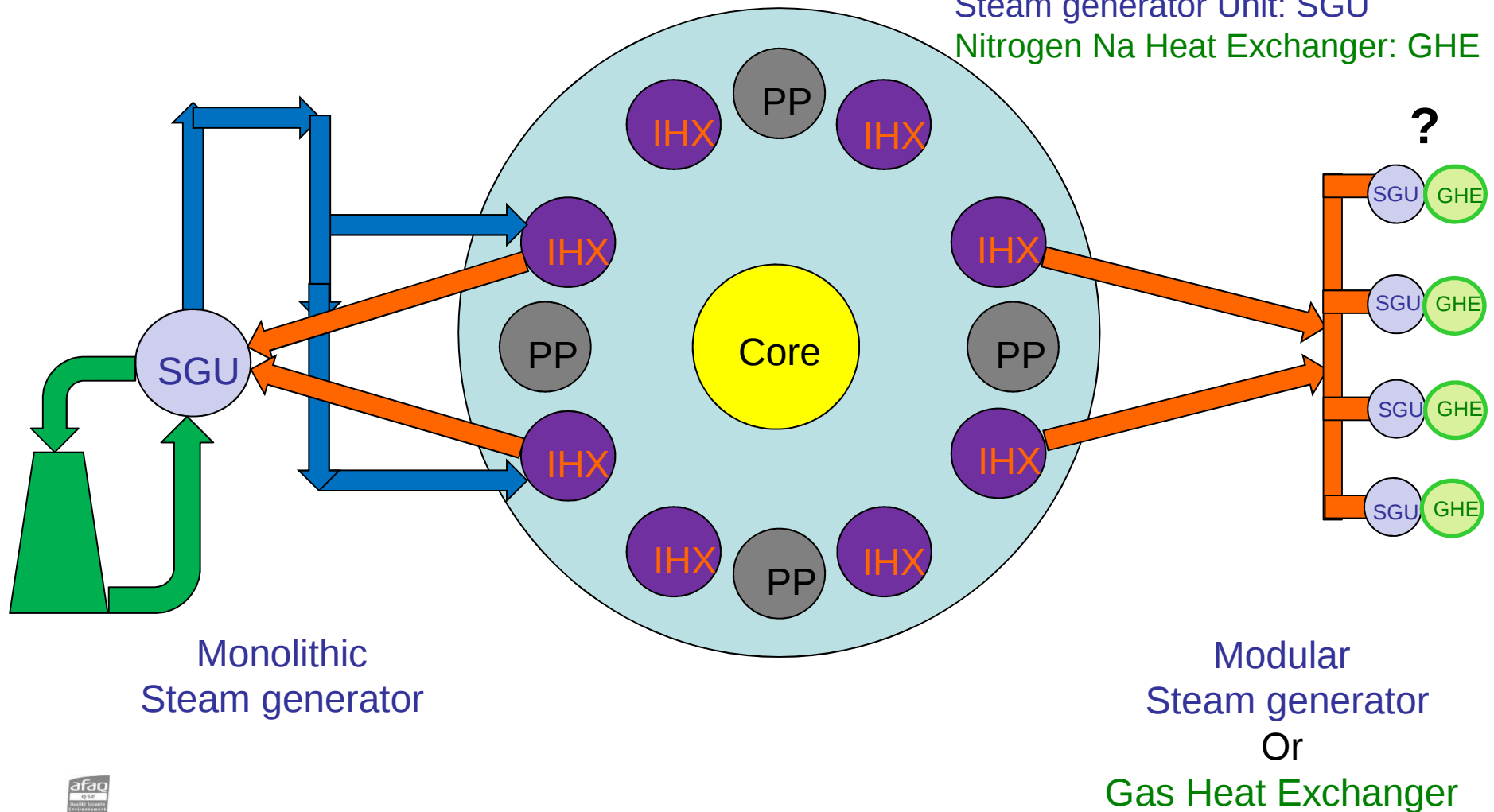
PRIMARY CIRCUIT OF SFR (POOL CONCEPT) 2/2

Primary pump: PP

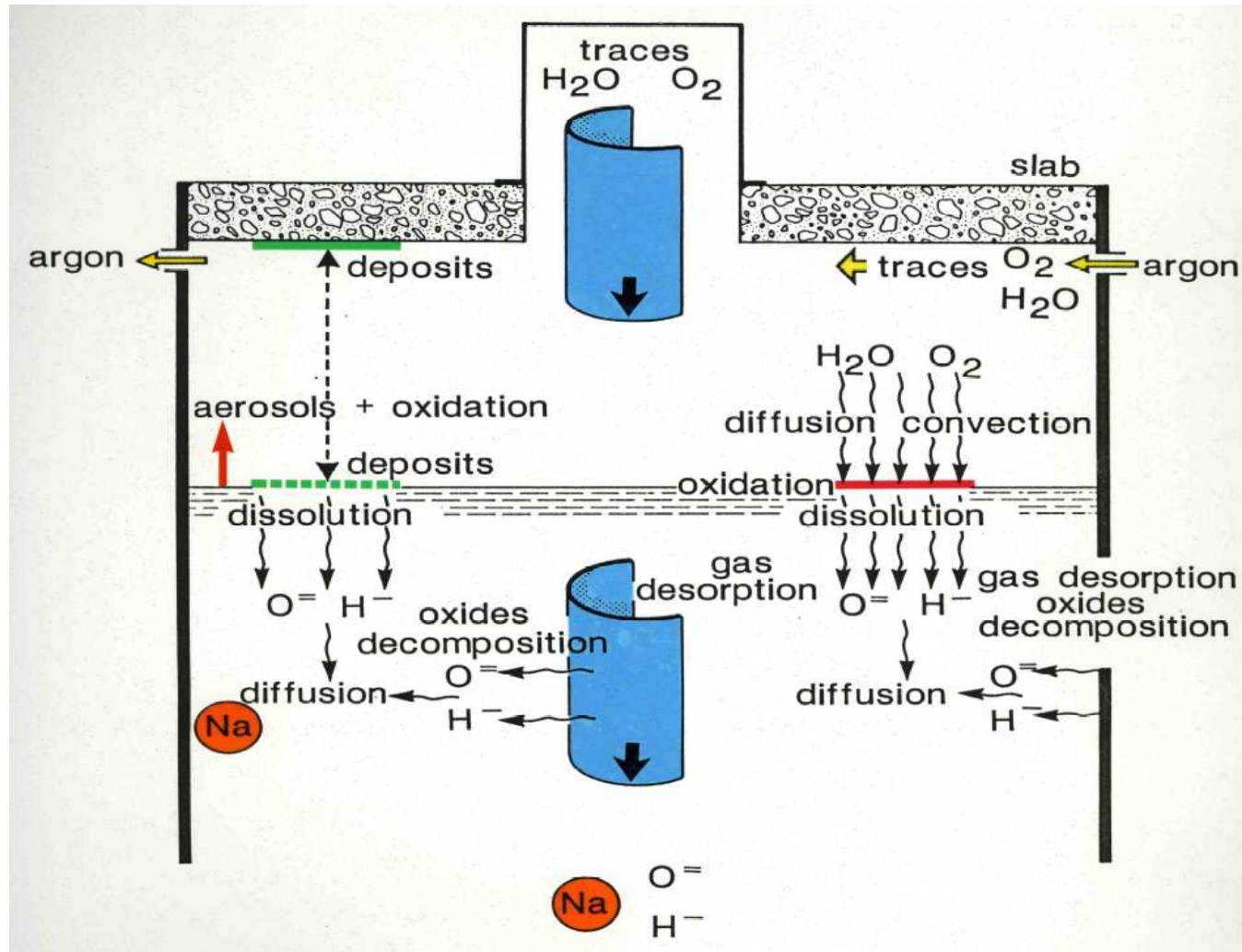
Intermediate Heat Exchanger: IHX

Steam generator Unit: SGU

Nitrogen Na Heat Exchanger: GHE



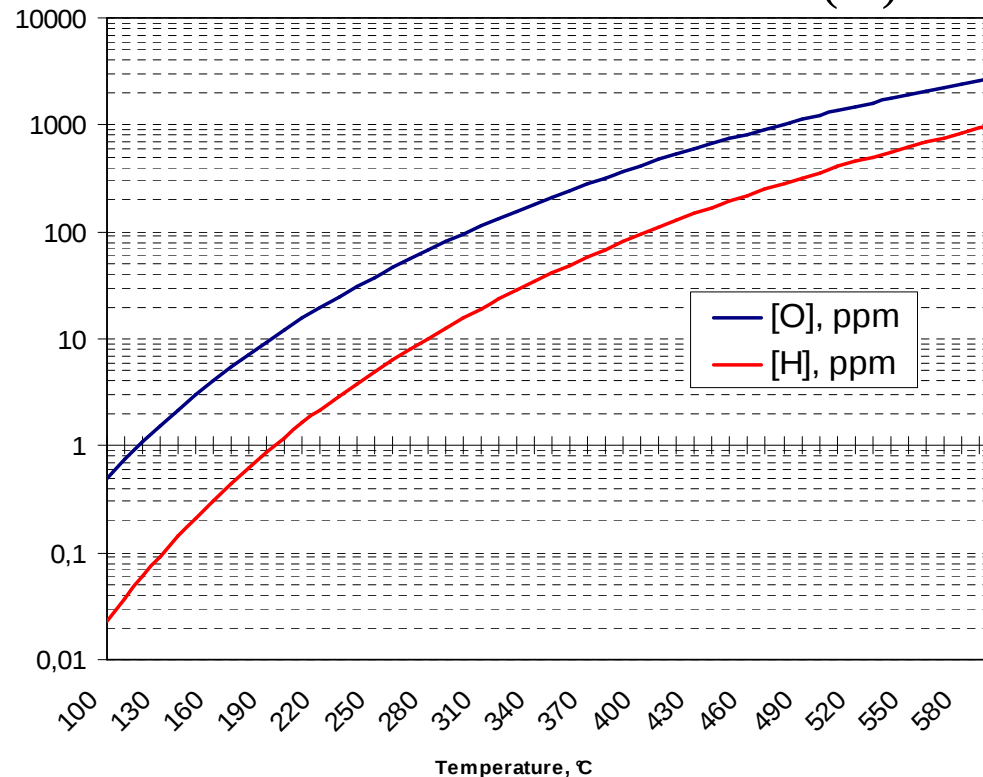
POLLUTION



SOLUBILITIES OF O AND H IN SODIUM

Wittingham solubility law

$$\log_{10}[H(ppm)] = 6.467 - \frac{3023}{T(K)}$$



Noden solubility law

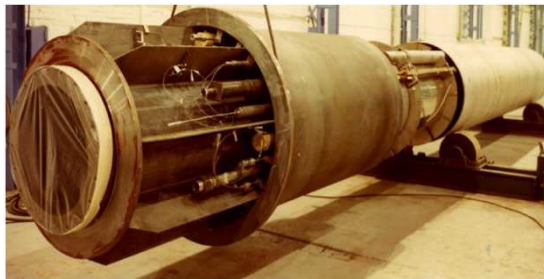
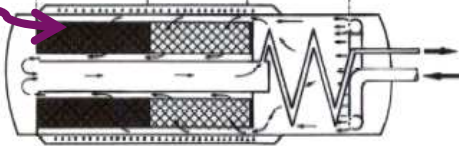
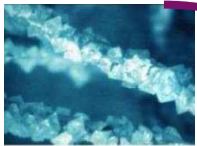
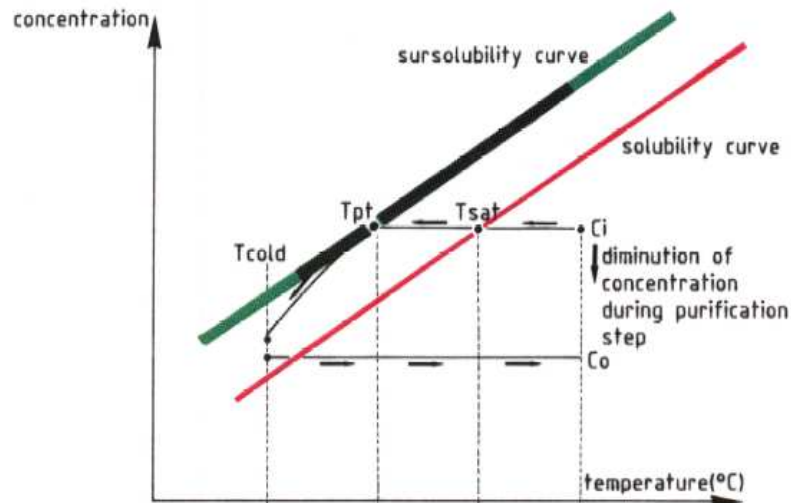
$$\log_{10}[O(ppm)] = 6.250 - \frac{2444.5}{T(K)}$$

