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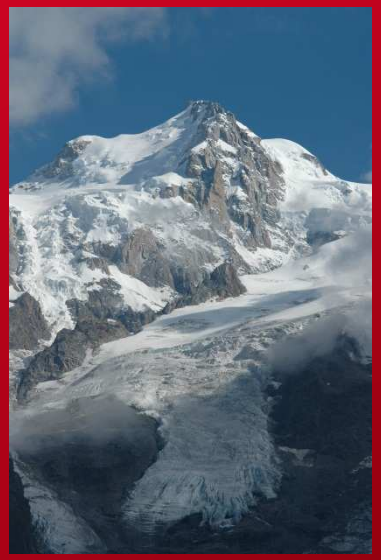

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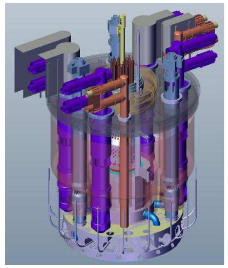
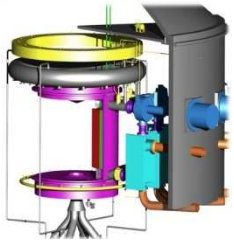
Joint ICTP-IAEA Workshop on
"Physics and Technology of Innovative Nuclear Energy Systems for Sustainable Development"
Trieste Italy
2018 August 20th-24th



Coolants for Fast Neutron Reactors Choice & consequences

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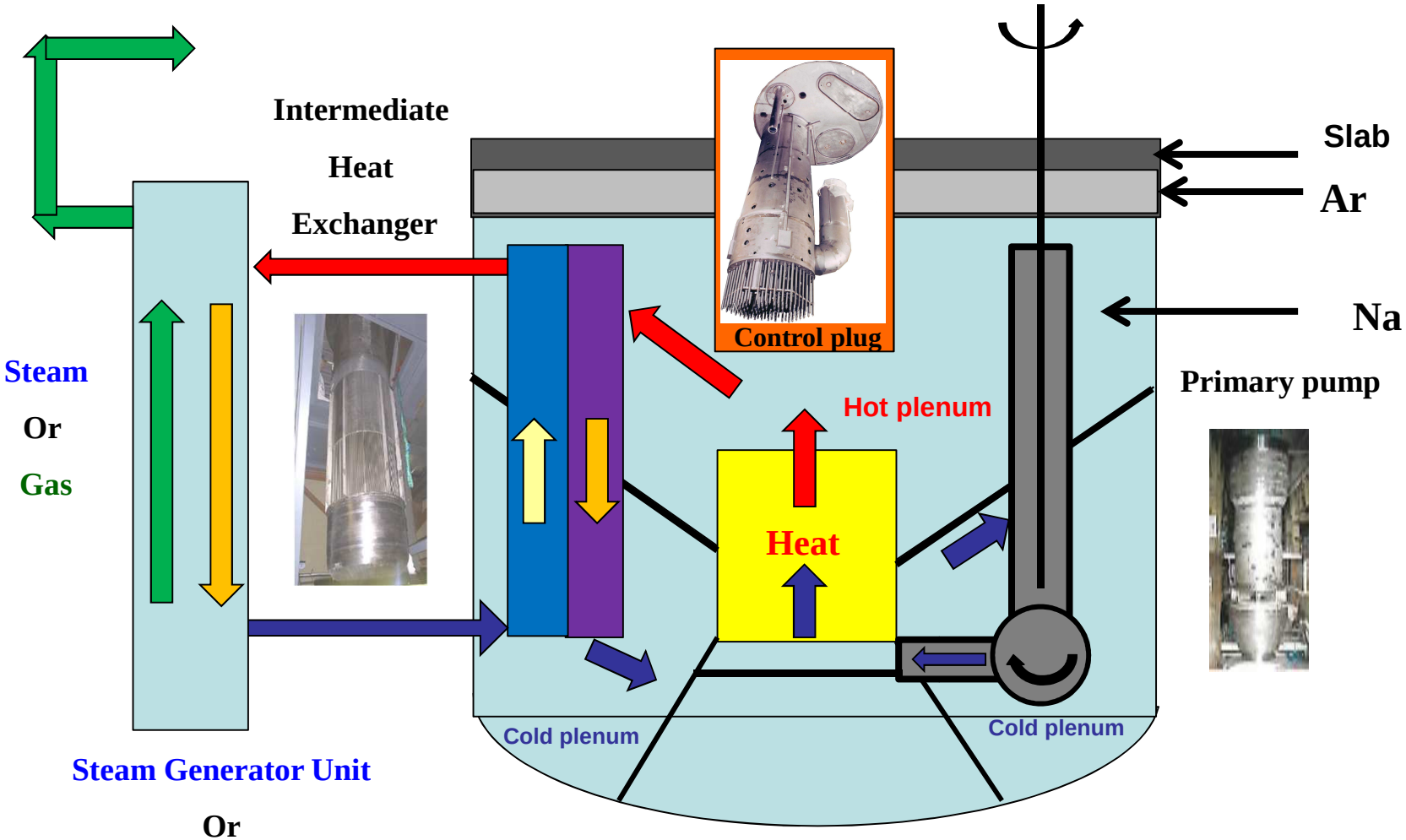
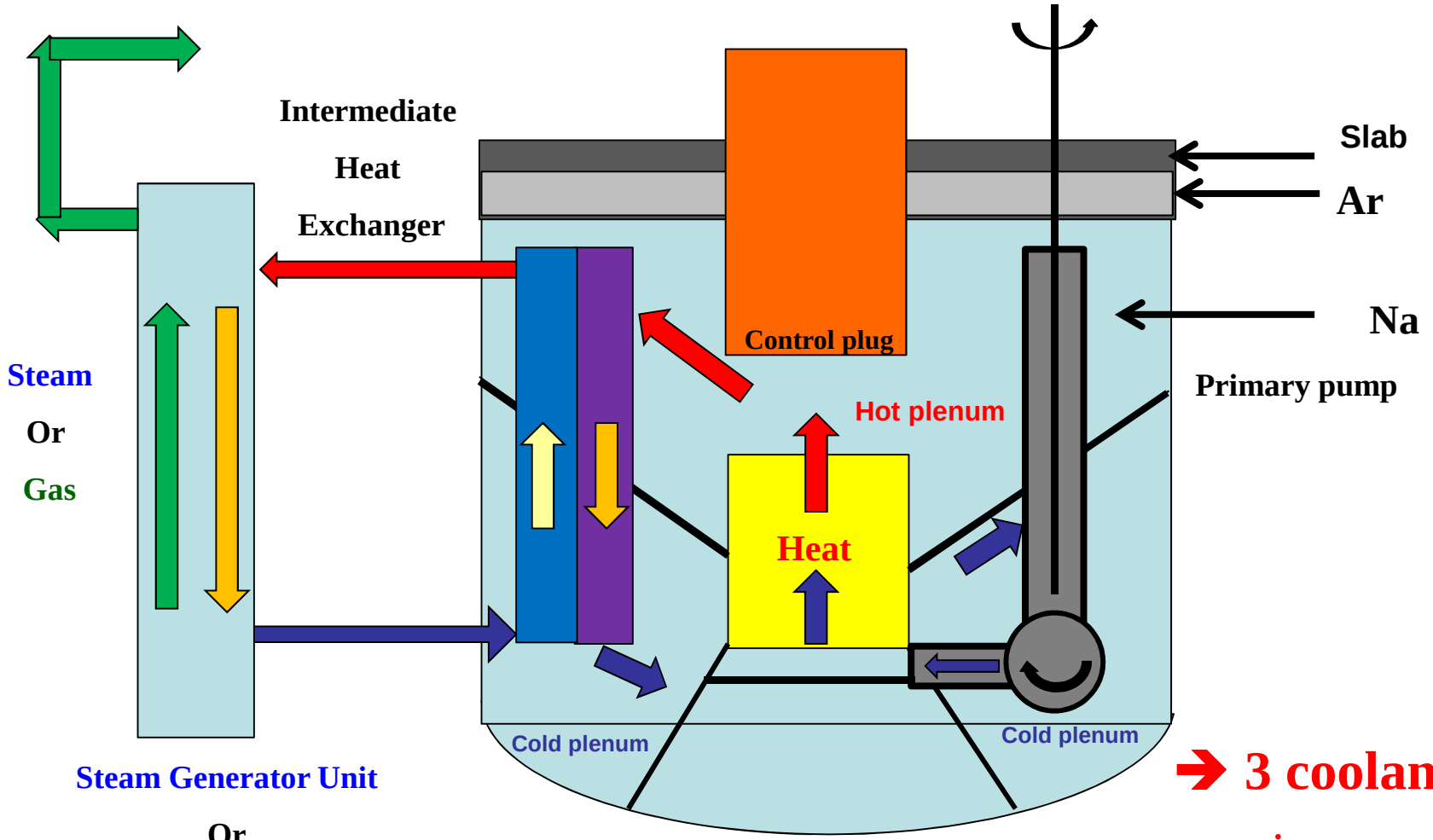
PRIMARY CIRCUIT OF SFR (POOL CONCEPT) 1/2



PRIMARY CIRCUIT OF SFR (POOL CONCEPT) 1/2



➔ **3 coolants:**

-primary pool

-intermediate loops

- Energy conversion system

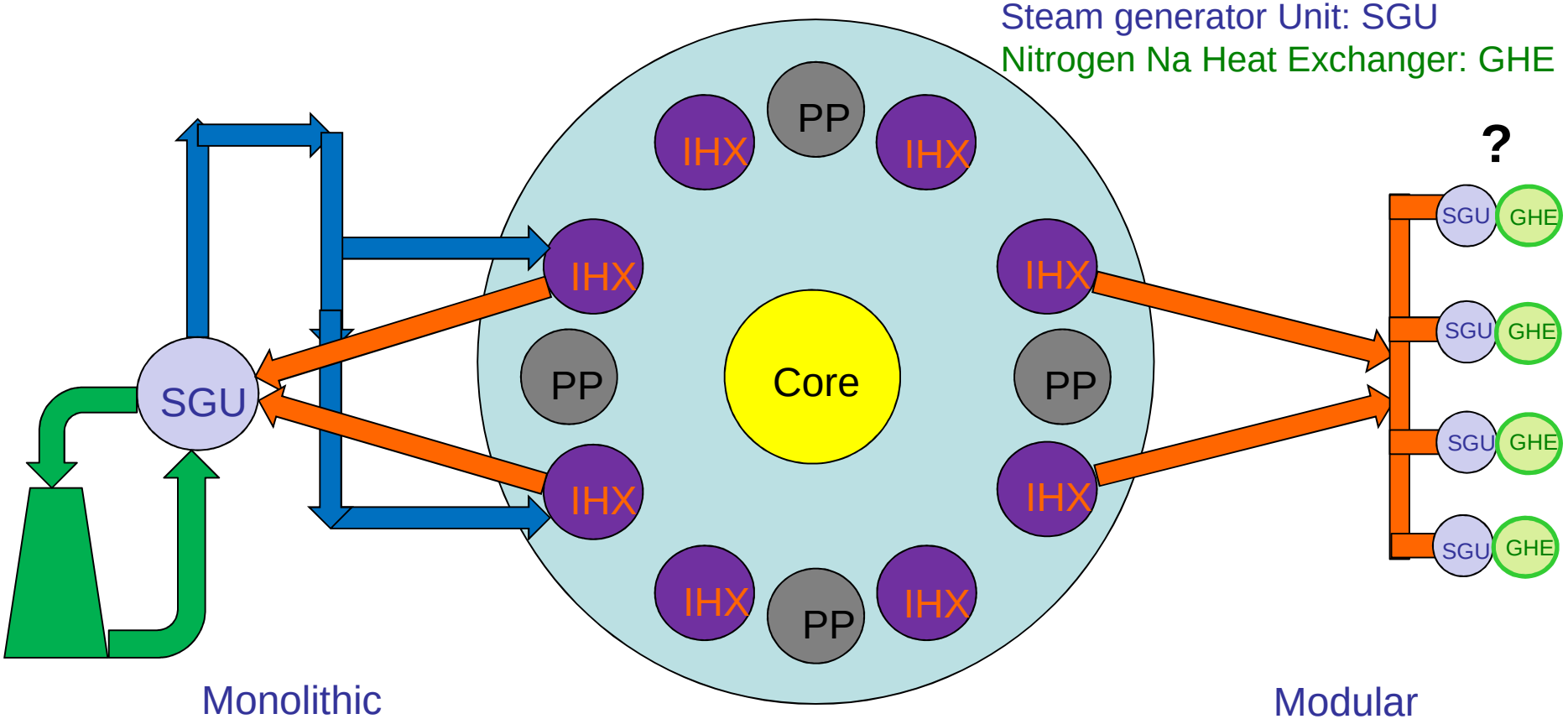
PRIMARY CIRCUIT OF SFR (POOL CONCEPT) 2/2

Primary pump: PP

Intermediate Heat Exchanger: IHX

Steam generator Unit: SGU

Nitrogen Na Heat Exchanger: GHE



Monolithic
Steam generator

Modular
Steam generator
Or
Gas Heat Exchanger

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SOME COOLANTS FOR NUCLEAR SYSTEMS

