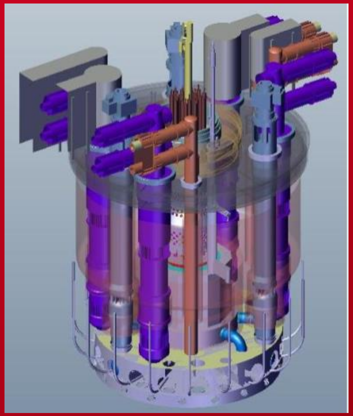
DE LA RECHERCHE À L'INDUSTRIE



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Joint ICTP-IAEA Workshop on
"Physics and Technology of Innovative Nuclear Energy Systems for Sustainable Development"
Trieste Italy
2022 December 12th – 17th

SODIUM COOLANT : FROM PROPERTIES TO DEDICATED TECHNOLOGIES
PART-1

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COOLANT FUNCTIONS FOR THE PRIMARY CIRCUIT OF SFR:

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 behaviour of structural materials**
- **Induce unacceptable safety conditions**
- **Induce insurmountable operating problems**
- **Lead to wastes which can't be processed during operation or dismantling**

Potential coolants

METAL		Molar mass, g/mol	Melting point, ° C	Boiling point, ° C	ΔT $T_m = T_b$, ° C
MERCURE	Hg	200,59	– 38,9	356,6	395,5
CESIUM	Cs	132,91	28,5°	690	661,5
GALLIUM	Ga	69,72	29,7	2 403	2 373,3
RUBIDIUM	Rb	85,47	38,9	684	645,1
POTASSIUM	K	39,10	63,7	774	710,3
INDIUM	In	114,82	156,6	2 080	1 923,4
LITHIUM	Li	6,94	180,5	1 317	1 336,5
SELENIUM	Se	78,96	217	684,9	467,9
TIN	Sn	118,69	231,9	2 270	2 038,1
BISMUTH	Bi	208,98	271,3	1 560	1 288,7
THALLIUM	Tl	204,37	303,5	1 457	1 153,5
CADMIUM	Cd	112,40	321,0	765	444
LEAD	Pb	207,19	327,3	1 740	1 412,7
SODIUM	Na	23	97,8	883	785,2

Other coolants: Na-K, Pb-Bi, Pb-Mg…

NTR(J) – NETER – NITRON-NATRUN-NATRON-NATRIUM

Réf. Wikipédia: The word **natron**, equivalent to « mineral soda », « carbonated soda ($Na_2CO_3 \cdot 10\ H_2O$, …) is close to latin word then german world « **natrium** », and from it the symbol **Na**, for sodium.

The word *natron* came from Arabian word **natrūn**, which seems originally from ancient greek **nítron**, and early from Aegyptian word

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

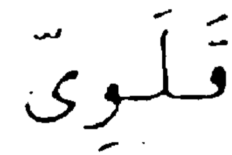
This **product** was **used for many applications** : home cleaning, antiseptic to avoid infection, conservation for food safety, drying agent for leather, additive for brazing, compound of blue colour (aegyptian blue), mommies preservation…

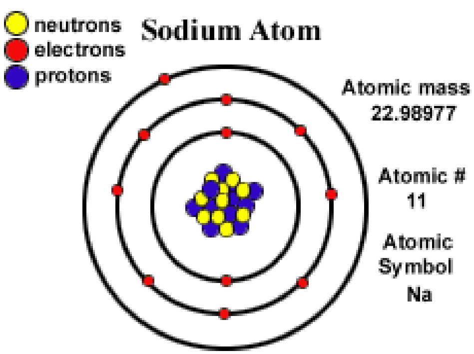
Wadi El Natrun

Blue colour

Toutankhamon

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



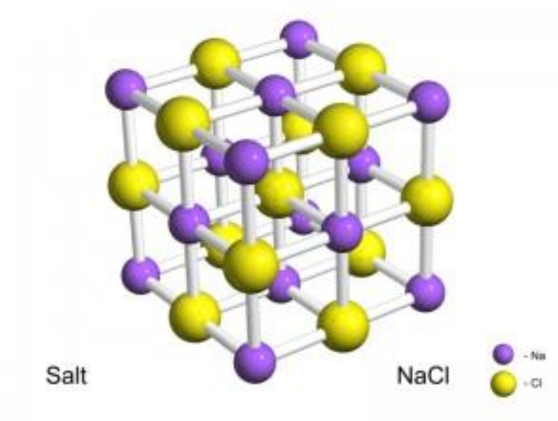


	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub						

6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

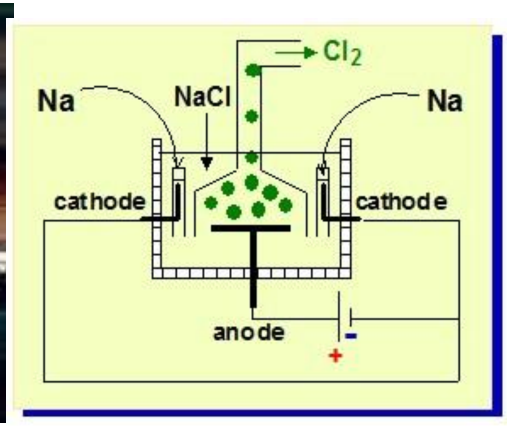
SODIUM PRODUCTION

Mine in Varangéville France



Produced by electrolysis of the eutectic NaCL/CaCl$_2$

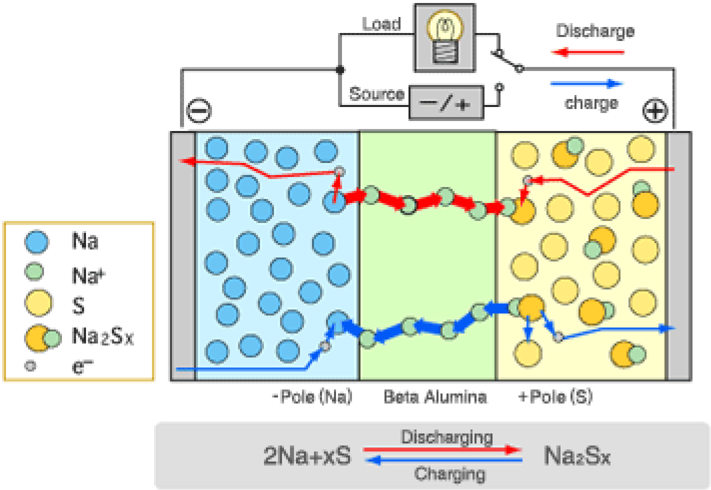
Electrolysers at MSSA plant Métaux Spéciaux (Moutiers France)