O and H solubilities are negligible close to 97.8° C

Consequences: Na can be purified by Na cooling, leading to crystallization of O and H as Na₂O and NaH in a "cold trap"

Quality of Na has been always well mastered with cold traps, in normal or transient situations (start-up purification, large air pollution in SPX)

Cold trap principle



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

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

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.ppmx.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).

n_X is the order of the crystallization process.

C* (kg/m³) is the saturation concentration (from solubility law.)

ρ_{Na} 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 Na_2O and NaH

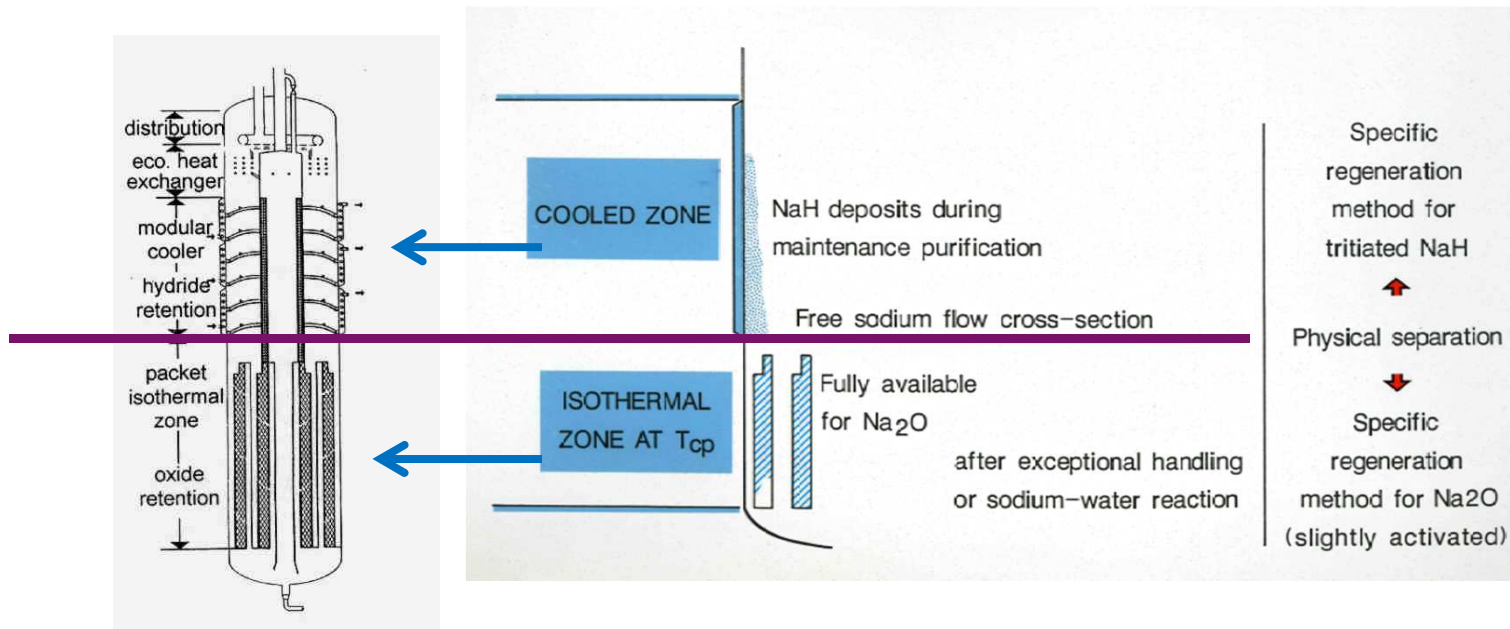
For a cold trap designed with an upper packless cold zone:

→ Na_2O crystallization only on wire mesh packing

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

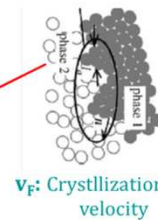
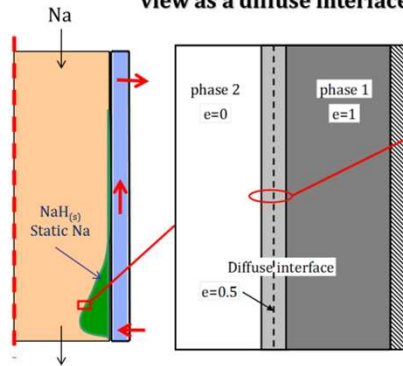
However, in case of a non-optimized packless cold zone, hydride might as well crystallize on wire mesh packing. Thus, co-crystallization occurs between sodium hydride and sodium oxide.