Fission:

➔ **Sodium** for fast neutron reactors (FNR) cooled by sodium (SFR)

➔ **Lead** for fast neutron reactors (FNR) cooled by lead (LFR) or subcritical reactors (ADS: Accelerated Driven Systems)

➔ **Lead-bismuth eutectic** for ADS spallation targets and Russian submarine FNRs

➔ **Gas:** He for Very High Temperature thermal Reactors (VHTR), for gas-cooled fast neutron reactors (GCR), He-N_2 or SC-CO_2 in innovative energy conversion systems (ECS) for SFRs

➔ **Mercury** for spallation targets

➔ **Molten salt** for molten salt reactors (MSR)

➔ **Water-steam** as the primary coolant in pressurised water reactors (PWR), supercritical water in supercritical water-cooled fast reactors (SCWR), etc. and water-steam in the steam 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)

Note:

- *In spallation targets, the lead-bismuth eutectic also serves to produce neutrons*
- *In fusion, lithium acts mainly as a generator of tritium and neutrons*

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FIRST FAST NEUTRON REACTORS

Year	Reactor	Country	Power	Coolant
1946	Clementine	USA	25 kW	Mercury
1951	EBR-1	USA	1,4 MW	NaK
1956	BR-2	USSR	100 kW	Mercury
1959	BR-5	USSR	5 MW	Na, NaK
1959	DFR	Great Britain	60 MW	NaK
1962	EBR-2	USA	62 MW	Na
1963	Enrico Fermi	USA	300 MW/60MWe	Na
1967	Rapsodie	France	20-40 MWe	Na
1969	BOR-60	USSR	60 MW	Na
1973	BR-10	USSR	8 MW	Na
1973	BN-350	USSR	1000 MW/250 MWe + Water	Na
1973	Phenix	France	250 MWe	Na
1974	PFR	Great Britain	250 MWe	Na

➔ **Very early, consensus on Na due to its** availability, cost, neutronic properties, Low operating temperature, heat removal capability, low corrosion. **IN OPERATION**

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FIRST FAST NEUTRON REACTORS

	Year	Reactor	Country	Power	Coolant
➡	1977	Joyo	Japan	140 MW	Na
	1978	KNK-II	Germany	20 MWe	Na
➡	1980	BN-600	USSR	600 MWe	Na
	1980	FFTF	USA	400 MW	Na
	1985	SNR-300	Germany	300 MWe	Na
➡	1985	FBTR	India	40 MW/13.2 MWe	Na
	1986	Superphenix	France	1200 MWe	Na
	1995	Monju	Japan	250 MWe	Na
➡	2010	CEFR	China	65 MW/20 MWe	Na
	2018?	**PFBR**	**India**	*500 MWe*	**Na**
➡	**2016**	**BN800**	**Russia**	**800 MWe**	**Na**

➡ **IN OPERATION**

COOLANTS FOR SUBMARINES

USS Seawolf (1957-1959)

- #2 after Nautilus, followed by PWR subs
- ***Sodium cooled Fast Reactor***
  - Conversion with super heated steam
  40% gain in NSSS compactness

USSR November-class Submarine K-27 (1963-1968)

- ***Two VT-1 PbBi cooled Fast Reactors***
  Prototype for Alpha-class submarines
  - Loss of reactor power accident &
  Releases of radioactive gases

USSR Alpha-class Submarines 7 Lira-class units (1969-1981)

- ***155 MW PbBi cooled Fast Reactor***
  > 74 km/h & > 800 diving depth
  + Compactness, long lifetime


USS Seawolf (1957-1959)


November-class K-27 (1963)


Alpha-class (1969-81)

COOLANT FOR THE FAST NEUTRON REACTOR SYSTEMS

➔ **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 coolant/gas heat exchanger + turbine to produce enectricity), or to a system which directly uses the heat: heavy oil extraction, thermochemical production of hydrogen, sea water desalination …**

- **Assure safety by providing the system with a degree of thermal inertia**

COOLANT FOR THE FAST NEUTRON REACTROR SYSTEMS

➔ **In a Fast Neutron Reactor, the coolant must not:**

- **Significantly slow neutrons, activate under flux, produce compounds which create unacceptable dosimetry**
- **Change the mechanical properties of structural materials**
- **Induce unacceptable safety conditions and insurmountable operating issues**
- **Lead to wastes which can't be processed during operation and dismantling**

COOLANT CHARACTERISTICS, CONSEQUENCES ON DESIGN&OPERATION 1/2

- **Melting temperature**, and impact on the reactor's cold shutdown temperature (for fuel element handling in primary vessel)

- **Boiling point** and **liquid phase temperature range** and impact on safety

- **Thermal stability : no difficulty with liquid metals or gas but a key parameter for molten salts** (decomposition close to high temperature + safety margin)

- **Thermal properties**: Cp, λ, Prandtl number,

- **Density** and therefore seismic resistance (sloshing…), pumping power required, internal dynamic pressures...

- **Interactions with structural materials:** Dissolution (solubility of metal elements) corrosion, embrittlement, etc. and potential mass transfer inducing radio-contamination (activated corrosion products)

- **Reactivity with surrounding fluids** (air, water, organic products, etc.) and impact on safety in operation

- **Opacity,** which can induce the necessity to develop dedicated in-service inspection (ISI) methods

COOLANT CHARACTERISTICS, CONSEQUENCES ON DESIGN&OPERATION 2/2

- **Vapor pressure law** and its impact on gas blanket composition, the presence of aerosols, and deposition on upper structures
- **Possibility of interaction with the neighbouring coolants**, with resulting impacts on corrosion, contamination, etc. (Energy conversion System, intermediate coolant, coolant of Decay Heat Removal Systems…)
- **Ability to be purified and meet again quality standards** after pollution ingress
- **Toxicity** and the need to confine the coolant during handling, repair, etc.
- **Ability to be processed during dismantling,** and ability of some specific components (i.e. purification systems for cold-trapping) to be dismantled,
- **Production of wastes which can't be processed** during operation or dismantling
- **Coolant availability:** A pre-requirement for developing the reactor system
- **Cost:** Must be analysed versus the overall facility's cost

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COOLANT FOR THE ENERGY CONVERSION LOOP:

Main requirements:

➔ **Ability to design and manufacture main electricity production components:**

➔ Heat exchangers and recovery systems, turbines, etc.

➔ **Absence of significant structural interaction (corrosion)**

➔ **In the absence of an intermediate loop, acceptability of ingress in primary system** (interactions, pressure increases, gas bubbles entering the core, etc.)

➔ This could be achieved through design provisions:

Double-walled steam generator (SG)

Degassing system (cyclone, etc.)

➔ **Ability to avoid any unacceptable tritium "release",** tritium produced in the primary system (tritium is the only radioactive contaminant able of diffusion through structural materials, and to meet release standards)

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METALS WITH MELTING POINTS < 330°C

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

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Metals with melting points < 330°C: more properties

ELEMENTS	Density (g/cm3) at 20° C	Thermal conductivity $W.m^{-1}.K^{-1}$ 300 K	Resistivity, μΩ cm	Viscosity, Pa.s	Cp $J.K^{-1}.g^{-1}$	Cp $J.K^{-1}.mol^{-1}$ Etat solide	Microscopic capture cross section, (barn) N Th
Bi	9,80 10,03 (300° C)	7,87	120	$1,662.10^{-3}$ à 304°C	0,122	25,52	0,034
Cd	8,64 8,009 (340° C)	96,8	7,6	$1,44.10^{-3}$ à 349°C	0,23	25,98	2450 $2,15.10^{-1}$ (NR)
Cs	1,87 1,691 (310° C)	35,9	37,39 (28,1° C) 20,0 (20°C)		0,24	32,17	28
Ga	5,91	40,6	17,4		0,37	25,86	2,8
Hg	13,546	8,34	94,1	$1,5410^{-3}$ à 20°C	0,14	27,98 26,80 à 200°C	389
In	7,31 6,93 (302° C)	81,6	8,37		0,23	26,74	191
K	0,86 0,744 (400° C)	39,8 (400°C ; 1 bar) 102,4	7,01 (22,8°C) 6,15 (273 K)		0,76	29,58 29,83 à 400°C	2,07 $2,28.10^{-2}$ (NR)
Li	0,534	84,7	12,17 (86,6° C) 8,55 (273 K)		3,57	24,77	71 Li6 0,2 keV $6,6.10^{-1}$ Li6 (NR)
Pb	11,34 10,51 (400°C)	35,3	20,648 (293 K)	$2,116.10^{-3}$ à 441°C	0,127	26,44	0,17 $4,66.10^{-3}$ (NR)
Rb	1,53	58,2	11,28 (0° C) 12,5 (20°C)		0,36	31,06	0,73
Se	4,82 3,91 (300°C)	2,04	0,01 (293 K)		0,32	25,36	12,3
Sn	7,30 6,834 (409°C)	66,6	11,5 (273 K)	$2,12.10^{-3}$ à 240°C	0,22	25,77	0,625
Tl	11,85	46,1	18,0 (0° C)		0,13	26,32	3,4
Na	0,971 0,857 (400°C)	141	4,2	$2,81.10^{-4}$	1,23	28,24	0,53 $2,80.10^{-3}$ (NR)

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SODIUM

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

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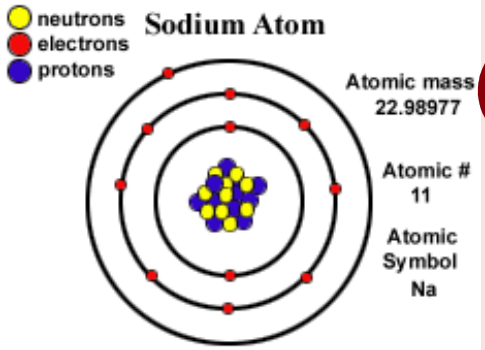
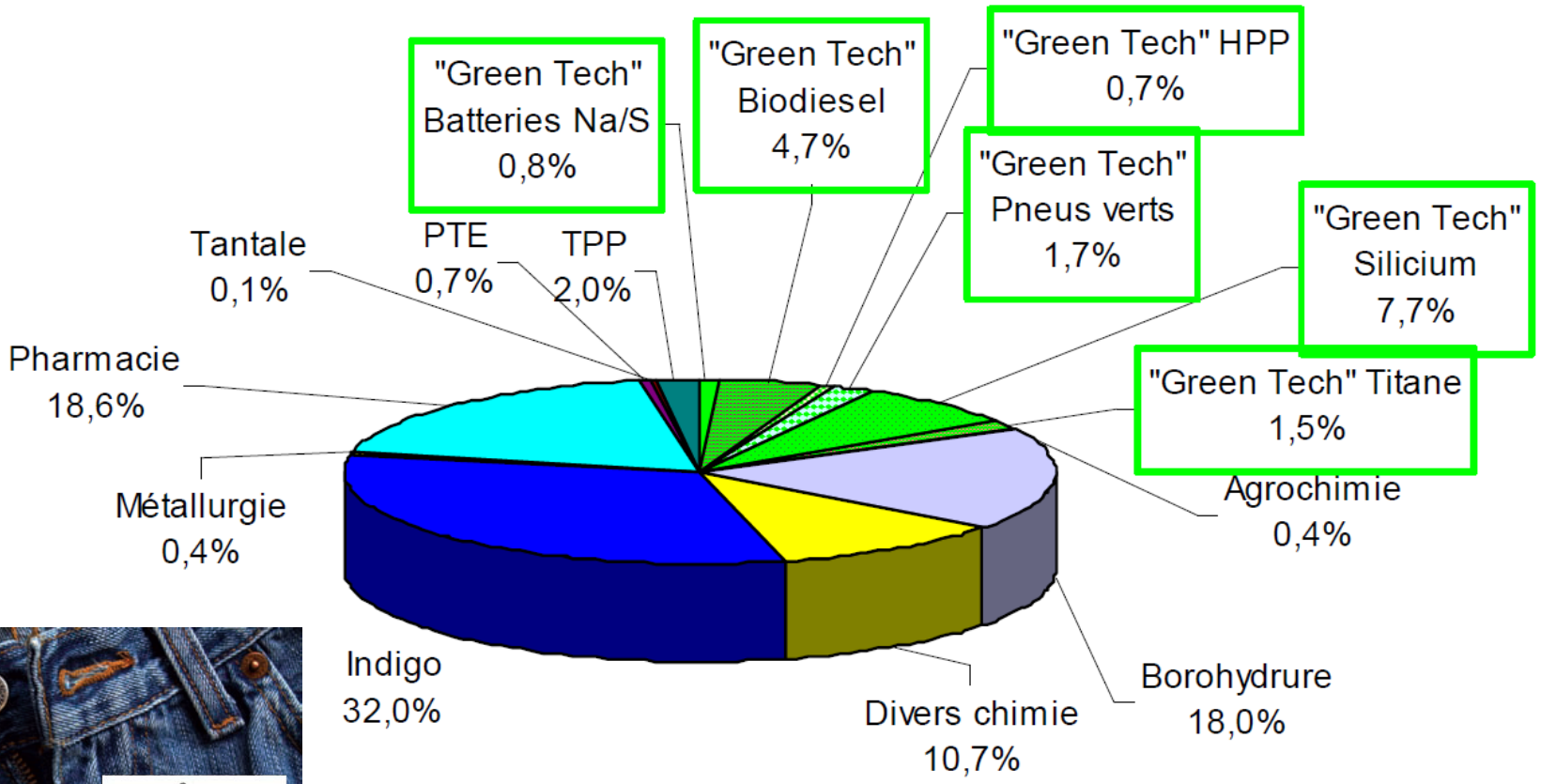
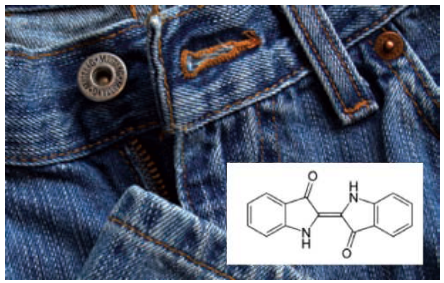