NA-S BATTERY

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

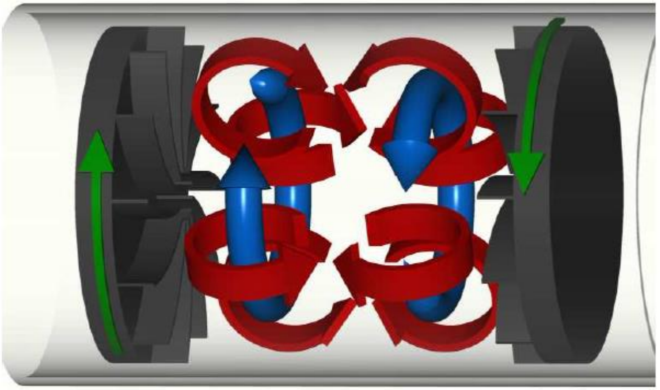
➔ Na separated by a beta-alumina solid electrolyte (BASE) cylinder (good conductor of Na ions) from the cathode (container containing molten sulfur adsorbed on a carbon sponge). When Na gives off an electron, Na^+ ion migrates to the sulfur container. The electron drives an electric current through the 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)

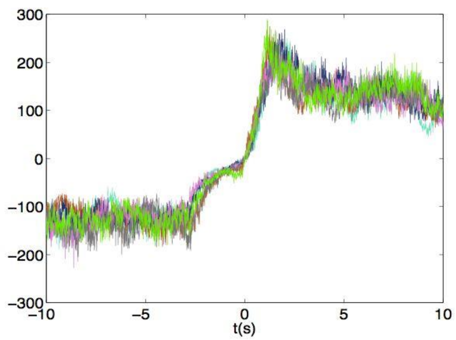


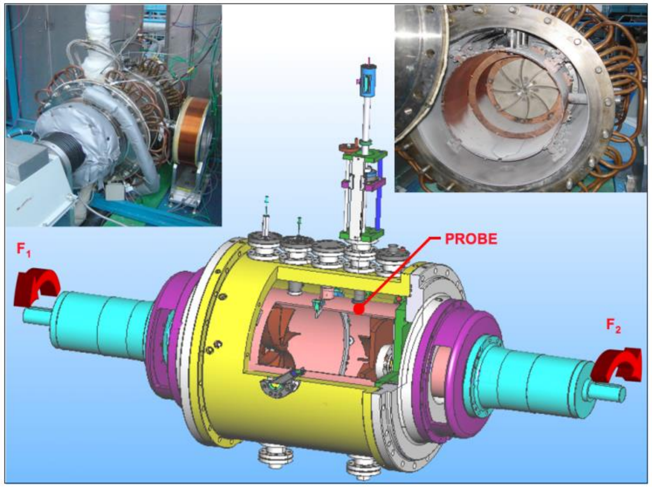
Exemple: 34 MW NAS alongside 51 MW Wind Farm Courtesy of NGK Insulators – Japan)

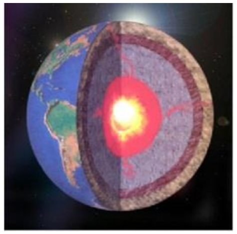
Dynamo experiments with Na

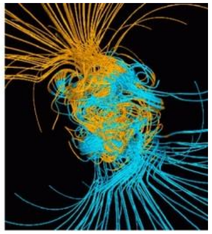
$R_m = 2\pi K \mu_0 \sigma R^2 f$

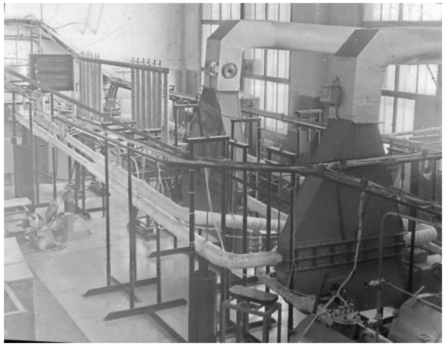


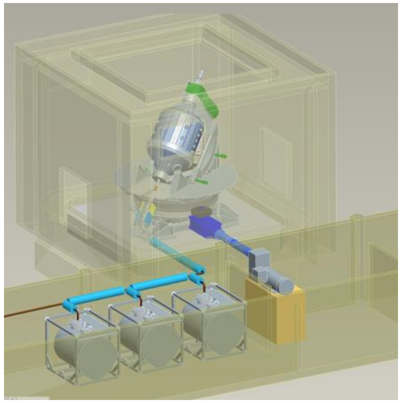












VKS in Cadarache

Na dynamo in IPUL (1991)

DRESDYN in HZDR

MOLTEN SODIUM METAL FOR METALURGY (IE TANTALUM)

The preparation of tantalum is the process of reducing pure tantalum compound to metal tantalum.

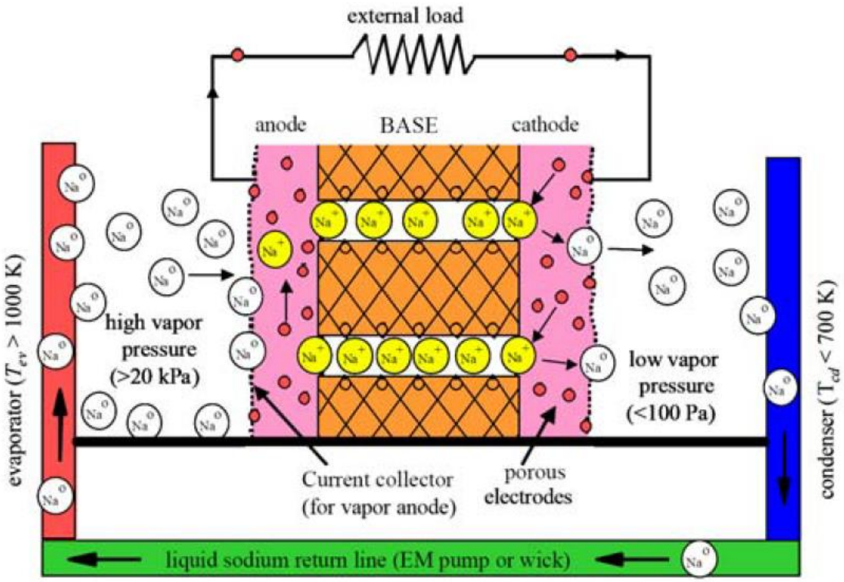
Raws materials are five tantalum oxide, tantalum chloride, five tantalum fluoride and fluoride (such as K_2TaF_7,).