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



MODELING OF MASS TRANSFER IN COLD TRAPS

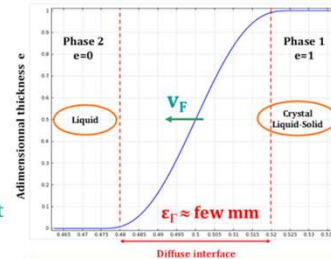
A deposit sodium hydride front view as a diffuse interface



v_F : Crystallization front velocity

Function of Nucleation and Growth kinetics, defined on wire mesh packing cold trap.

Introduction of a new variable « e » to determine the phase field: Na/NaH



$$\frac{\partial e}{\partial t} + \vec{v}_{FS} \cdot \nabla e = \beta \nabla \cdot \left[(e_1 \nabla e) - e(1-e) \left(\frac{\nabla e}{|\nabla e|} \right) \right]$$

β refers to a reinitialization parameter (m/s)

Crystallization Front velocity

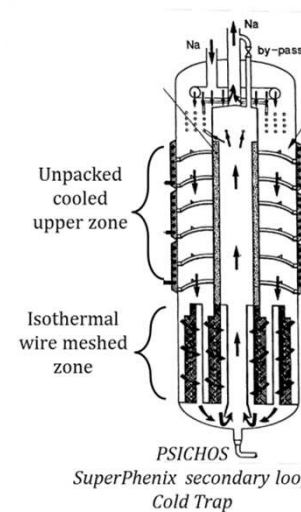
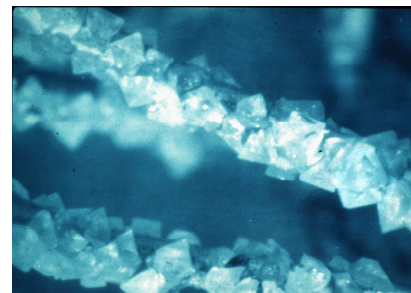
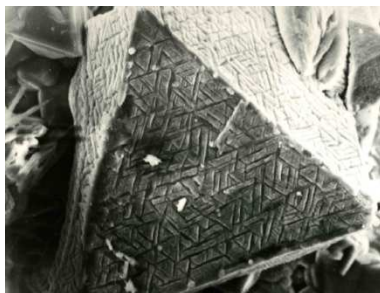
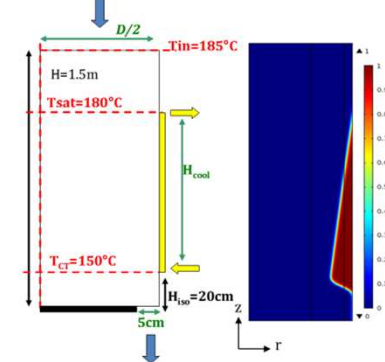
Front velocity corresponds to the translation rate of the diffuse interface, such that each elementary volume over the interface keeps the same porosity during its translation. Hence, over the thickness of the diffuse interface, the material derivative of porosity is set to be equal to zero:

$$\frac{D\phi}{Dt} = \frac{\partial \phi}{\partial t} + v_F(r) \frac{\partial \phi}{\partial r} = 0$$

$$v_F(r) = \left\| \vec{v}_F \right\| = \left\| \frac{\partial \phi}{\partial t} \right\|_{\text{fixed}} \quad \text{for } [\partial \phi / \partial r \neq 0]$$

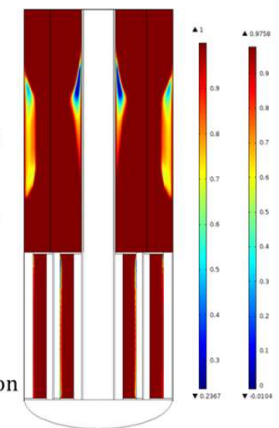
Parameter to initially define

Example of Sodium Hydride Deposit location



- Both Impurities: H and O
- Hydrogen crystallization on cold walls
- Cocrystallization on wire mesh packing
- Duration: > 5 years
- Purification specifications to apprehend
- Design and operation to optimize

Porosity profiles on walls and packing



N. Khatcheressian et al "Development of a mass transfer model for Na purification system in a SFR". IAEA Conférence FR13 Paris March 2013

NA VALVES (COURTESY OF DUCROUX)



Sodium-Gas compact heat exchanger

Heat exchangers -> large component (190 MWth)

- 1 component = assembly of 8 compact heat exchanger "module"
- 2 module designs with / without external pressure vessel
- (Collaboration with Rolls Royce/UK)

R&D focused on :

- 1 - fabrication/performances of heat exchanger « module »
Fabrication process under development (HIP) -> small scale prototypes
Test program (DIADemo test loop, 2013-2015)
- 2 - characterization of HIP-316 L material
- 3 - specific inspection needs and applicable technics



Sodium channels entry



Gas channels entry



DIADemo test
mock-up (2013)
40 kW

Electro-Magnetic Pump for large Na flow-rates ($2\text{m}^3/\text{s}$)

Primary pumps

Mechanical pumps, conventional design

Secondary pumps

Electro-magnetical pumps (passive cooling)