	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 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 USES (COURTESY OF MSSA)





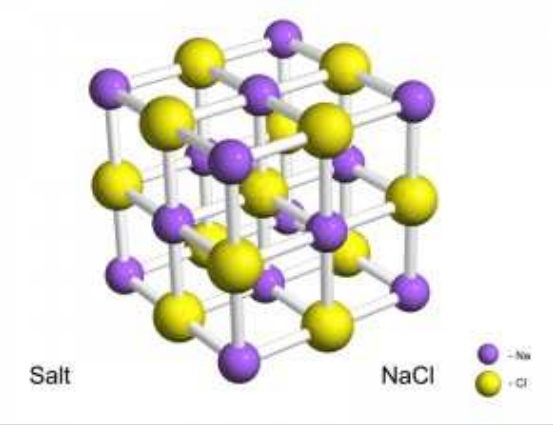
Green Tech =17,2%

Some explanations:

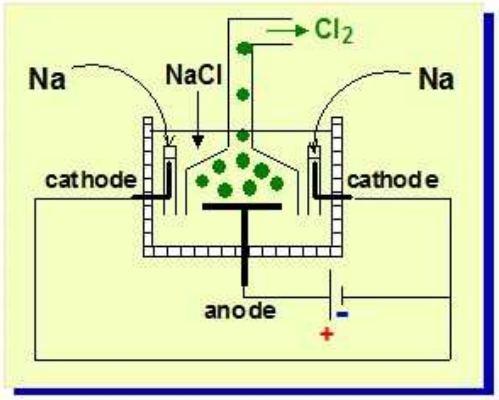
-TPP triphenyl phosphine used for the synthesis of vitamin A

-HPP High Performance Pigment

SODIUM MANUFACTURING



Varangéville France



Electrolysis battery in Métaux Spéciaux (France)

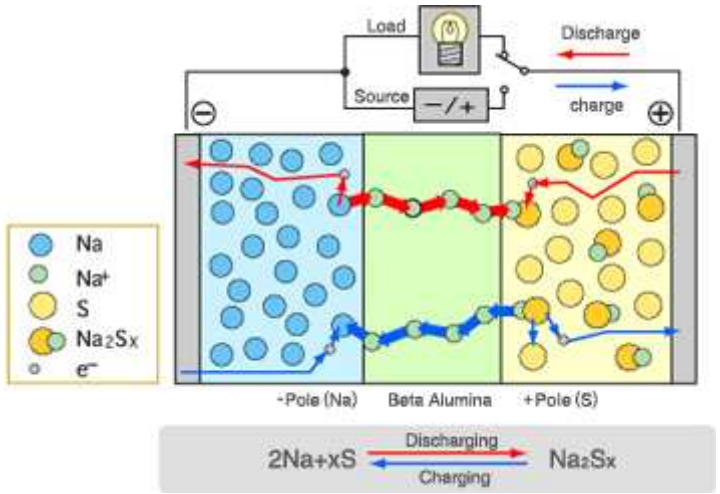
➔ Produced by electrolysis of eutectic NaCL/$CaCl_2$

➔ **Annual production:** about 200 000 tons/year from halite (NaCl), trona [$Na_3(CO_3)(HCO_3)2H_2O$],

NA-S BATTERY

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

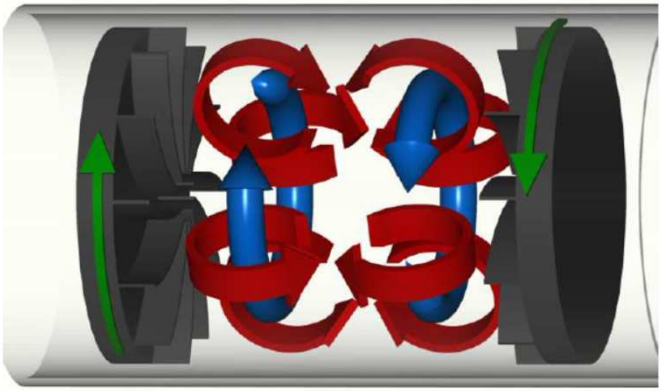
➔ Na separated by a beta-alumina solid electrolyte (BASE) cylinder (good conductor of Na ions) from the cathode (container containing molten sulfur adsorbed on a carbon sponge). When Na gives off an electron, Na^+ ion migrates to the sulfur container. The electron drives an electric current through the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

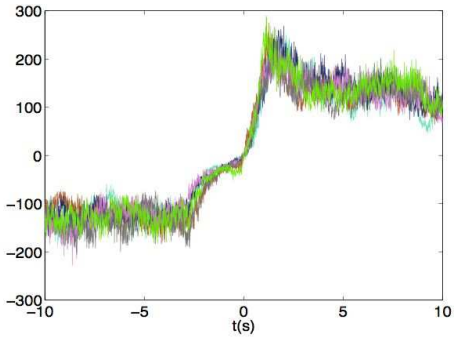


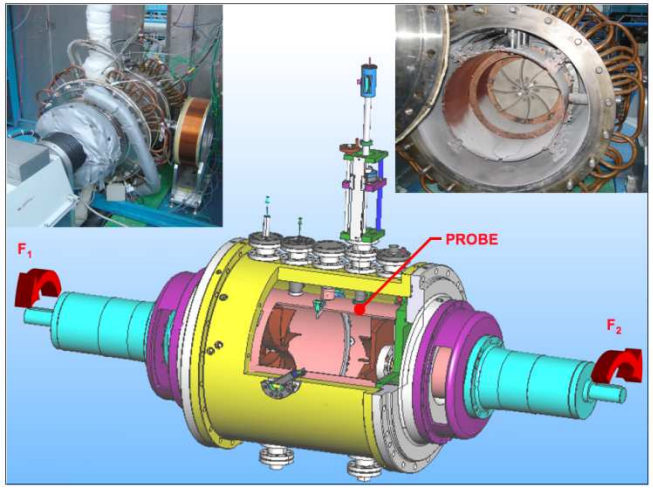
Exemple: 34 MW NAS alongside 51 MW Wind Farm Courtesy of NGK Insulators – Japan)

Dynamo experiments with Na

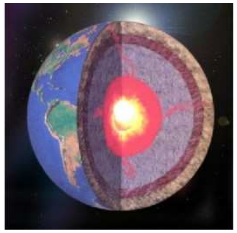
$R_m = 2\ \pi\ K\mu_0\sigma\ R^2 f$

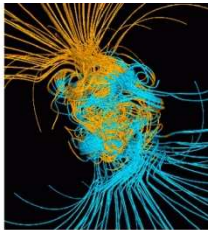


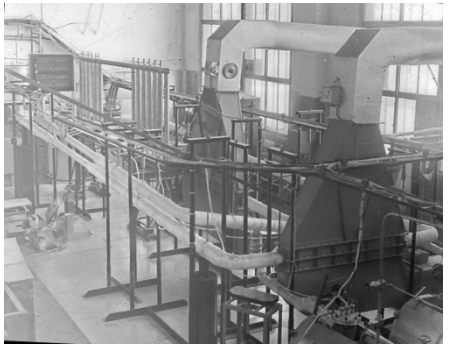




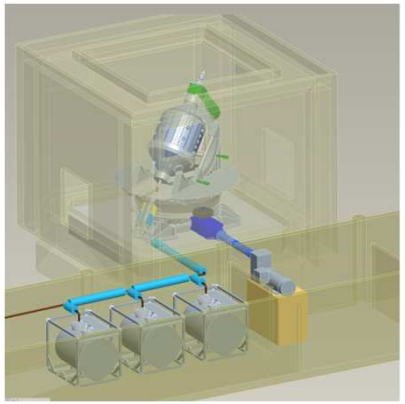
VKS in Cadarache







Na dynamo in IPUL (1991)



DRESDYN in HZDR

MAIN SODIUM CHARACTERISTICS

➔ **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 (2.5 €/Kg)**

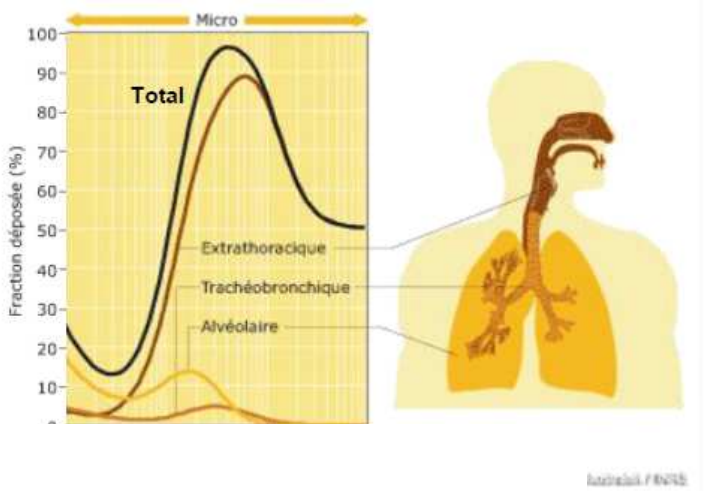
Earth's crust:	**23 000 ppm**
Sea water:	**10 500 ppm**

Main ressources:

Halite ("NaCl"Mines)

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

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



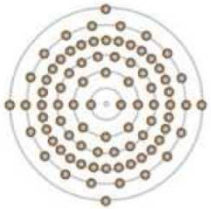
Dépôt total et régional chez l'homme, en fonction du diamètre des particules inhalées (d'après INRS, 2009).

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

LEAD

- ➔ **high economic value,**
- ➔ **relatively low cost, (2€/Kg in 2018)**
- ➔ **two main production routes:**
- **primary production from mined lead ore**
- **secondary production, where it is recovered**

from recycled products or from residues arising from the production process is of enormous importance (due to its high toxicity) (In the US >80% , Europe > 60%).

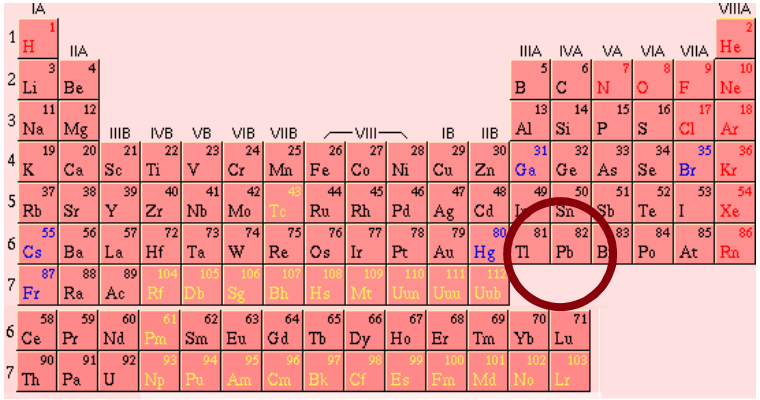


Lead Properties

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/cm^3
Colour: bluish

Courtesy of ILA

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

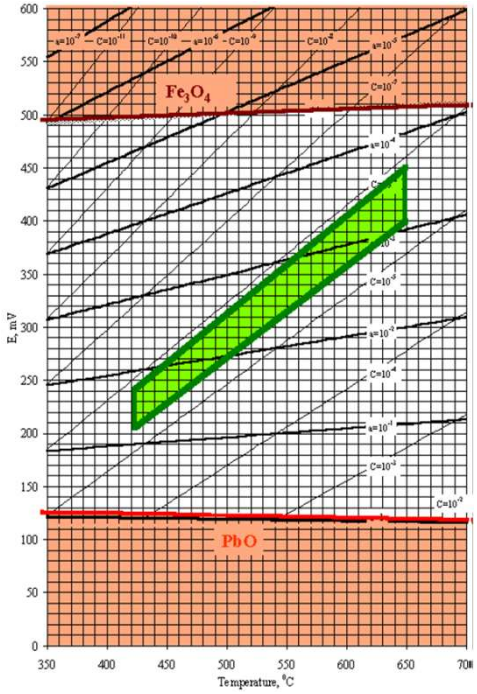


COOLANT: Lead / sodium

Main advantages for lead:

- only physical interaction between Pb and H_2O (possibility to foresee elimination of intermediate loops)
- no significant chemical reactivity with air (ie fire), but oxidability and necessity to foresee a treatment to eliminate PbO
- High Boiling Point of lead (1749℃ at 1 bar): risk of core voiding due to boiling reduced…

at 500℃		
	sodium	lead
Melting point (℃)	98	327
Boiling point (℃)	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 24Na 15h	207Pb 52h



Main drawbacks:

- Corrosion (efficient O control or necessity to foresee reliable coating)
- Toxicity
- Seismic resistance
- High melting point (SG: materials)
- Density (pumping power, impact on FA)
- Dismantling (chemical conversion not possible)
- no operational feedback (except LBE)….