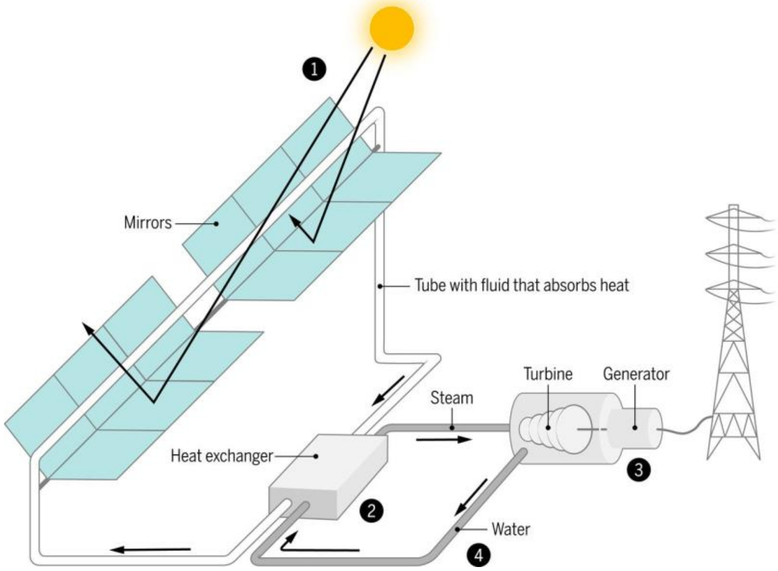
Reducing agent: sodium, magnesium and other active metals and carbon and hydrogen. The melting point of tantalum is as high as 3669K, so it is powder or spongy metal after reduction. It is necessary to further smelting or refining, in order to get dense metal.

➔ Sodium thermal reduction of potassium tantalate is the most widely used method.

Courtesy ICD Europe

Several projects in renewable energies: Concentrated Solar Power plants (CSP) can use molten salts (HYTEC
➔ See VAST projects in Australia, AZELIO in Sweden….





AMTEC Cell (Alkali-Metal Thermo-Electrical Converters) (Courtesy KIT) with β-aluminate solid electrolyte + as electrical insulator

See Ref: W. Hering, R. Stieglitz, 2011, Qualification requirements for innovative instrumentation in advanced nuclear systems, PAMIR-8, Int. Conf. on Fundamental and Applied MHD, 529-533.

BINARY ALLOYS WITH MELTING POINTS < 330°C

	NaK-78	Bi-Pb	Li-Pb	Pb-Mg
Mass percentage	K : 78 %	Bi : 55 %	Pb : 99,3 %	Pb : 97,5 %
Density (g/cm^3)	0,868 at 20°C	10,5 à 20° C 10,19 at 400°C	9,43 at 400°C	9,36 at 250°C 10,6 liquid
Viscosity (Pa.s)	2,050.10^{-4} at 400°C	1,38 . 10^{-3} at 450° C	1,37.10^{-3} at 400°C	2,86.10^{-3} at 250°C
Vapor tension (atm)	1 mm Hg at 350°C	1,5. 10^{-8} at 500°C		
Microscopic capture cross section, (n th) in barns	1,7	0,094		0,17
Boiling point (° C)	784	1 670	1 665	1 103
Cp (J/kg. °C)	0,879.10^3 at 400° C	0,1493.10^3 at 400° C	0,189.10^3 at 400° C	0,148.10^3 at 400° C

SODIUM PROPERTIES 1/6

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

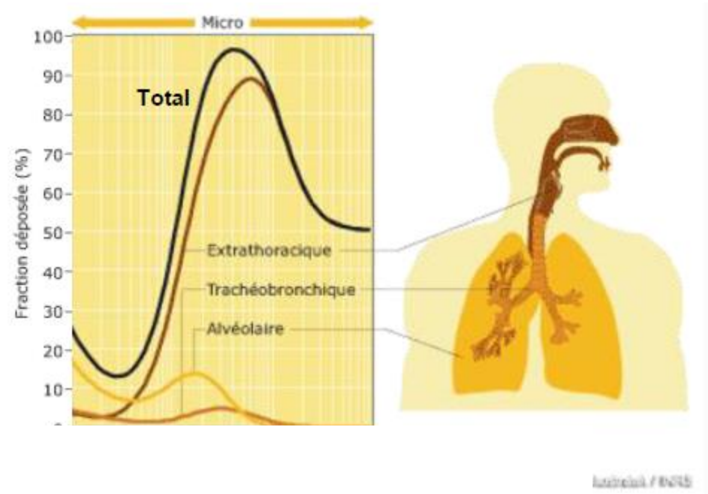
Biological utility: essential

Daily recommended consumption: 2 to 15g;

MNa in human body (70kg): 100g

- Bones: 10 000 ppm

- Blood: 1970 mg/l



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

➔ **large availability and cheapness**

Earth's crust:	**23 000 ppm**
Sea water:	**10 500 ppm**

Main ressources:

Halite ("NaCl"Mines)

Trona: $Na_3(CO_3)(HCO_3),2H_2O$

Yearly output: c. 200 000 ton.year^{-1}

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

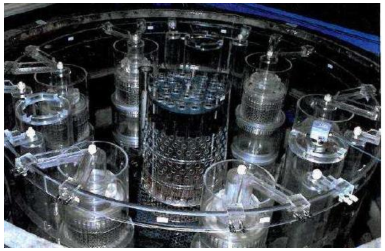
SODIUM PROPERTIES 2/6

➔ **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):**

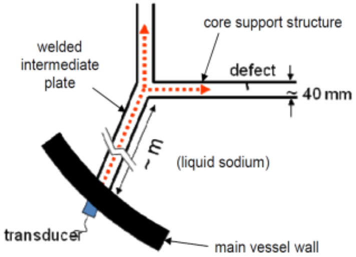
- Flexibility for Na uses as a cooling media

Exemple of mock-up for a SFR

➔ **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.



➔ **a high sound velocity in Na**

- allows In Service Inspection in Na thanks to US transmission

$$C\ (m/sec) = 2\,577{,}2 - 0{,}5234\ \theta \qquad 100 < \theta < 370°C$$

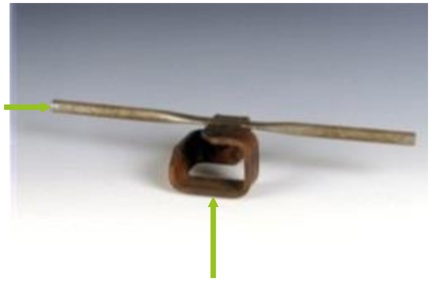
SODIUM PROPERTIES 3/6

➔ **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, leak detection systems…



➔ **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

NA LEAK DETECTION

Experimental objectives: ***Improvement of Na leak detection system, to reduce detection time and mitigate consequences***

Chemical behavior under insulating material in case of sodium leak (corrosion phenomena)

FUTUNA 2 – well mastered leak flow rate experiment:

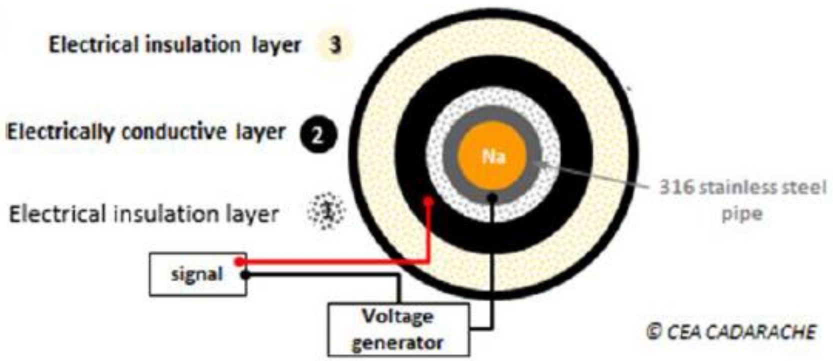
- **Dynamic test section with a sodium leak rate range:** 0,05 up to 30 cm^3/min
- **Temperature range of leaking sodium:** 250-550°C
- **Maximum pressure:** 250 mbar rel.