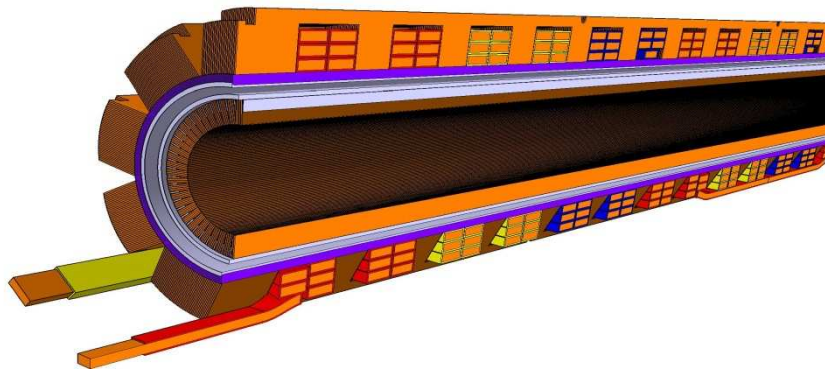
Design: collaboration with Toshiba/Japan

R&D: collaboration with IPUL, University of Latvia, CNRS – SIMAP Grenoble (PhD: L. Goldsteins)

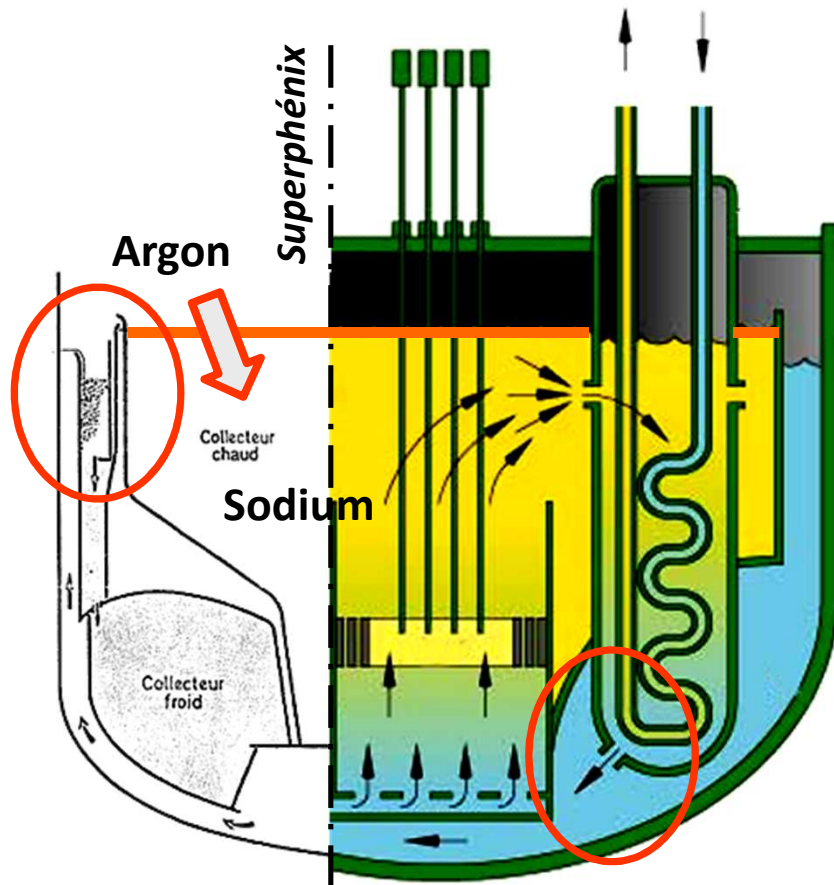
Dynamic behavior of Electromagnetic pump, MHD code assessment

Test program (PEMDYN, 2014-2015)

Small scale prototype



Bubble presence in primary sodium



CAUSES

- Dissolution ► Nucleation in oversaturated areas (Henry's law)
- Entrainment phenomenon
 - Weir (« waterfall effect »)
 - Pumps shafts
 - Vortex
- Neutronic reactions ($^{41}\text{K} \rightarrow ^{41}\text{Ar}$, $\text{B}_4\text{C} \rightarrow \text{He} \dots$)
- Auxiliary circuits

CONSEQUENCES

- Acoustic properties modifications of liquid Na
 - Attenuation
 - Velocity
- Risk of gaz pocket accumulation

ISSUES

- The mastery of the origins of this gas presence
- The evaluation of its consequences
- The validation of computational codes (VIBUL...)
- The response to a request from French Nuclear Safety Authority

OBJECTIVES

CHARACTERISATION OF :

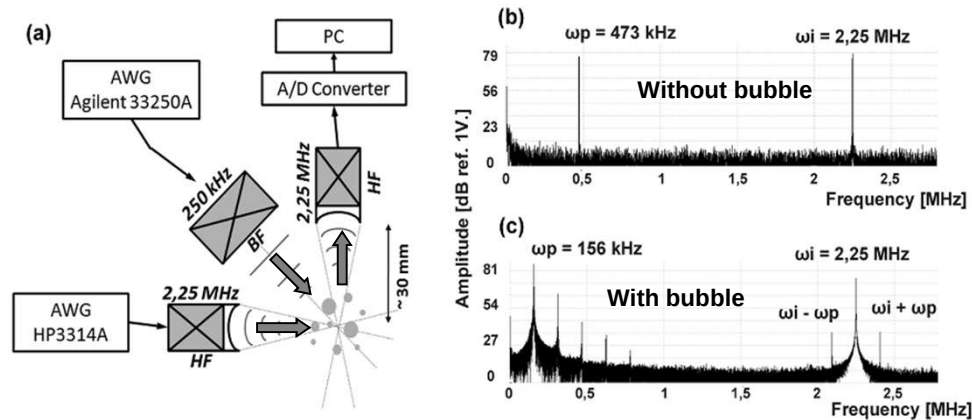
VOID FRACTION ($V_{\text{BUBBLES}}/V_{\text{TOTAL}}$)
($\tau \approx 2,5 \cdot 10^{-6}$ for Superphénix)