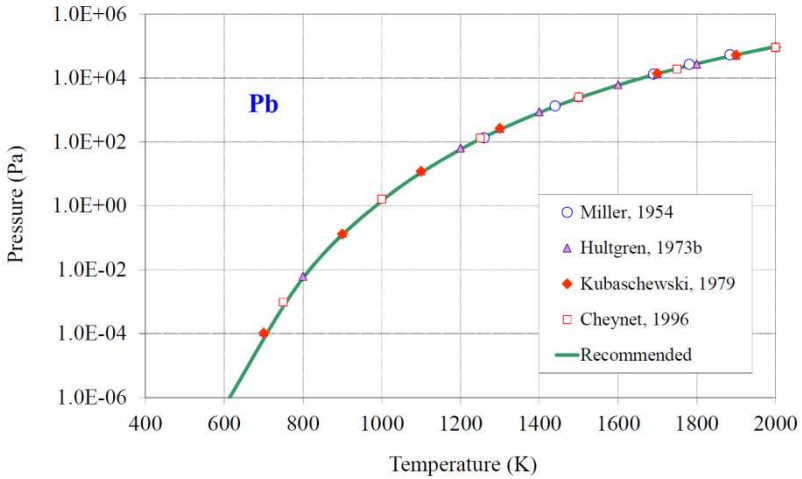
LEAD: MAIN ADVANTAGES IN MORE DETAILS

- Absence of chemical reaction (like with Na) with H_2O & but physical interaction: design without intermediate loops (and intermediate IHX) possible, nevertheless double-wall Steam-Generators Units (SGU) required.

- The absence of coolant fire and the very low saturated vapour pressure prevents the release of very toxic Pb vapours

- Good capability of lead to circulate under natural convection (Grashoff number)

Saturated vapour pressure of liquid lead versus temperature



LEAD: MAIN DRAWBACKS IN MORE DETAILS

- **High density:**
  - Fuel elements must be fixed to compensate buoyancy
  - Specific provisions with regards earthquakes; potential impact on structural integrity (Compact design better)
  - Loop type reactor not selected due to the difficulty to design piping supports.

- **High melting temperature:**
  - refueling must be performed at about 380°C (Melting poi nt: 325°C)
  - difficulty to maintain the passive oxide layer on the sliding parts of the Fuel Assembly.(Hard coating?)

- **Lead-material compatibility:** necessity to limit the lead velocity (<2m/s) to reduce erosion of the structural material

- **Poor wetting capability:** in addition to high shut-down temperature, impact on In Service Inspection technologies (US devices) («acoustic coupling » between coolant and structures)

- **Absence of chemical reaction:** difficulty to develop efficient clean-up process (FA, components), before inspection and repair or decommissioning.

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BINARY ALLOYS WITH MELTING POINTS < 330℃

	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

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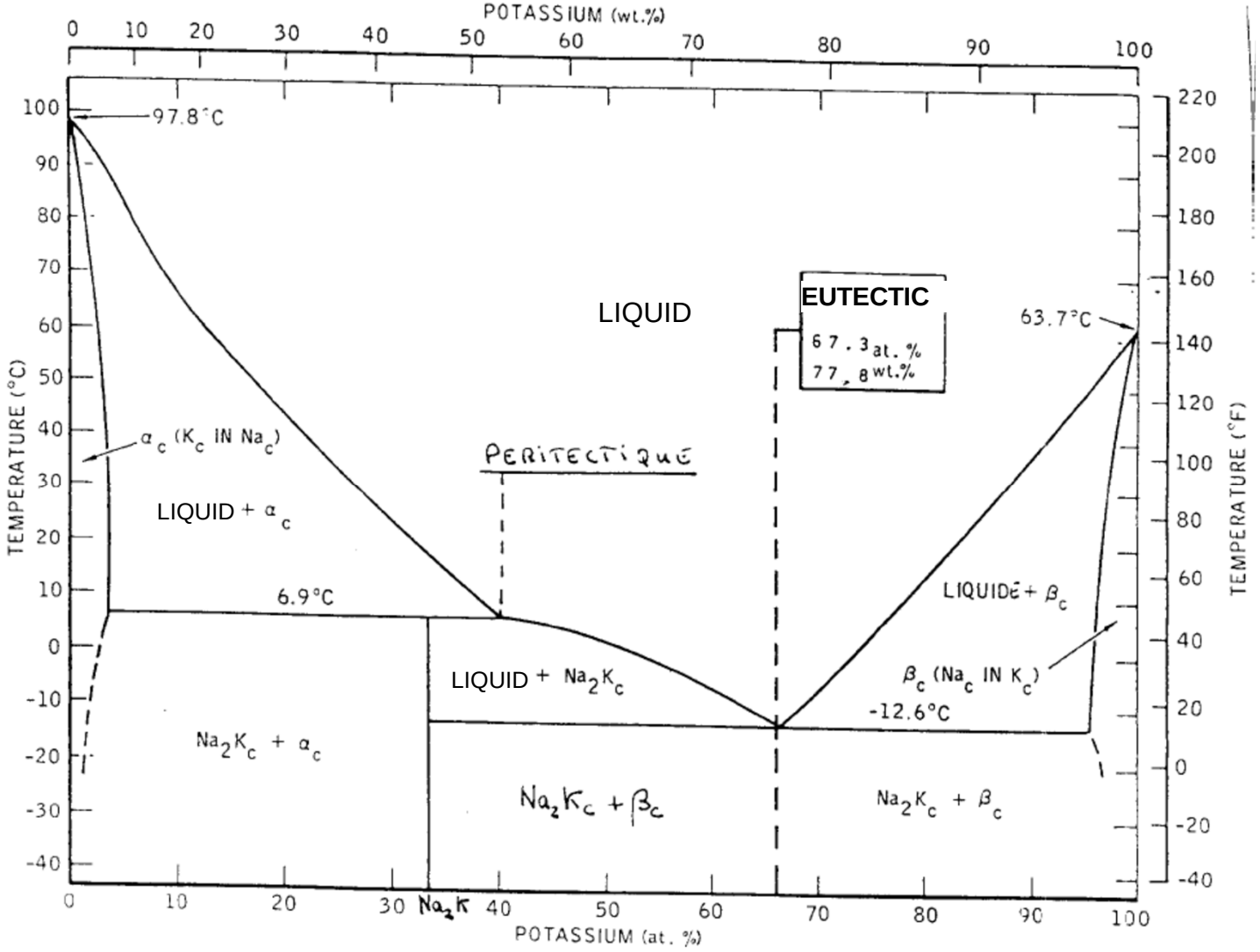
SODIUM-POTASSIUM PHASE DIAGRAM



SODIUM-POTASSIUM ALLOY PROPERTIES

	Melting point, ° C	Boiling point, ° C	Density, g/cm³	Thermal conductivity, W/cm.° C
Sodium	97,8	881	0,968 à 20 °C 0,856 à 400 °C	0,860 à 100 °C 0,722 à 400 °C
Potassium	63,7	756	0,855 à 20 °C 0,750 à 400 °C	0,522 à 100 °C 0,408 à 400 °C
NaK-77,8	- 12,6	785	0,870 à 20 °C 0,785 à 400 °C	0,232 à 100 °C 0,262 à 400 °C
NaK-56	6,9	812	0,898 à 25 °C 0,892 à 50 °C	0,216 à 50 °C
Water	0	100	~ 1	0,007 à 100 °C

77.8 mass% K ←→ 67.3 at.% K
52 mass% K ←→ 40 at.% K

SODIUM-POTASSIUM ALLOY

NaK has been used for certain Fast Neutron Reactors (DFR (UK), EBR1(USA)
➔ because it is liquid at ambient temperature (no preheating necessary to melt the metal).
➔ Nota: this alloy was considered for Rapsodie but not selected

➔ It is also used in the following applications:
- coolant in cold traps
- ultrasound waves transport fluid in Visus device
- irradiation systems
- inert gas (argon) purification system (sparger)

But it reacts with oxygen as a reducing agent and forms:

- Na_2O	sodium oxide	white
- K_2O	potassium oxide	white -> yellow at 250° C
- Na_2O_2	sodium peroxide	yellow
- K_2O_2	potassium peroxide	yellow
- KO_2	potassium superoxide	yellow

(or K_2O_4, potassium tetroxide)

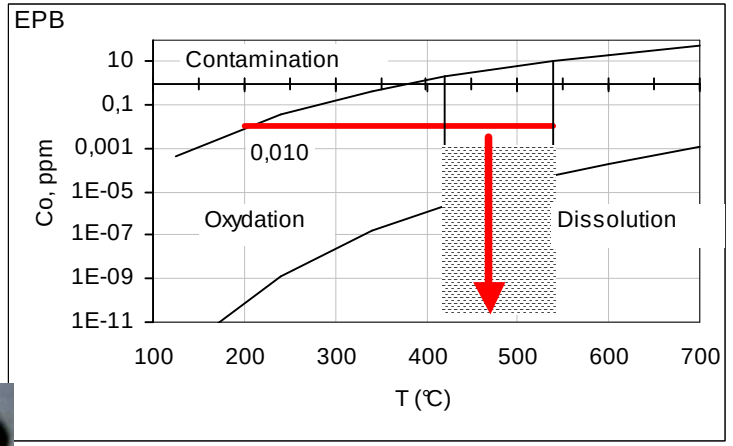
K_2O_2: Violent reaction or even explosion with liquid water
KO_2: Explosive reaction with alkaline substances
➔ For handling potentially oxidised NaK, the greatest care must be taken in establishing the procedures

LEAD-BISMUTH PROPERTIES (55.5% BI):

- **Low melting point (125℃)**

- **No chemical reaction with water (but water may violently vaporise depending on conditions)**

Lead oxidised with possible precipitation of PbO



Significant corrosion➔ protective coating required: Aluminium coatings, or oxygen content controlled to maintain a protective oxide film at the surface (introduction of steam+H2 or oxygen by an equilibrium method using PbO pellets)

Possible interaction with Na (if foreseen as intermediate coolant for SFR): Exothermal formation of $BiNa_3$ (137 kJ/mol LBE)

Very large operating feedback available on this coolant in ADS, especially with spallation targets (TECLA, MEGAPIE, EUROTRANS, VELLA programmes)

AVAILABILITY OF BISMUTH

➔ **Bismuth is currently a by-product of the lead industry, which looks for ores poor in bismuth.**

More than 60% of lead comes from recycled batteries, thus the bismuth level is already low. The lead market is relatively stable, so Bi production from lead will remain limited (unless Bi demand causes Pb producers to take an interest in other mines).

The bismuth market is relatively small (cosmetics, pharmaceuticals, metallurgy, etc.).

There are mines rich in bismuth but very few are exploited. However, increased production of Bi has been reported, as it's also a by-product of tin, tungsten and fluorine mines (cf. Chinese production).

Example in Canada: Fortune Minerals Ltd. mine (NICO): Estimated deposits: 34,500 tonnes

➔ Situation differs from that of sodium (easily accessible and widely used in industry) or lead

➔ Cost: 25 to 30 €/Kg (depends on the purity, volume….)

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AVAILABILITY OF BISMUTH: PRODUCTION AND REFINING (USBM)

World Mine Production and Reserves:

	Mine production		Reserves[2]
	2013	2014[e]	
United States	—	—	—
Bolivia	10	10	10,000
Canada	35	35	5,000
China	7,500	7,600	240,000
Mexico	824	824	10,000
Russia	40	40	NA
Other countries	—	—	50,000
World total (rounded)	8,400	8,500	320,000

World Resources: Bismuth, at an estimated 8 parts per billion by weight, ranks 69th in elemental abundance in the Earth's crust and is about twice as abundant as gold. World reserves of bismuth are usually based on bismuth content of lead resources because bismuth production is most often a byproduct of processing lead ores; in China, bismuth production is a byproduct of tungsten and other metal ore processing. Bismuth minerals rarely occur in sufficient quantities to be mined as principal products; the Tasna Mine in Bolivia and a mine in China are the only mines that produced bismuth from bismuth ore.