INNOVATIVE LEAK DETECTION SYSTEMS

- **Stakes:** Safety & operation
  - If it takes to long to detect a small Na leak in a pipe, this leak will eventually worsen and can lead to a large fire, with significant consequences

- **Requirements:**
  - Detection of small Na leaks (< 10 cm³/min) in large thermal insulated pipes (secondary and auxiliary circuits) with continuous monitoring in nominal operating conditions.
  - Detection system requirements: reliable, short detection time (< 10 hours), precise location of the leak, easy to assemble, a 10-year service life.

- **Multilayer detection system (MDS):**
  - Concept:



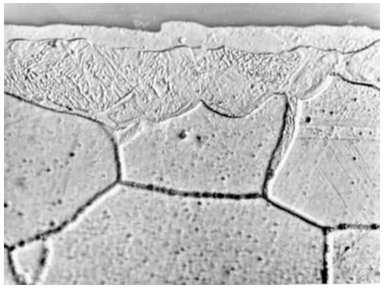
  - Principle: in the event of a sodium leak, the liquid sodium will flow through the first layer of electrical insulation (1) to come into contact with the second layer which is conductive (2). The electrical properties of sodium will trigger the detection circuit which, in turn, will trigger an alarm.

Detection of small leaks (around 1 $cm^3.min^{-1}$) within few minutes or few tens of minutes depending on the conditions

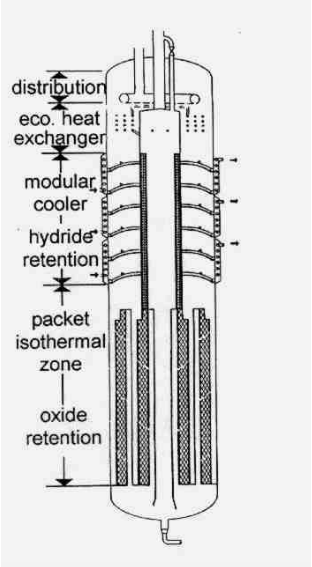
SODIUM PROPERTIES 4/6

➔ 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.



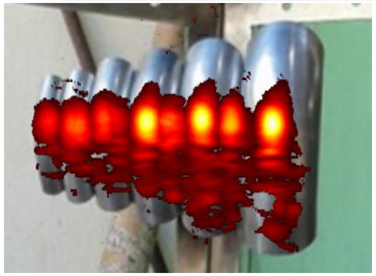
➔ a **very limited amount of particles in sodium**, due to the instability of ternary oxides (except NaCrO2) and high dissolution rates in Na, due to its reducing properties.



➔ **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 6/6

➔ a coolant which **does not slow down the neutrons**, and does not change fast spectrum properties

➔ a **very limited activation*** **with short decay** periods (^{22}Na: 2.6 y, ^{24}Na: 15 h),

Reaction	Product		Types of decay	Half-life
n, γ (21)	$^{24}_{11}Na$		β- (1) 0.28 MeV(0.05%) β-(2) 1.39 MeV (99.94%) β- (3) 4.14 MeV (0.003%) γ (1) 1.00 MeV(0.001%) γ (2) 1.37 MeV (99.992%) γ (3) 2.75 MeV (99.94%) γ (4) 2.87 MeV (0.000 2%) γ (5) 2.87 MeV (5.2 %) γ (6) 4.24 MeV (0.0008%)	14.98 h
n,2n (21)	$^{22}_{11}Na$		β+(1)0,545 MeV (89.8%) K (1) 1.567 (10.11%) K (2) 2.842 (0.0002%) β+(2) 1.820 MeV (0.06%) γ 1.275 MeV	2.60 y
n, p (2)	$^{23}_{10}Ne$		β-4.39 MeV (67%) 3.95 MeV (32%) 2.40 MeV (1%) γ 0.44 MeV (33%) 0.47 MeV (100%) 0.88 MeV (8%)	38 sec
n, α (2)	$^{20}_{9}F$		β-5.42 MeV (100%) γ 1.63 MeV (100%)	11 sec

*** But must be of "nuclear grade" (see next slide)**

➔ **low capturing power** (small cross section)

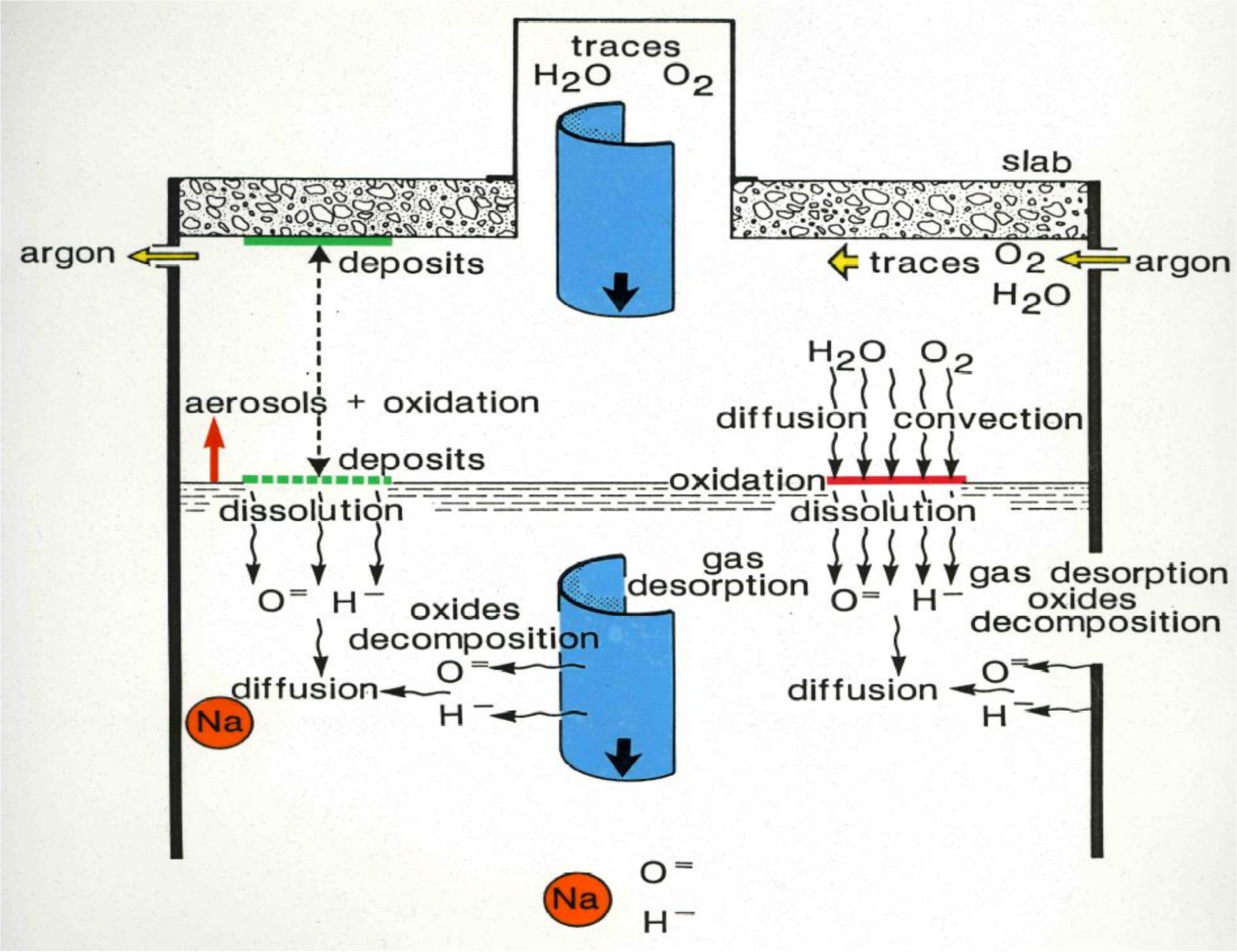
➔ Doesn't produce any α contamination (ie ^{210}Po)