MICROBUBBLES RADII HISTOGRAMS
($10\mu\text{m} \leq R \leq 100\mu\text{m}$ pour SPX – estimation)

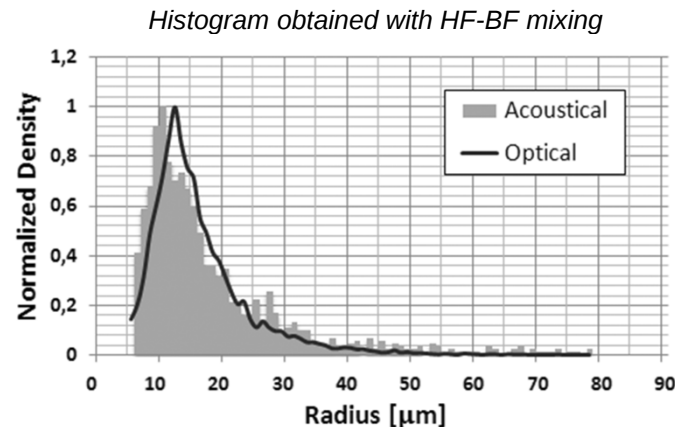
Nonlinear frequency mixing (HF-LF or HF-HF)

■ Based on the nonlinear behavior of a resonant bubble

- A resonant bubble insonified with two frequencies leads to the apparition of mixed frequencies



■ Detection of resonant bubbles allows determining the radii bubble histogram



- Excellent results have been obtained in water¹
- Experiments with sodium compatible transducer and then in liquid sodium are scheduled

¹ M. Cavarro, C. Payan, J. Moysan, F. Baqué - Microbubbles cloud characterisation by nonlinear frequency mixing – J. Acoust. Soc. Am., Express Letters, 129(5), EL179-EL183, May 2011

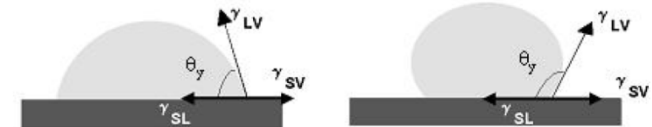
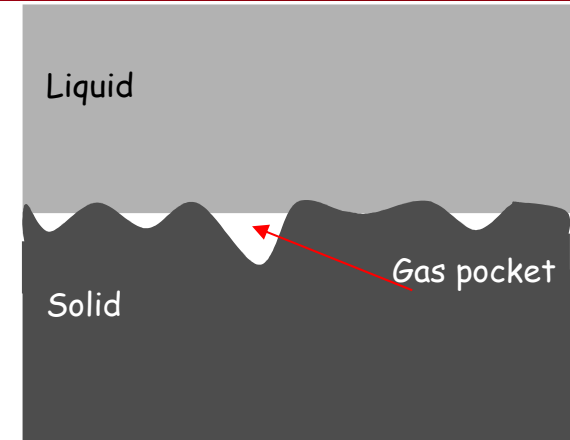
Are ECFM usable as free gas detector?

If yes, what are its limits (void fraction and bubble sizes)?
Is the characterisation (not only the detection) possible?

WETTING PHENOMENA

Wetting phenomena, which depend of gas adsorption, structural material oxidation,... are key interface phenomena between the coolant and the structural material. Therefore it is considered as a key factor with regards the following items:

- **accuracy of measurements** for some instrumentation devices such as ultra-sonic based traducers, electro-magnetic flow-meters, electro-chemical cells,...
- **interactions between structural material and liquid metal:** corrosion, embrittlement, stress corrosion cracking....
- **mass transfer** such as activated corrosion products, tritium,...
- **thermal exchanges in Heat Exchangers**, liquid metal targets,...
- **Technology developments, cleaning of residual layer,...**



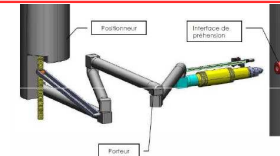
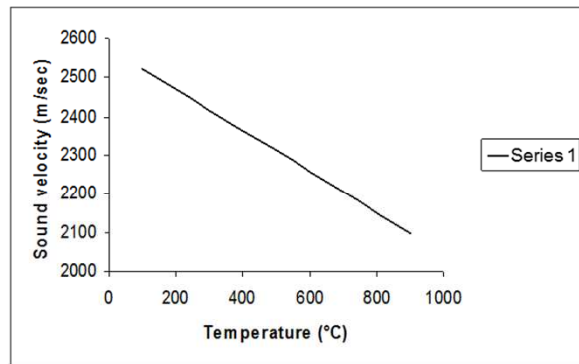
- ➔ Due to non-significant material embrittlement in Na, there is no necessity to foresee coatings to prevent wetting and its deleterious consequences.
(except to prevent from wearing & fretting effects)
- ➔ Na: a strong reducer: a very good wetting is obtained, even at low temperature (ie $T=180^\circ\text{C}$) thanks to the possibility to reduce oxygen content down to a very low value ($< 3\text{ppm}$)

SODIUM OPACITY: ULTRA-SOUND TECHNOLOGIES

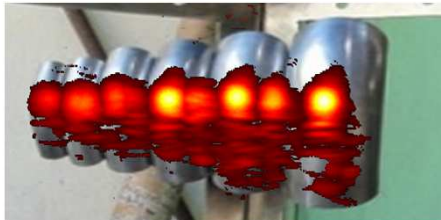
- As all liquid metals, sodium is opaque;
- necessity to develop adapted technologies for telemetry and visualization