Bismuth is an environmentally friendly substitute for lead in plumbing and many other applications, including fishing weights, hunting ammunition, lubricating greases, and soldering alloys.

U.S. Geological Survey, Mineral Commodity Summaries, January 2015

AVAILABILITY OF LEAD: PRODUCTION AND REFINING (USBM)

World Mine Production and Reserves: Reserves estimates for Australia, Canada, and Peru were revised based on information from Government and industry sources.

	Mine production		Reserves[6]
	2013	2014[e]	
United States	340	355	5,000
Australia	711	720	35,000
Bolivia	82	75	1,600
Canada	20	4	247
China	2,900	2,950	14,000
India	106	110	2,600
Ireland	51	40	600
Mexico	210	220	5,600
Peru	266	270	7,000
Poland	90	40	1,700
Russia	195	195	9,200
South Africa	53	27	300
Sweden	62	62	1,100
Turkey	78	65	NA
Other countries	324	324	3,000
World total (rounded)	5,490	5,460	87,000

World Resources: Identified world lead resources total more than 2 billion tons. In recent years, significant lead resources have been demonstrated in association with zinc and (or) silver or copper deposits in Australia, China, Ireland, Mexico, Peru, Portugal, Russia, and the United States (Alaska).

U.S. Geological Survey, Mineral Commodity Summaries, January 2015

Main motivations of He for GFR

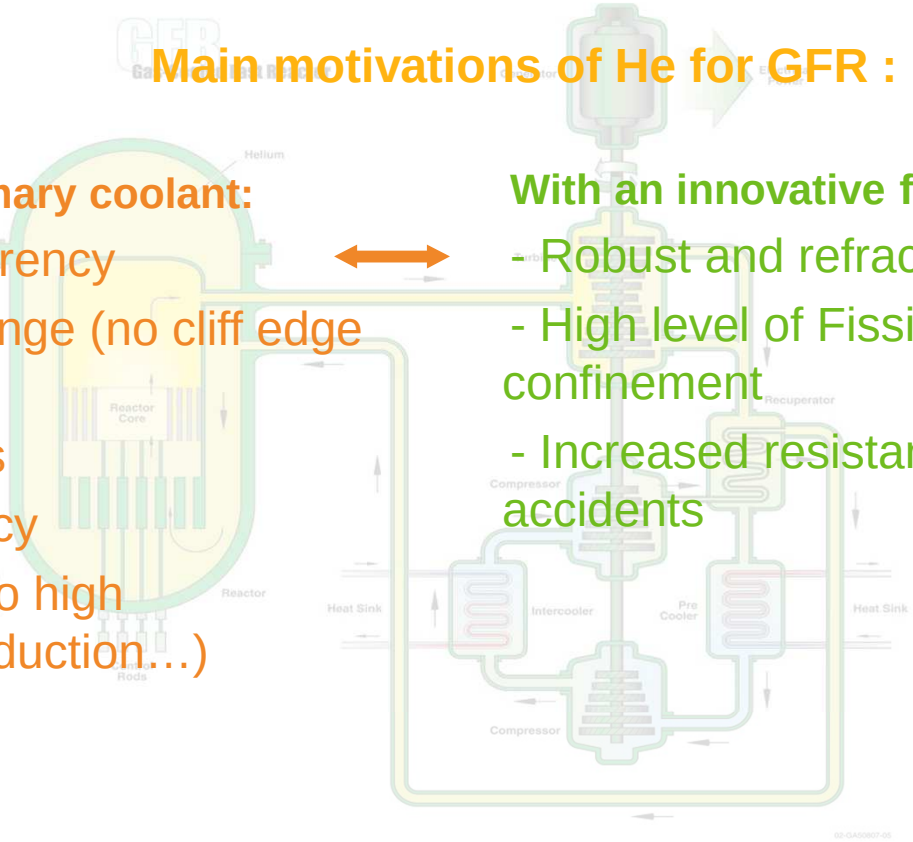
Main motivations of He for GFR :

The use of He as primary coolant:

- Neutronics transparency
- Without phase change (no cliff edge effects)
- Chemical inertness
- Optical transparency
- Opening the gate to high temperatures (H production…)

With an innovative fuel

- Robust and refractory
- High level of Fission Products confinement
- Increased resistance to severe accidents



Possible use of high temperatures
with
Sustainable resources management

SPECIFIC MOTIVATIONS FOR HE

	Water	CO2	He	Ar	Na
	150 bar, 300℃	60 bar, 500℃	60 bar, 500℃	60 bar, 500℃	1 bar, 500℃
ρ kg/m3	725,53	40,86	3,7	37,29	857
Cp J/kg/K	5476	1182	5190	525	1262
λ w/m/K	0,56	0,06	0,303	0,037	66,3
μ 10^{-5} Pa.s	8,83	3,33	3,73	4,54	24.3

Confirmation of He as a good gas coolant, the main drawback being its low capability regarding natural convection

MOLTEN SALTS FOR PRIMARY CIRCUITS

– **Nitrates**

• Already used as coolants for solar applications, nitrates unstables above 550℃

– **Chlorides**

• production of ^{36}Cl under neutronic flux (^{36}Cl (301 000 ans) is a radioactive waste very chemicaly reactive and thus quite difficult to manage

• Reactivity with water (production of HCl)

–**Fluorides**

• HF production in presence of water, low solubility in water

➔ **Only fluorides taken into consideration : several uses in Nuclear Reactors:**

- As primary coolant in Reactor with solid fuel

- As coolant producing tritium in fusion reactors

- As liquid fuel and coolant in MSR it has to contain fuel and fission products

➔ **Main properties of molten salts (fluorides):** good Cp, thermal conductivity rather low, dynamic viscosity close to water, high melting temperature (400-600℃), necessity to control Red-Ox potential to limit corrosion,....

Key points for FRs: stability as coolant under irradiation and at high temperature, low saturation pressure, fuel solubility, fission products management,...

➔ MSFR (reference): 77,5%7LiF- 20%ThF4,-2,5%233UF4 (Operating temperature : 625 - 775 ℃)

SPECIFIC CASE: COOLANTS FOR SFR INTERMEDIATE LOOPS

➔ Possible detrimental effects due to Na reactivity with air and water when the heat conversion is performed with a conventional Rankine cycle.

➔ In order to reduce the constraints due to potential sodium-water interactions on design, investment (safety instrumentation,…), reactor availability, dedicated operational procedures, several alternative options were investigated:

1 To develop an alternative Energy conversion system (Brayton cycle) (using gas i.e. pure N_2, SC-CO_2 ,…), or

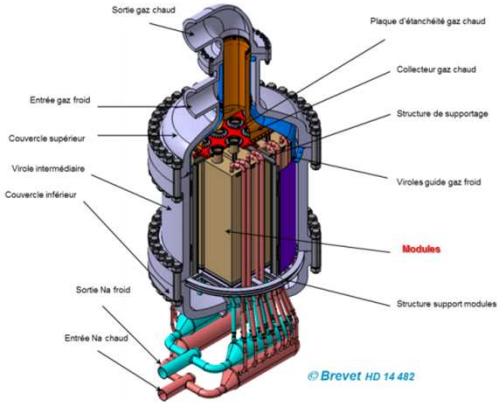
2 To keep the Rankine option (water steam) associated with:

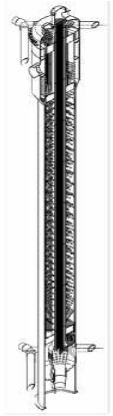
- Implementation of intermediate loops fitted with improved safety monitoring system for Na-H_2O interaction, and improved associated procedures (pressure decrease, H_2O draining,

- Implement of modular SGU or improved "monolithic" SGU (ie with helical tubes)

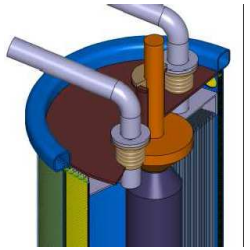
- Implementation of double-wall Steam Generator Units,

3 To design an intermediate loop, with an alternative coolant (next slides), avoiding potential detrimental effects due to coolant-water interaction.





Helical tubes

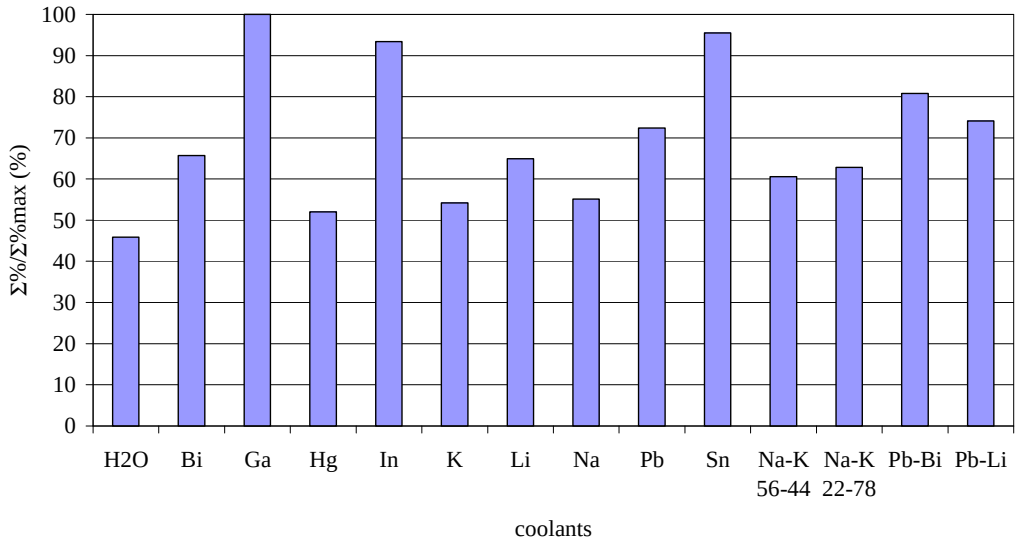


IHX-SGU integrated intermediate loop

MELTING AND EVAPORATION TEMPERATURES; LIQUID PHASE TEMPERATURE RANGE

$$A = \frac{\left(1/T_f\right)}{\left(1/T_f\right)_{\max}} + \frac{\left(T_v\right)}{\left(T_v\right)_{\max}} + \frac{\left(T_v - T_f\right)}{\left(T_v - T_f\right)_{\max}}$$

Temperature operating range



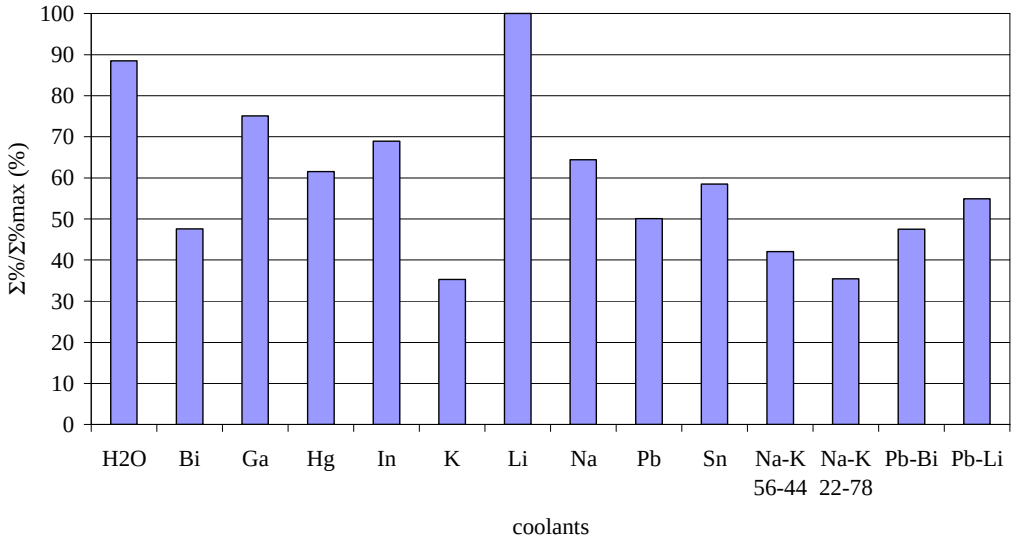
Ref: THERMAL CRITERIA TO COMPARE FAST REACTOR COOLANTS FOR THE INTERMEDIATE LOOP
M. SAEZ (CEA) Global 2007 Boise USA