NUCLEAR GRADE SODIUM (MSSA): SPECIFICATIONS (IN PPM)

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

POLLUTION



traces
H2O O2
slab
argon
deposits
traces O2
H2O
argon
H2O O2
aerosols + oxidation
diffusion convection
deposits
oxidation
dissolution
dissolution
gas
desorption
gas desorption
O= H−
oxides
decomposition
O= H−
oxides
decomposition
O=
diffusion
H−
Na
diffusion
O=
H−
Na
O=
H−

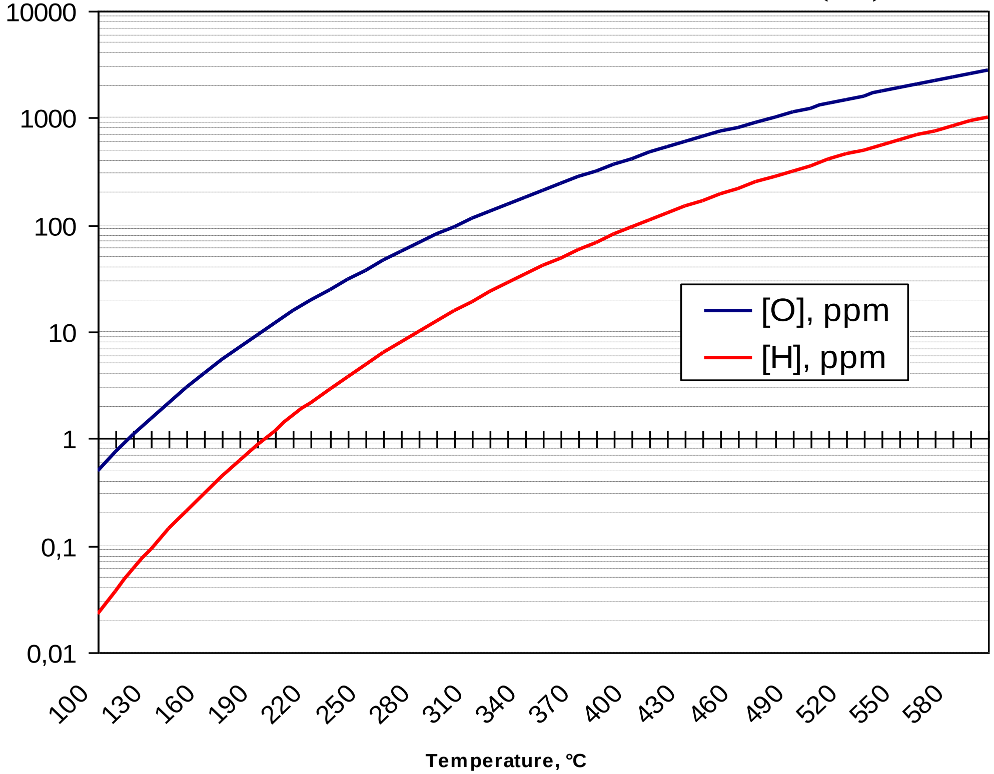
SOLUBILITIES OF O AND H IN SODIUM

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 Na_2O 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)

C. LATGE, *"Sodium quality control, In International Conference on Fast reactors",* Kyoto, Japan, (December 2009).

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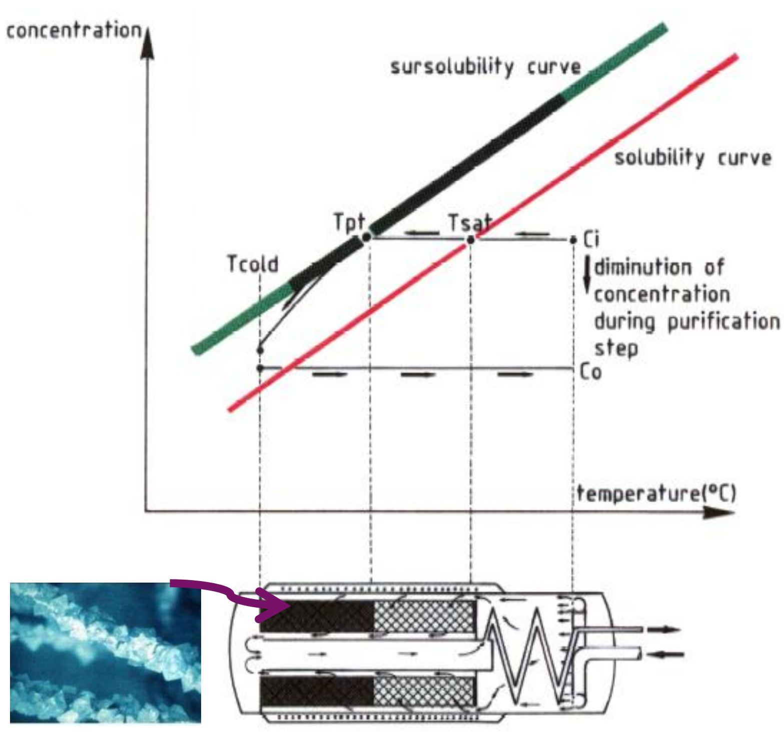
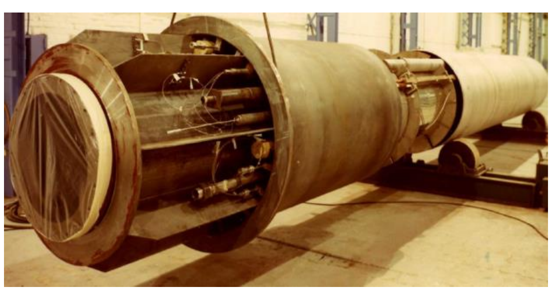
Cold trap principle





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

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

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.)
ρNa is the sodium density in (kg/m³)
(C-C*) is the supersaturation at temperature T(K).