Sound velocity in sodium varies little with temperature and is given by the following relationship:

$$C \text{ (m/sec)} = 2577.2 - 0.5234 \theta \quad 100 < \theta < 370^\circ\text{C}$$



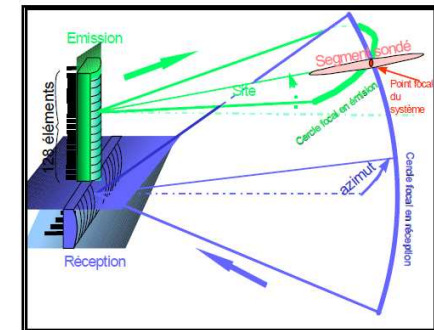
Consequences: Property used for telemetry and visualisation in sodium facilities, and for acoustic detection of events in Na



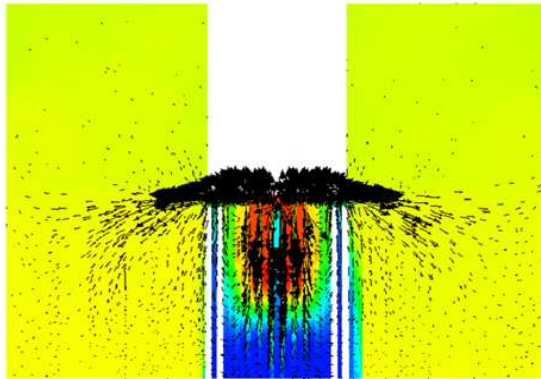
F. Baqué et al: "Sodium Fast Cooled Fast Reactor: R&D Program for improving periodic examination and repair". Science and technology of nuclear installations Journal, July 2012



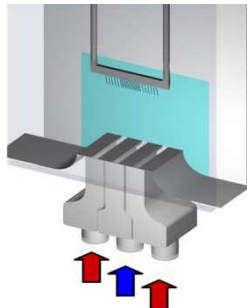
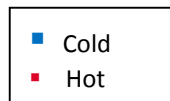
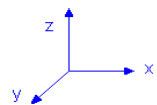
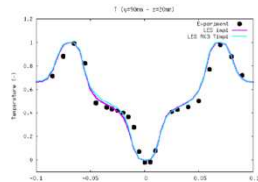
Multireflector mock-up



- Surface mapping (imaging) of submerged structures/components,
- Integrity inspection of structure/component surfaces (including the detection and sizing of opened cracks),
- Determination/confirmation of robotic system positioning,
- Fuel assembly identification,
- Detection, localization and sizing of immersed objects (including migrating bodies).



Temperature and speed vector field in sodium-cross section of a SFR reactor (CFD simulation)

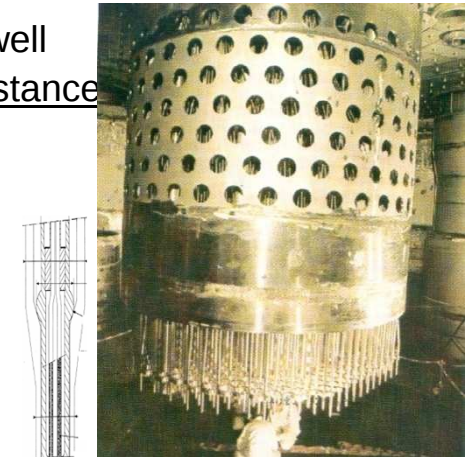
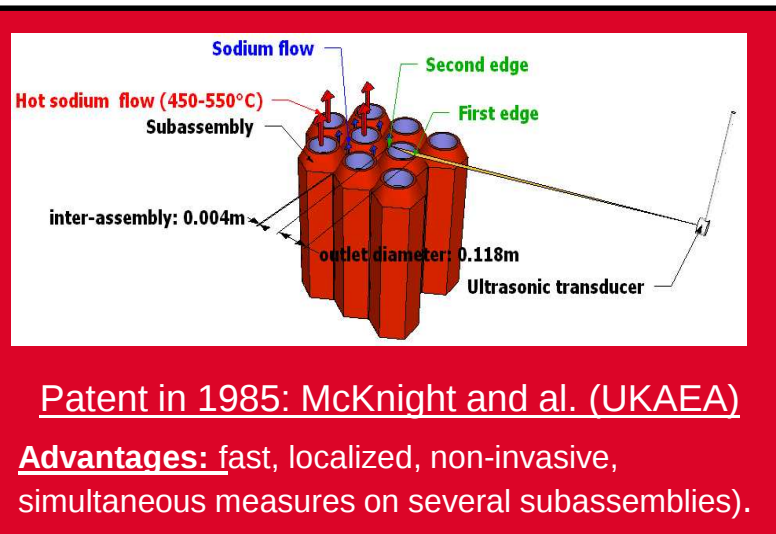


PLAJEST experiment geometry *



N. Massacret et al: "Simplified modeling of liquid sodium medium with temperature and velocity gradient using real thermal-hydraulic data. Application to ultrasonic thermometry in SFR". DENVER - 39th QNDE Congress July 2012

Thermocouple restrictions: need of a thermowell above each monitored subassembly, minimal distance between thermowell and subassembly outlet.



≈350 thermowells, containing 2 thermocouples each. (Time response SPX: 1.1s)

Ultrasonds propagation depends of :

- Temperature: Inhomogeneities of temperature inside the sodium ($\Delta T_{max}=50K$)
- Speed flow field: Turbulent flow ($Re=60\ 000$), speed (about. $4\ m.s^{-1}$), speed gradient ($1.5m.s^{-1}.cm^{-1}$).
- Induces deviation and diffusion of ultrasounds.