HEAT TRANSPORT AND TRANSFER

$$B = \frac{\left\langle \frac{(Cp)}{(Cp)_{max}} + \frac{(\rho Cp)}{(\rho Cp)_{max}} + \frac{\left(\rho^{9/4} Cp \mu^{-1/4}\right)}{\left(\rho^{9/4} Cp \mu^{-1/4}\right)_{max}} \right\rangle}{\left\langle \frac{(Cp)}{(Cp)_{max}} + \frac{(\rho Cp)}{(\rho Cp)_{max}} + \frac{\left(\rho^{9/4} Cp \mu^{-1/4}\right)}{\left(\rho^{9/4} Cp \mu^{-1/4}\right)_{max}} \right\rangle_{max}}$$

$$+ \frac{\left\langle \frac{\left(Cp\beta^{-1}\right)}{\left(Cp\beta^{-1}\right)_{max}} + \frac{\left(\rho^{9/8} Cp \beta^{1/2} \mu^{-1/8}\right)}{\left(\rho^{9/8} Cp \beta^{1/2} \mu^{-1/8}\right)_{max}} \right\rangle}{\left\langle \frac{\left(Cp\beta^{-1}\right)}{\left(Cp\beta^{-1}\right)_{max}} + \frac{\left(\rho^{9/8} Cp \beta^{1/2} \mu^{-1/8}\right)}{\left(\rho^{9/8} Cp \beta^{1/2} \mu^{-1/8}\right)_{max}} \right\rangle_{max}}$$

Heat transport and heat transfer



$$C = \frac{\left\langle \frac{\left(\lambda^{0,2} (\rho Cp)^{0,8}\right)}{\left(\lambda^{0,2} (\rho Cp)^{0,8}\right)_{max}} \right\rangle}{\left\langle \frac{\left(\lambda^{0,2} (\rho Cp)^{0,8}\right)}{\left(\lambda^{0,2} (\rho Cp)^{0,8}\right)_{max}} \right\rangle_{max}} + \frac{\left\langle \frac{\left(\lambda^{0,5} \beta^{0,25} (\rho Cp)^{0,5}\right)}{\left(\lambda^{0,5} \beta^{0,25} (\rho Cp)^{0,5}\right)_{max}} \right\rangle}{\left\langle \frac{\left(\lambda^{0,5} \beta^{0,25} (\rho Cp)^{0,5}\right)}{\left(\lambda^{0,5} \beta^{0,25} (\rho Cp)^{0,5}\right)_{max}} \right\rangle_{max}}$$

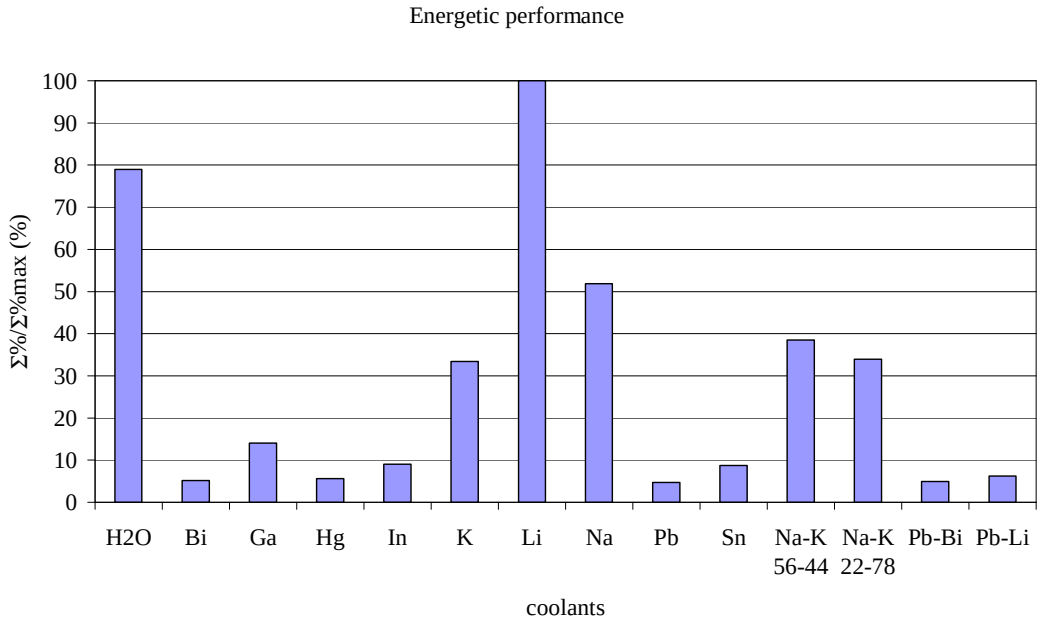
$$\boxed{D = \left(B/B_{max}\right) + \left(C/C_{max}\right)}$$

Heat transport capacity ➔ impacts dimensioning of pipes and pumps.
Heat transfer capacity ➔ impacts exchanger size (exchange surface area).

Ref: THERMAL CRITERIA TO COMPARE FAST REACTOR COOLANTS FOR THE INTERMEDIATE LOOP
M. SAEZ (CEA) Global 2007 Boise USA

ENERGY PERFORMANCE (RELATED TO CYCLE EFFICIENCY)

$$F = \lambda^{0,2}\,\rho^{-0,2}\,Cp^{0,8}\,\nu^{-0,25}$$



Ref : THERMAL CRITERIA TO COMPARE FAST REACTOR COOLANTS FOR THE INTERMEDIATE LOOP
M. SAEZ (CEA) Global 2007 Boise USA

GALLIUM

Gallium has attractive properties, especially its broad liquid phase region. **("by-product of Al, Cu, Sn ore")**

Annual production: about 30t/year

➔ But it forms Ga_2O_3 in the presence of oxygen.

Cp and λ lower than for Na:

Cp_{Ga} (30° C): 381.3 $J.kg^{-1}.C^{-1}$ at 30° C

(CpNa (400° C): 1278° C)

λ_{Ga} (77° C): 28.7 $W.m^{-1}C^{-1}$

(λ Na (450° C): 68.8 $W.m^{-1}.K^{-1}$)

Density: 5907kg/m^3 at 293K

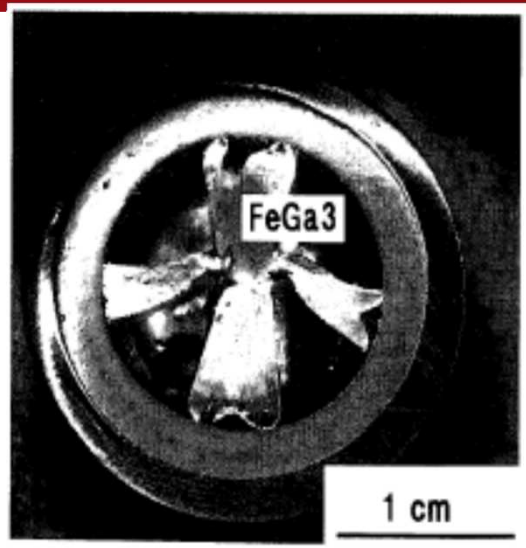


FIG. 2. Cross section of iron specimen exposed to gallium at 400 °C for 140 h. The sample located in the alumina crucible exhibits a cruciform pattern entirely made of $FeGa_3$.

Compatibility with martensitic steel and 316L steel: Studied in the presence of Ga:

➔ Very severe attack on the materials and embrittlement

Formation of $FeGa_3$, (400℃, 140 hours)*

Strong corrosion with:

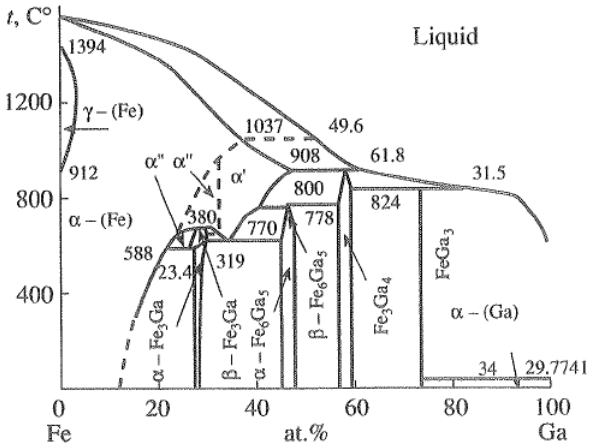
Fe: 1.9mm/d at 400℃!!!!

Cr ($CrGa_4$): 0.04mm/d at 400℃

Ni (Ni_2Ga_3 and $NiGa_4$): 0.21 mm/d at 400℃

➔ **Need for protective coatings**

(vanadium-based alloys suggested)



Corrosion of martensitic and austenitic steels in liquid gallium. F. Barbier and all J. Mater Res Vol 14 No. 3 March 1999

INTERACTION BETWEEN NA AND LBE (BISMUTH)

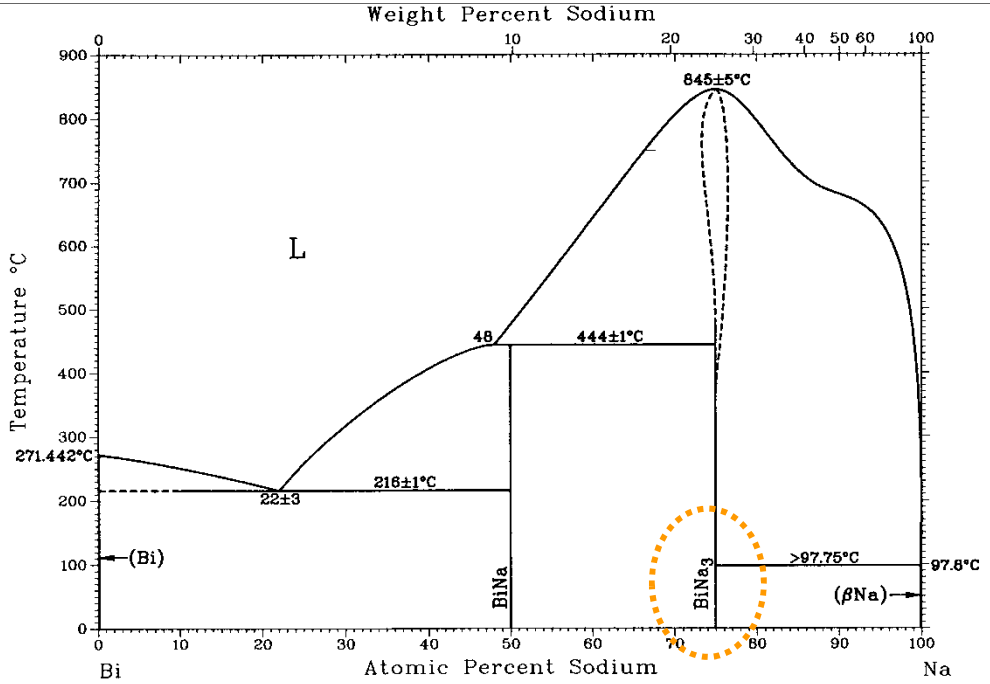
Reactivity between Bi and Na :

Production of $BiNa_3$, stability up to 845°C

Low solubility of Bi in Na up to 650°C.

JAEA, study (Icone 2003) : Pb-Bi in liquid Na.

Exothermal reaction 137 kJ/mol Pb-Bi.



MOLTEN SALTS INVESTIGATED AS POTENTIAL COOLANTS

There are number of molten salts.

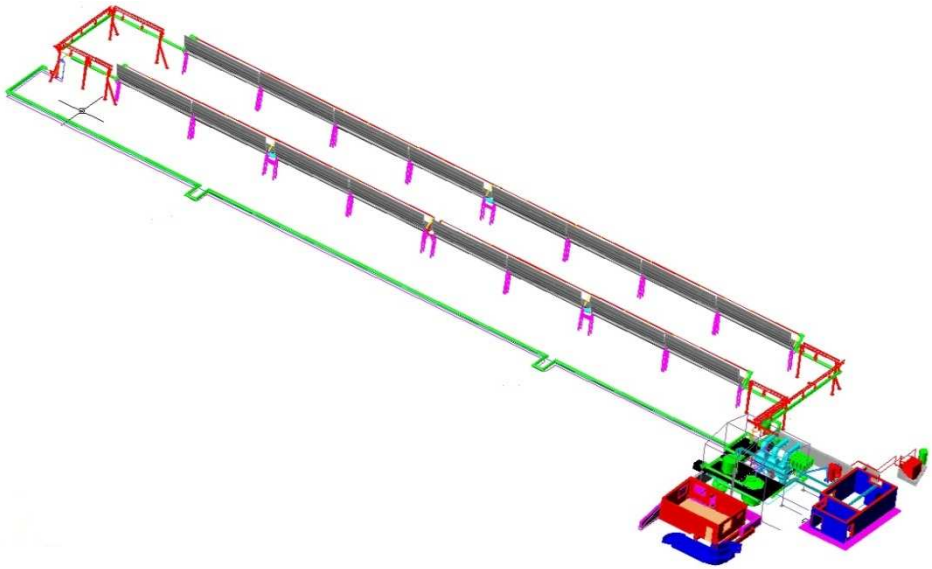
However, their melting points are often high.