Phenomena	**Nucleation (N)**		**Growth (G)**	
Impurity	Na_2O	NaH	Na_2O	NaH
E (kg/mol)	-60	-450	-45	-43.6
n	5	10	1	2

CORROSION IN NA

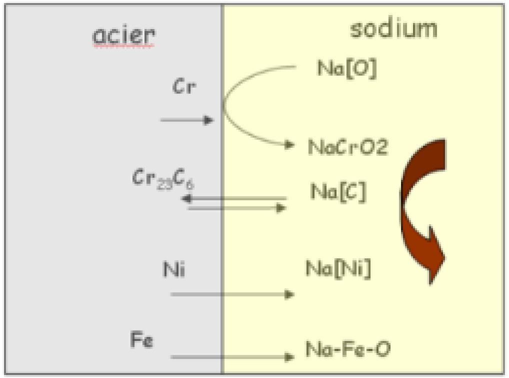
Background:

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 (IHX)…,

Consequences:

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

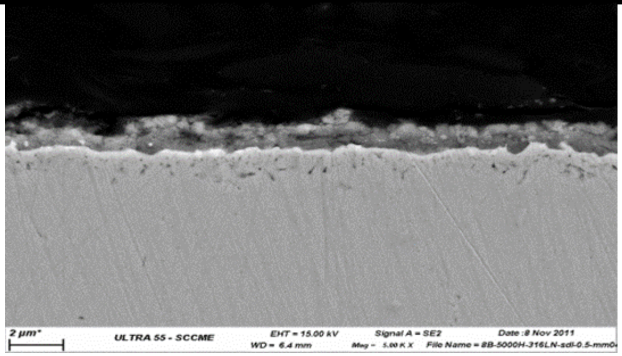
Basic research to improve the knowledge:

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

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

➔ Development of new corrosion models

➔ Development of a **new transfer model** (OSCAR-Na)

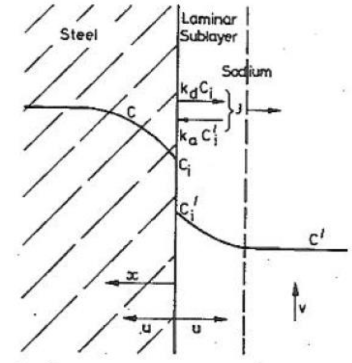


ACTIVATED CORROSION PRODUCTS IN NA

Mass transfer (Fe, Ni, Cr, …)

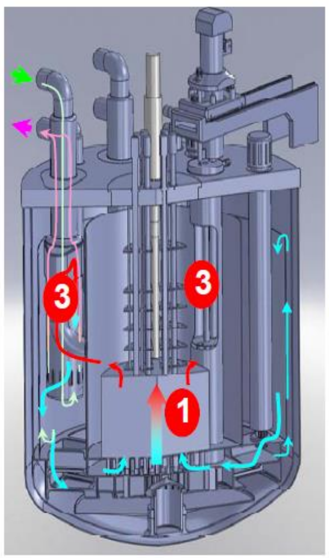
Is due to solubility difference between hot parts and cold parts of species in the sodium

- ➔ Steel solution in hot regions (bulk corrosion)
- ➔ Precipitation in cold regions (bulk deposition)



(a) Release

Radioactive corrosion product transfer (^{54}Mn, ^{60}Co, ^{58}Co, …)



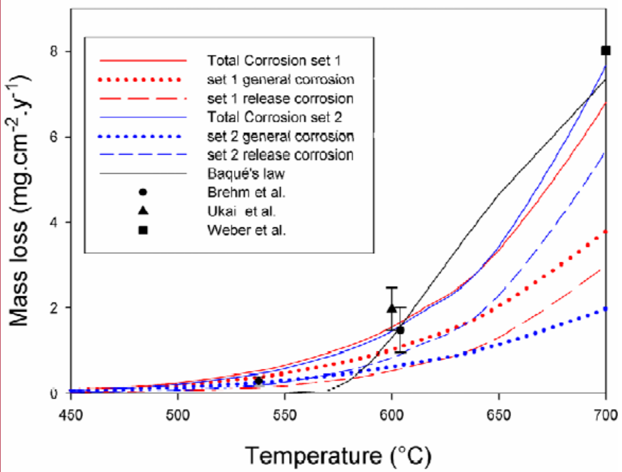
1) Release from the activated cladding

- Bulk corrosion of cladding steel
- Preferential release of highly soluble elements

2) Transfer in the flowing sodium
(parameters : T, velocity, [O])

3) Contamination of out-of-flux surfaces (IHX, primary pumps, …)