Goal: Define an appropriate model for ultrasonic propagation (in T, v field)

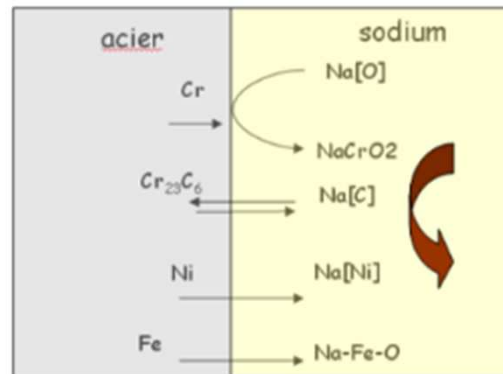
Background:

Very good compatibility of steels with pure sodium ($[O] < 5$ ppm)
for steels used with operating conditions of the existing reactors.

Nevertheless, new needs for ASTRID and SFR

- Life duration for structures: 60 years (316LN...)
- New materials: ODS, advanced austenitic steels,....

Na	Normal conditions	Transients
1	370-550°C - max 650°C 8-12 m/s - $[O] < 5$ µg/g	850°C (s- min) $[O] = 15$ µg/g/ 100 h
2	300-550°C - some m/s $[O] < 5$ µg/g	$[O] = 200$ µg/g/ 2000h



Corrosion: homogeneous phenomena but several mechanisms: dissolution, oxidation, intergranular diffusion (C, O, H, B), mass transfer

Parameters: température, duration, hydrodynamics, $[O]$, activities, minor alloy compounds (ie Mo), microstructure, neutron flux, ΔT (heat exchanger)

Consequences:

- mainly release of activated corrosion products,
- réduction of thickness (to a less ext)

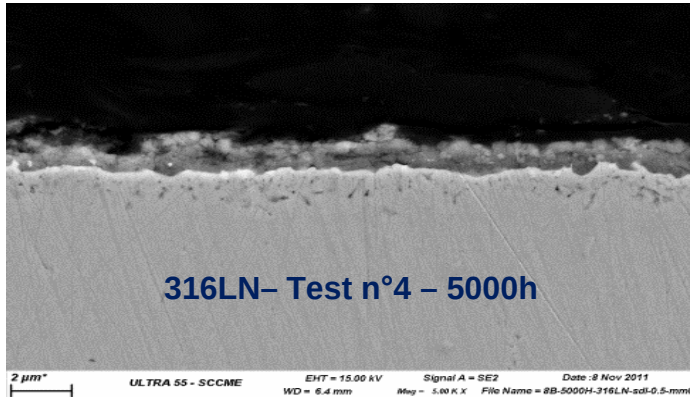
Basic research required to improve the knowledge:

- ternary oxides behaviour (Na_4FeO_3 ...),
- effect of solvation,
- diffusivities, ...

Up to now Semi-empirical modeling: (Baqué – Thorley)

→ Development of new corrosion models

→ On-going development of a **new transfer model** (OSCAR-Na)



- Kinetics available up to 5000 h at 550°C for [O] < 10 µg/g
- Ferritic steels more sensitive to oxidation and carburization than austenitic steels
- At lower temperatures, very low corrosion → no critical issue



CORRONa facility (CEA-DPC)

JL Courouau et al "*Corrosion by oxidation and carburization in liquid sodium at 550°C of austenitic steels for sodium fast reactors*" FR13
Paris March 2013

Impact on heat transfer:

Heat transfer, that occurs according to different mechanisms, mainly:

- convection in gas,
- radiation from the sodium surface towards emerged structures,

- Evaporation / condensation of sodium vapours. Sodium deposits but very limited amounts

→ Potential mechanical consequences on handling or rotating systems,...due to Na deposits (condensates):

Difficulties with control rods of PHENIX (one event),

→ Gradual decrease of magnetic lifting surface; lifting force < rod weight (lifting of the rod impossible)

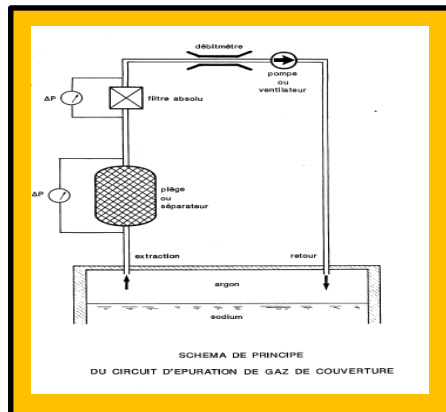
→ local cleaning solved the problem

→ Impact on viewing technologies in cover gas,...

→ Impact on thermal insulation performances

→ Impact on contamination and dosimetry (Cs,...)

→ Impacts on decommissioning ...



→Evaporation kinetics:

Based on $Sh = 0,643.(Gr.Sc)^{0.25}$ (Boolter relation)

$$R_{evap} = 0.643 D \cdot \rho_s / \Phi \cdot (Gr.Sc)^{0.25} \text{ kg/s.m}^2$$

With $Gr = g \cdot \Phi^3 / \nu^2 \cdot (1 - \gamma_s / \gamma_\infty)$

And $Sc = \nu / D$

With :

D = diffusion coefficient (m^2/s)

ρ_s = Na density at Na-gas interface (kg/m^3)

Φ = diameter of the free surface (m)

ν = viscosity (m^2/s)

$g = 9.81 \text{ m/s}^2$

γ_s = gas density at Na-gas interface (kg/m^3)

γ_∞ = gas density at infinite (kg/m^3)

Gas circuits are equipped with condensers and aerosol traps



Liels paldies

Merci beaucoup pour votre attention

Thank you for your kind attention