Their thermal stability determines the maximum temperatures at which they can be used.

Some of their components generate corrosion (fluorine, chlorine, etc.).

The molten salts already used in solar applications deserve further analysis (stability range close to intermediate loop specifications).

Couretesy ENEA/La Casaccia



EVALUATION OF HYDROXYDES COMPOUNDS AS POTENTIAL COOLANTS

Binary NaOH-KOH seems attractive:

T_E=170°C, T_{eb} >> 1000°C (low partial pressure at 550°C)

High stability up-to800°C

But

➔ **Reactivity with Na :**

- **highly corrosive (particularly if hydroxide is hydrated: risk of stress corrosion cracking),**
- **H production and dissolution in Na and H_2 in equilibrium in gas plenums.**

Thermal properties :

High Cp, low λ

➔ **Generalized corrosion**

Only Ni bases SS can be used up to 550°C:
Necessity to investigate:
Coatings ?
Inhibitors?

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EXAMPLES OF MOLTEN SALTS FOR INTERMEDIATE LOOPS OF SFRS

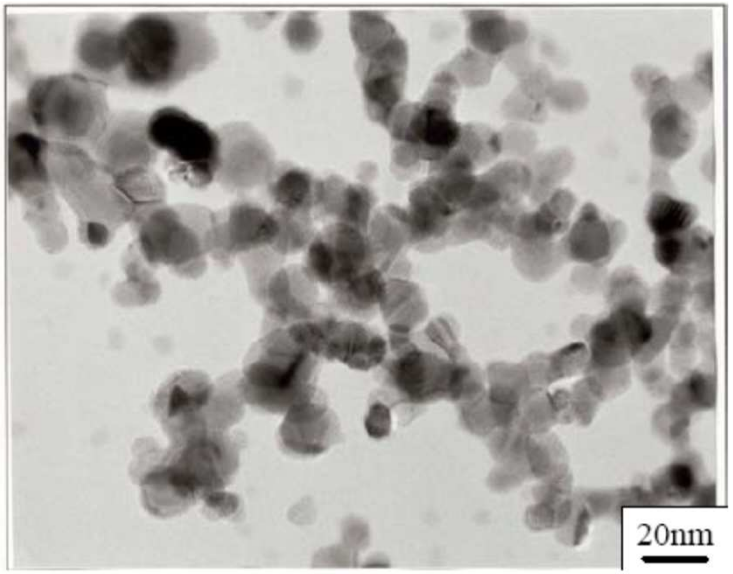
Salt	Composition	$T_{melting}$	T_{max}	Density at 300°C	Used in solar power stations
Hitec	7%$NaNO_3$ 40%$NaNO_2$ 53%KNO_3	**142°C**	**535°C**	**1.6**	**THEMIS (2.5MWe)**
Drawsalt	46%- 60%$NaNO_3$ 54%- 40%KNO_3	**220°C**	**600°C**	**1.9**	**SOLAR 2 (10MWe)**

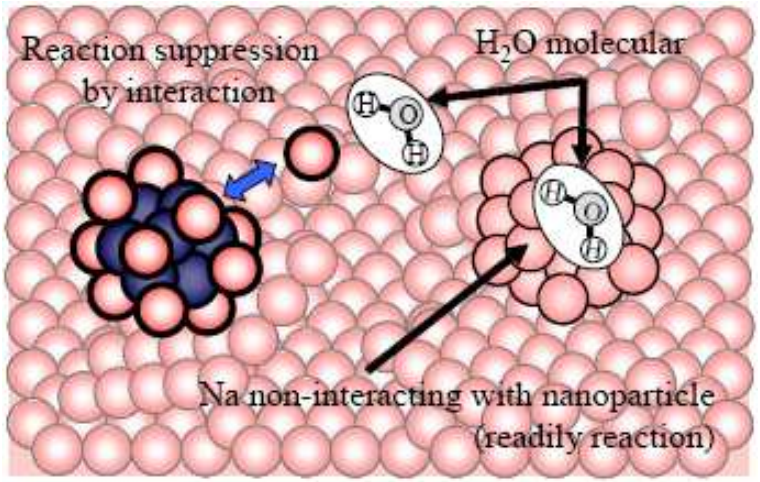
➔Corrosion (but can be controlled by adding oxides)

Note: Fluorides under consideration for AHTRs and MSRs

Courtesy ENEA/La Casaccia

NA WITH NI OR TI NANO-PARTICLES



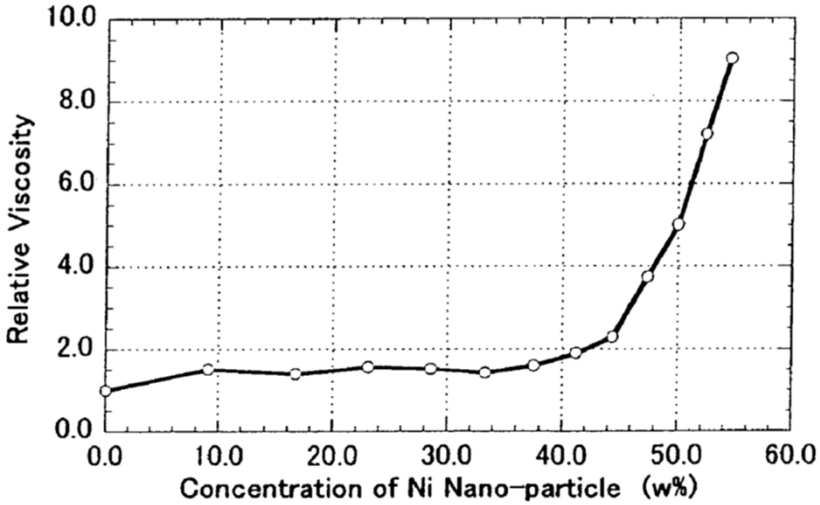


US 2006/0054869 A1

Necessity to study the following points:

- **Manufacturing methodology**
- **Stability**
- **Erosion, corrosion,**
- **Impact on Na-H2O interaction in realistic conditions,…**

Studies already carried out by JAEA and Hokkaido University (Japan)



GAS COOLANTS FOR ENERGY CONVERSION SYSTEMS

The main gas coolant possibilities are as follows:

- **Helium**
- **Helium-nitrogen or helium-argon**
- **Supercritical CO_2**
- **Nitrogen peroxide (dinitrogen tetroxide/nitrogen dioxide mix)**
- **Steam**
- **Supercritical water**

CO not considered because highly toxic and explosive.
H_2 not considered because forms explosive mixtures with air (cf. Shapiro diagram).

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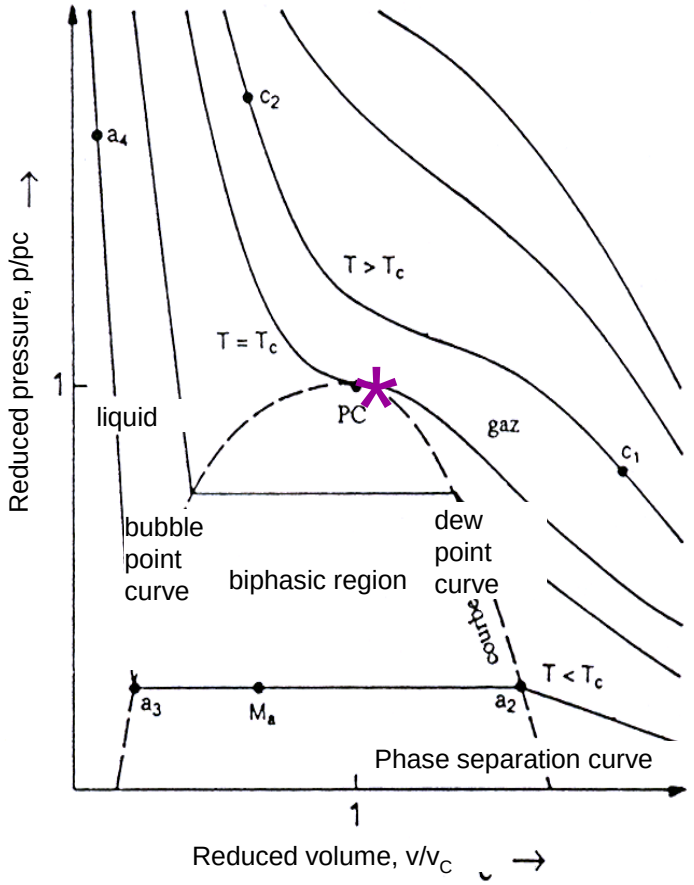
GAS COOLANTS: PROPERTIES

ELEMENTS	Molar mass, g/mol	Tf en K	Te enK (sous 1 bar)	Density (g/L) 273 K ; 1 bar	Thermal conductivity $W.m^{-1}.K^{-1}$	Cp $J.kg^{-1}.K^{-1}$	Viscosity, Pa.s (0,1 MPa 300 K)	Capture cross section (barn) (barn) Nth
Hélium	4,0025	3,6 K 0,95 K sous pression	4,215 K Tc =5,20 K	0,1785	0,152 à 300 K (1 bar)	$5,193.10^{3}$ (293 K, 1 bar)	$1,941.10^{-5}$	0,007
Dioxyde carbone (CO_2)	44,010	329,8 et 5,1 atm (Point triple)	194,7 sous Pression atmosphérique	1,962	$1,458.10^{-2}$ (273 K ; 1 bar) $3,058.10^{-2}$ à 473 K	$9,20.10^{2}$ à 100°C $1,157.10^{3}$ à 773 K	$1,48.10^{-5}$	
Nitrogen peroxide N_2O_4 NO_2	92,016	262	294,3	1,458 à 15°C 1,75 (sol)	$1,673\ 10^{-1}$ (323 K ; 1 bar)		$1,32.10^{-5}$	
Dry air	28,900		Tc = 132,55	1,205	$2,632\ 10^{-2}$ (300 K ; 1 bar)	$1,006.10^{3}$ à 300 K	$1,827.10^{-5}$	
Nitrogen	14,0067	63,29	77,4 Tc = 126,2	1,2506	0,02598 à 300 K	$1,485.10^{3}$ à 300 K	$1,74.10^{-5}$	1,88 $2,95.10^{-3}$ (NR)
Argon	39,948	83,78	87,29 Tc = 150,8	1,784	0,0177 à 300 K	$0,52.10^{3}$ à 300 K	$2,21.10^{-5}$	0,66
Oxygen	15,9994	54,8	88 Tc = 154,6	1,429	0,2674 à 300 K	$1,835.10^{3}$ à 300 K	$1,82.10^{-5}$	2.10^{4} $9,5.10^{-3}$ (NR)

Supercritical fluid: Critical isotherm: Horizontal tangent to the L/G equilibrium curve

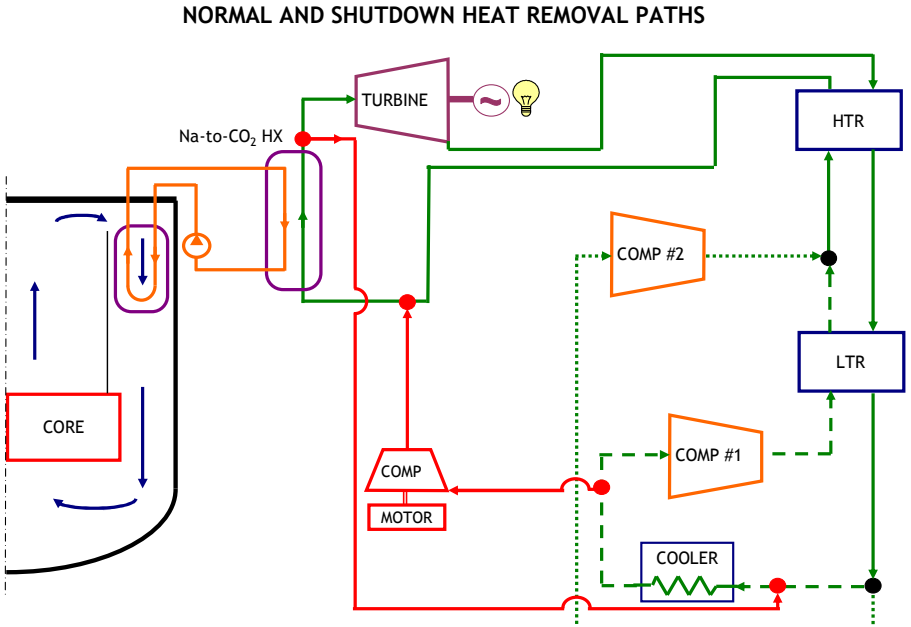


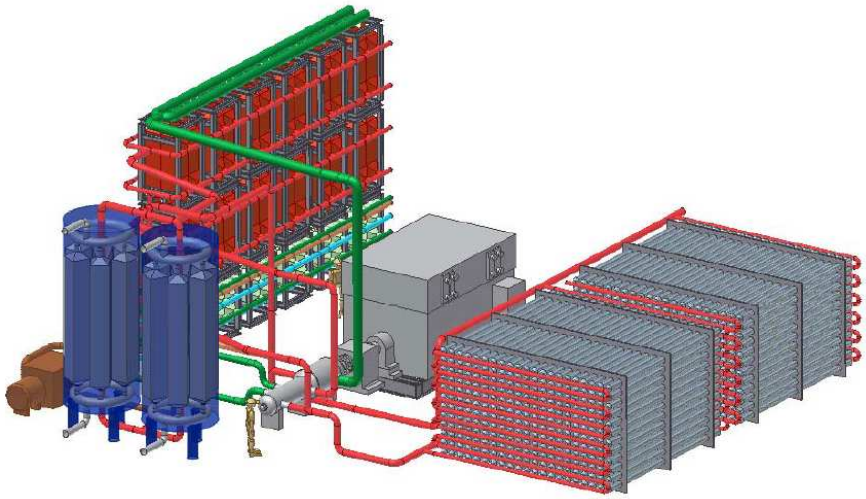
$$\left(\frac{\partial P}{\partial v}\right)_{T_C} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_C} = 0$$