- Diffusion in the steel
- Precipitation on cold surfaces



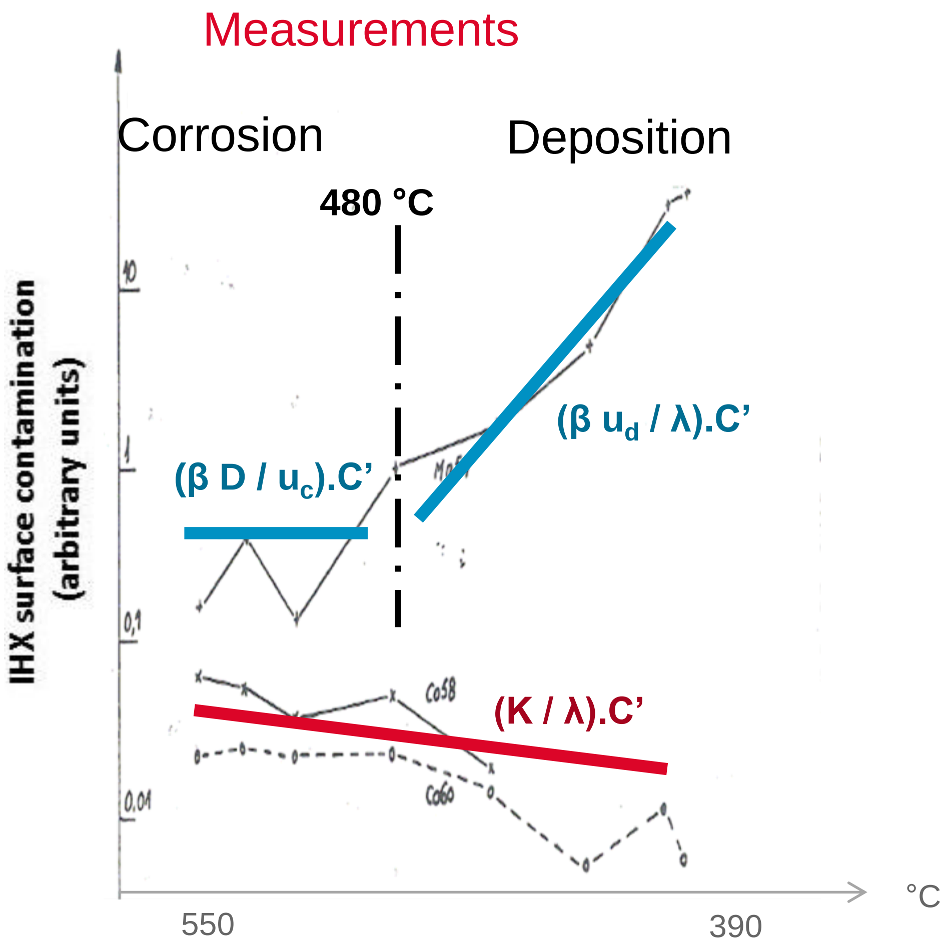
L. Brissonneau, "New considerations on the kinetics of mass transfer in sodium fast reactors: an attempt to consider irradiation effects and low temperature corrosion", Journal of Nuclear Materials 423 (2012) 67-78

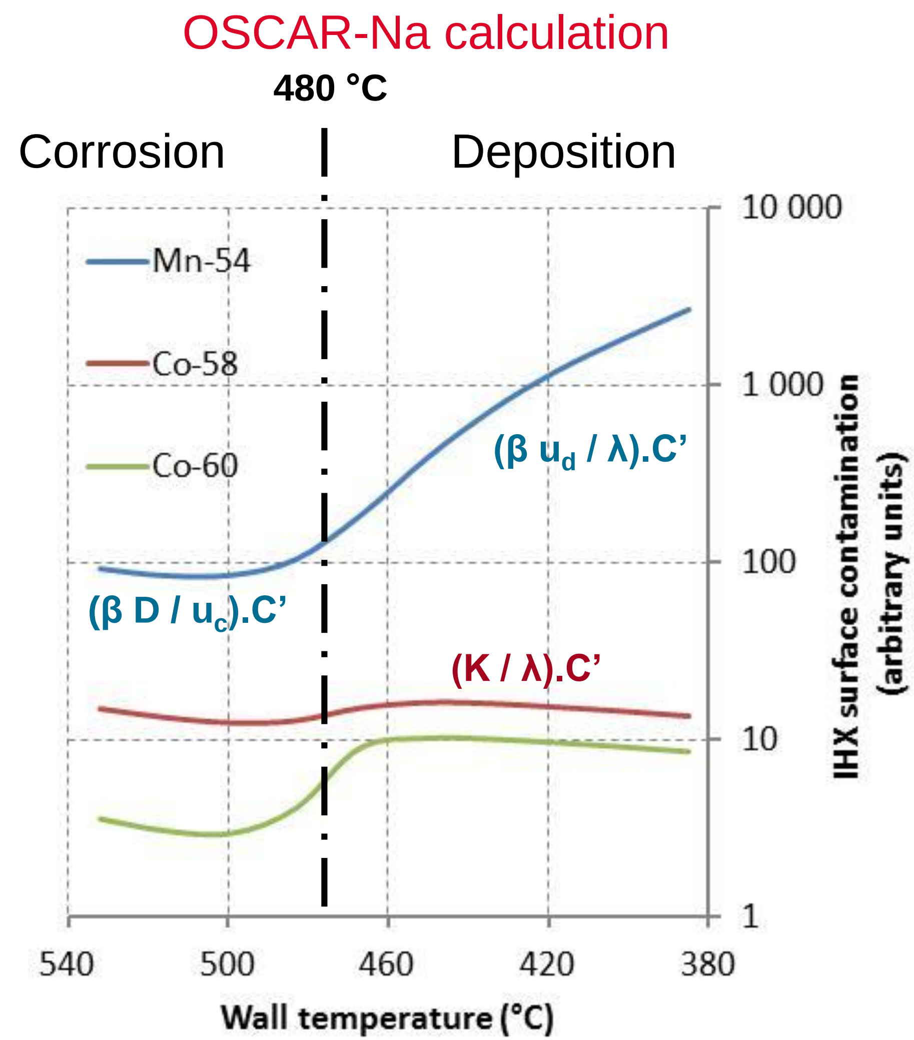
Industrial issues of contamination

- Personnel exposure to radiation
- Plant design
- Waste management
- Decomissionning

Contamination and dosimetry in SFR are low in comparison with PWRs

Contamination profiles on PHENIX IHX (1st OSCAR-Na validation)

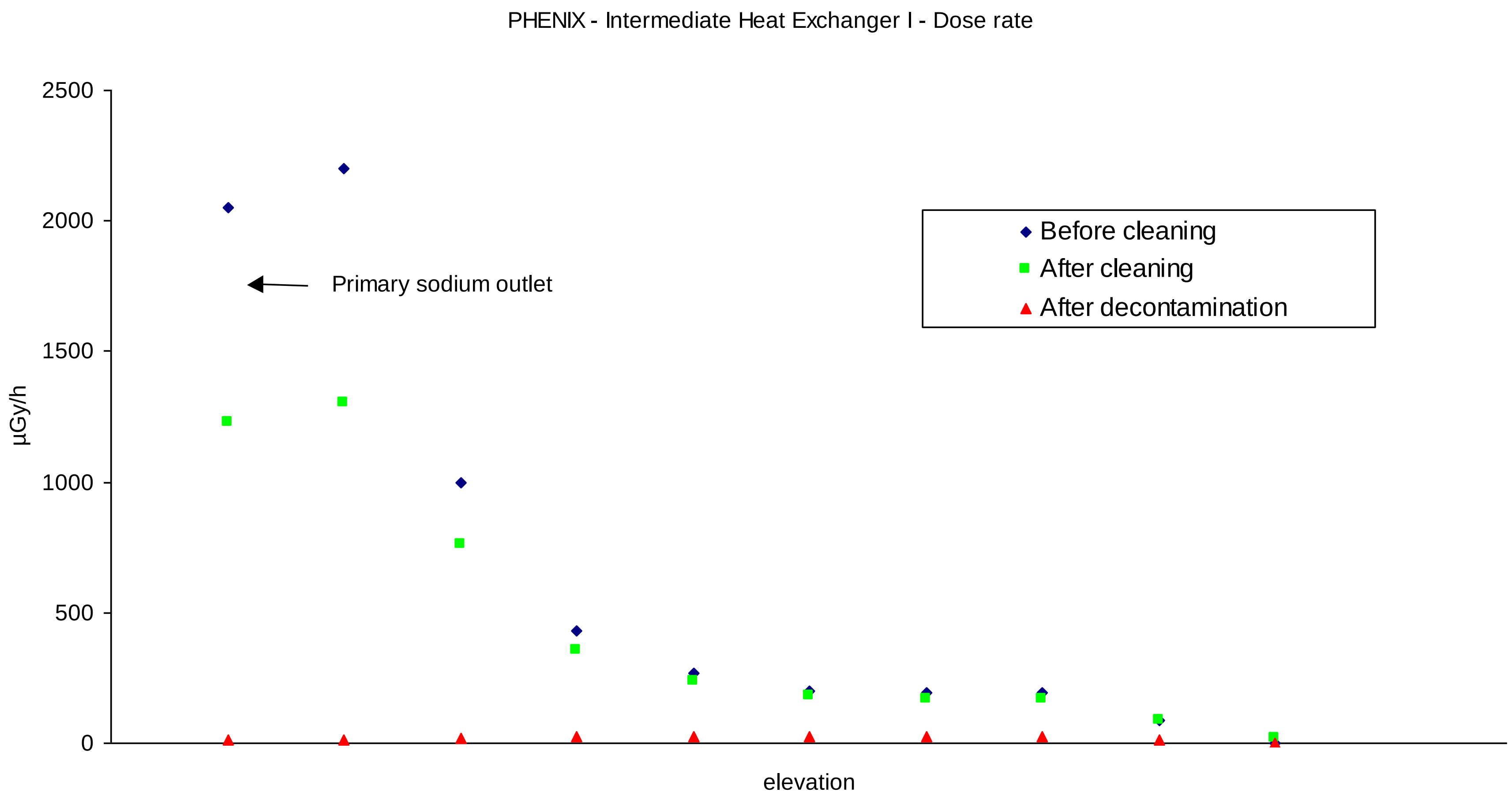




Global contamination as well as contamination profiles on PHENIX IHX are correctly simulated

J.-B. Génin et all *"OSCAR-Na V1.3: a new code for simulating corrosion product contamination in SFR reactors"* Conf. IAEA FR13, Paris March 2013

PHENIX IHX ACTIVITY (EXEMPLE)



Prior to repair or inspection, Na cleaning (with steam) is well mastered, in safe conditions.
Decontamination with Sulfo-phosphoric process is very efficient
➔ Low dosimetry during handling operations

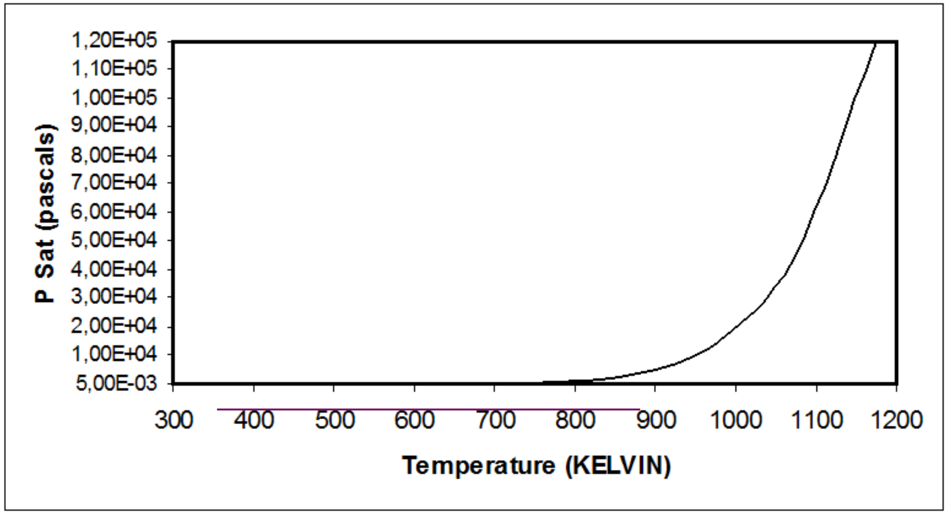
SATURATION VAPOUR PRESSURE

The empirical relationship for the saturation vapour pressure is given by the formula:

$$P_S = \mathrm{Exp}\left[A + \frac{B}{T} + C \mathrm{Ln} T + D T^E\right]$$

for 371 < T < 2573 K

Where A= 23.99, B= - 12.580, C= - 0.2241, D= 1.712 10^{-22} , E= 6



Consequences:

- very few aerosols and thus low gas phase transfer
- very low flames in case of ignition (T> 140°C if in puddle)
- vacuum distillation cleaning ineffective ➔ hot gas cleaning used

Sodium's chemical affinity for oxygen

Self-ignition of sodium:

- Na in puddle: T around 140°C
- Dispersed Na: As soon as Na becomes liquid

➔ Sodium fires $2\,Na + \frac{1}{2}\,O_2 \rightarrow Na_2O$

and $2\,Na + O_2 \rightarrow Na_2O_2$

Low flames, limited thermal radiation

Extinguished with Marcalina powder (sodium carbonate, lithium carbonate and graphite)

Limited expansion by partial confinement (collecting compartments)

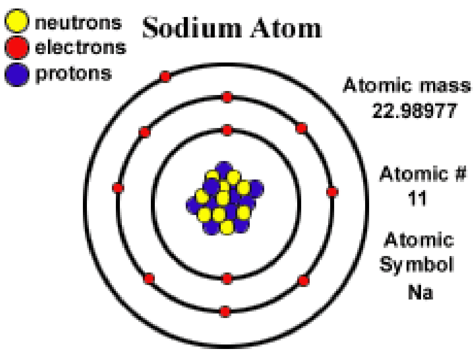
➔ Combustion phenomenological models + admospheric dispersion models

Na fire studies dedicated to SFRs are relevant for any non-nuclear systems using sodium as a fluid and/or coolant

SODIUM PROPERTIES 5/6

➔ **a very large reactivity with water:**

- possible deleterious effects in Steam Generator Units (SGU), in case of pipe rupture,
- allowing efficient components cleaning, prior to repair and Na treatment during decommissioning phase (conversion into sodium hydroxide then sodium salt, without any inherent toxicity).



➔ **Na-H_2O interaction in SGU:**

- to be avoided or mitigated by design (ie selecting a modular SGU)
- to be detected, thanks to the production of hydrogen, (Ni membrane + mass spectrometer, electro-chemical H-meter) without rupture of the confinement.

➔ **For cleaning pits or Na treatment processes**, the risk of explosion due to hydrogen has to be mitigated, thanks to dedicated means such as inertization or recombiners and appropriate design of buildings.

➔ **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, confinement or dedicated powder extinguishers (Na + Li carbonate + graphite).

Thank you for your kind attention!

Merci beaucoup pour votre attention!