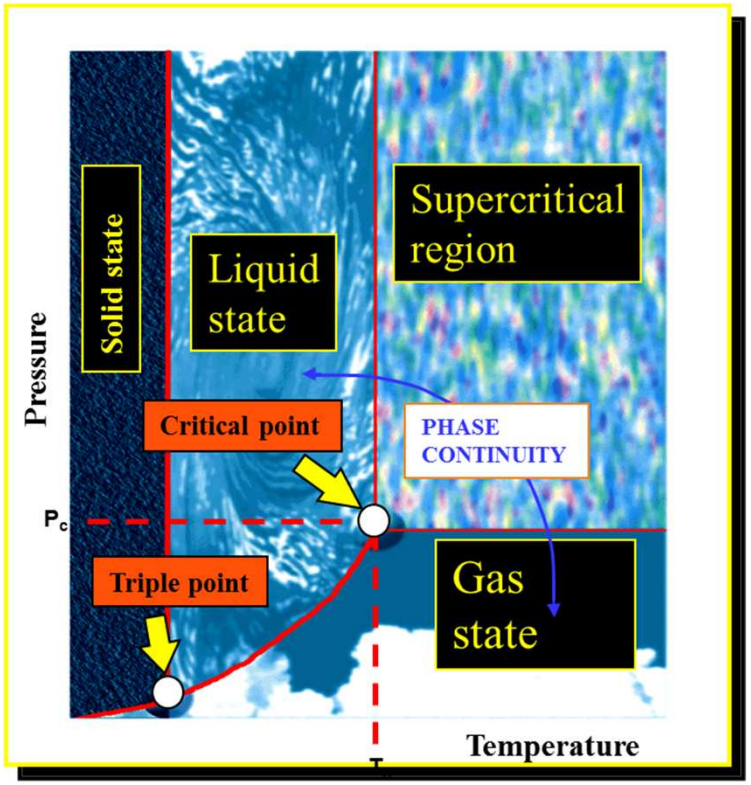
Compound		T_C (in ° C)	P_C (in bar)	ρ_C (in kg.m-3)
He	Helium	- 268	2,3	70,0
N_2	Nitrogen	- 147	34	314
O_2	Oxygen	- 118	50,4	436
CO_2	**Carbon dioxide**	31	73,8	466
C_2H_6	Ethane	32	48,7	207
N_2O	Dinitrogen oxide	36	72,5	453
C_3H_8	Propane	97	42,5	220
NH_3	Ammonia	132	113	235
C_3H_7OH	Isopropanol	235	47	273
C_2H_5OH	Ethanol	243	63	276
H_2O	Water	374	221	322

Supercritical region: $P > P_c$ and $T > T_c$

EXAMPLE OF SC-CO_2 BRAYTON CYCLE (SMFR PROJECT)







Wide range of variation for physical properties, especially ρ

Critical point of carbon dioxide (CO_2):
P_C = 7.38 MPa
T_C = 304.15 K
ρ_C = 466 kg.m^{-3}

SUPERCRITICAL CO_2

A few essential points:

The triple point corresponds to - 56.6° C and 5.11 atm (P_T).
Its sublimation point at atmospheric pressure is -78.5° C. (Pc)
The critical point is : 31.1° C and 73.84 bar.
Pure carbon dioxide is not very chemically reactive. In the presence of moisture, CO_2 forms carbonic acid and becomes corrosive.

How materials behave in the presence of CO_2: Several UK studies on Magnox and AGR CO_2 reactors (T<400° C for Magnox and 650° C for AGRs, service life up to 250,000 hours or 28.5 years)

➔ **Carbon deposition and carburisation**

9Cr steels: Two oxide layers form:
Outer layer from the reaction between the gas and metal ions in the grain boundaries:

$$3Fe + 4CO_2 \rightarrow Fe_3O_4 + 4CO$$

Inner layer at the metal-oxide interface:

$$3M + 2CO_2 \rightarrow M_3O_4 + 2C$$

Austenitic steels: Oxides form and grow in thickness ➔ impact on hydraulic diameter, pressure drops. Need for alloys with Si or coatings (Al, etc.).

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ROWLANDS, GARRETT, POPPLE, WHITTAKER AND HOAKSEY

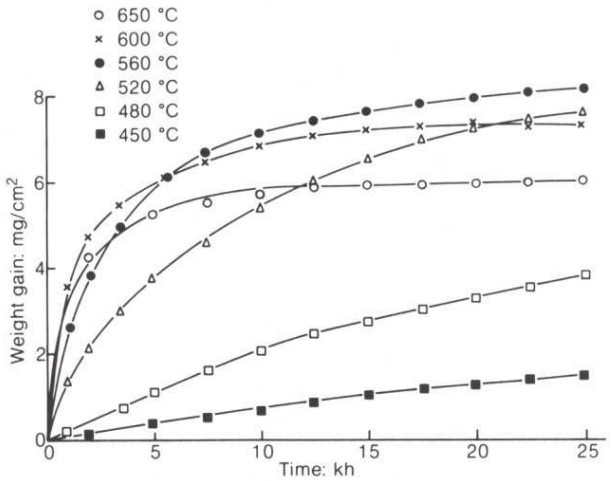


Fig. 12. Oxidation weight gain versus time for austenitic steels at various temperatures

NA/SC-CO_2 INTERACTION

- Low temperature, < 500° C

Na/CO_2 reaction

Complex intermediates:

$Na_2C_2O_4$, Na_2CO_3, Na_2O, C, etc.

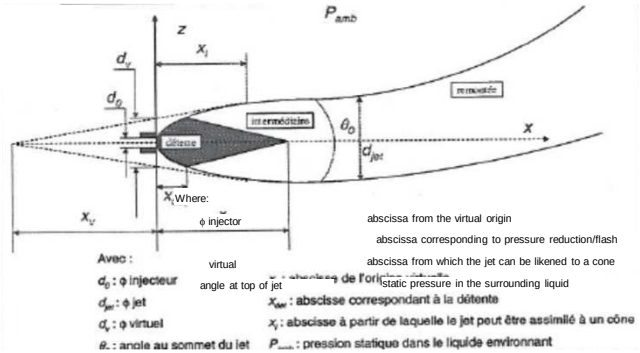
CO formation

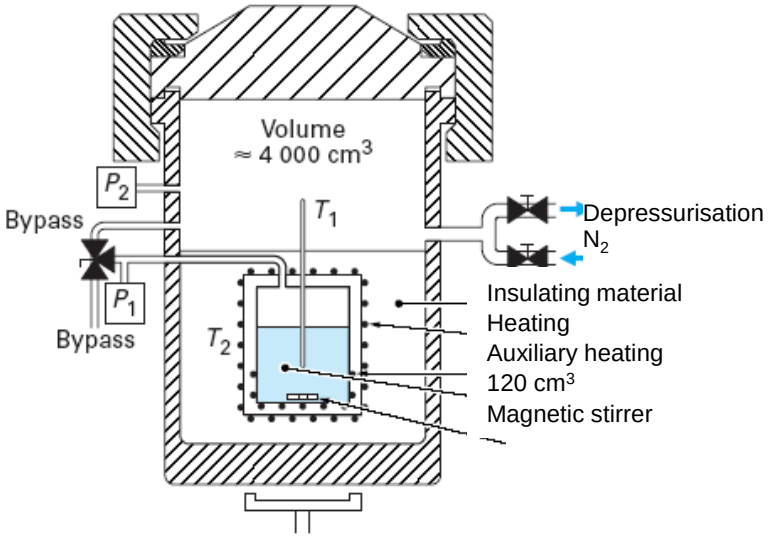
Na-CO reaction: induction period

- High temperature, 500-600° C

Na/CO_2 reaction is more rapid and global

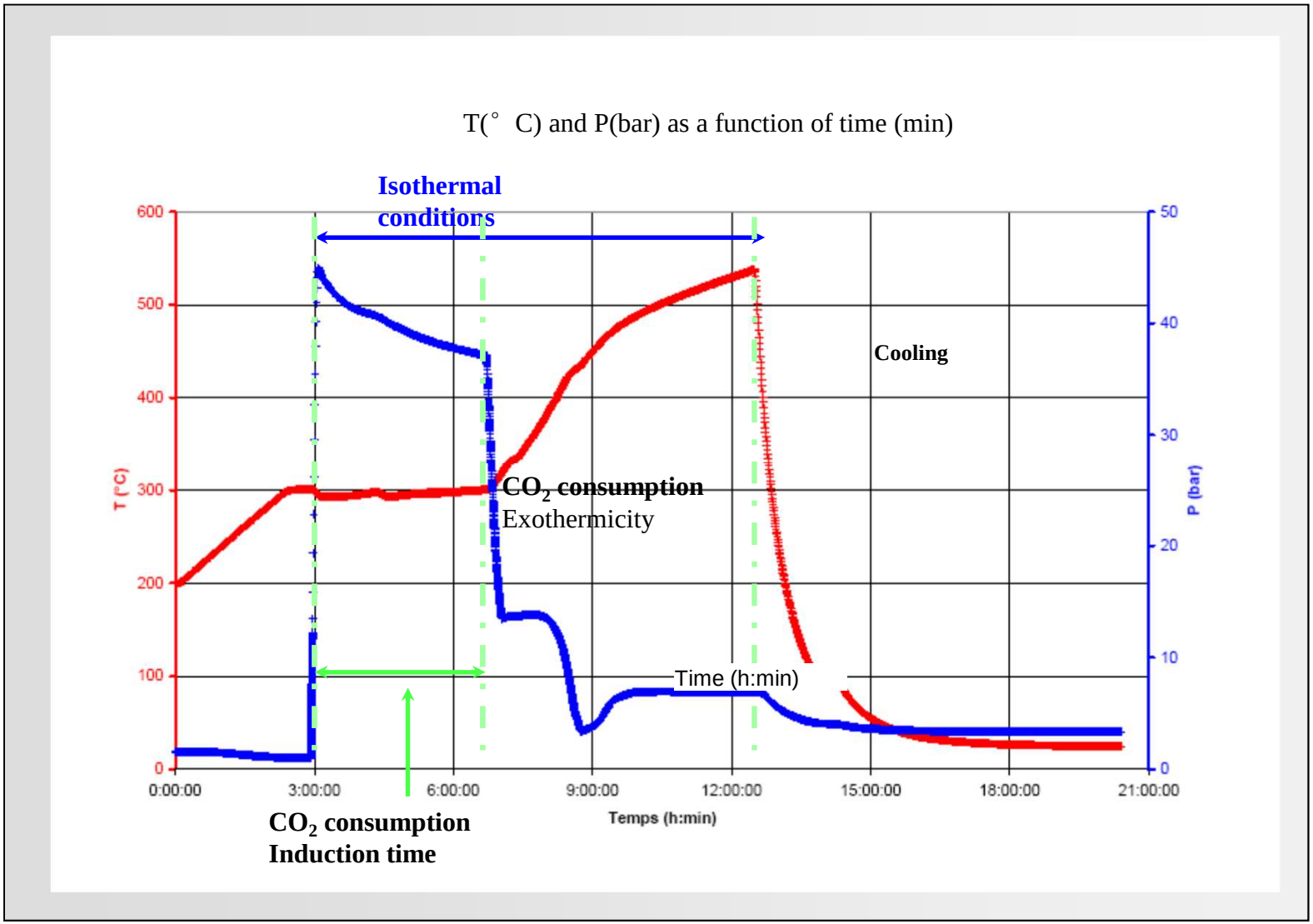
$Na + CO_2 \rightarrow Na_2CO_3 + C$





VSP analysis (Na-CO_2 interaction)

Isothermal test



Thank you very much for your kind attention!