TOPIC 3

Fuel, Clad, Structural and Coolant Materials

Sub topic 3.3:

Compatibility of Fast Reactor Structural Materials with Liquid Metal Coolants (Part 1)

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Outline

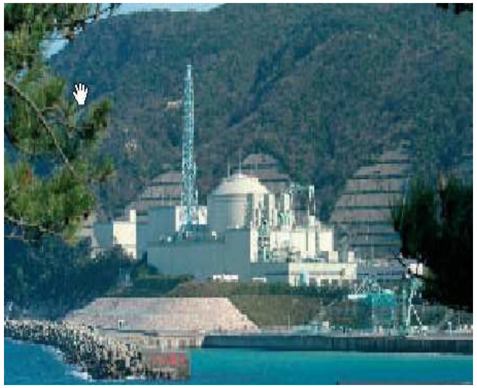
- Sodium Fast reactors (SFR)
- Why sodium as coolant
- Sodium chemistry/corrosion
- Materials for SFRs
- Materials corrosion in sodium
- Conclusions

Sodium Fast Reactor (SFR)

Sodium Fast Reactor : **world-wide developed since the 1950's, A very promising candidate for the development of fast neutron reactors, due to its very attractive nuclear, physical and even some of its chemical properties.**

Reactors in operation in Japan, India, Russia and China

Monju



Joyo

FBTR

BOR 60

BN600

CEFR

SFRs in Commissioning Phase

BN800 (Russia) 800 MW_e (criticality last June 2014) →

PFBR (India) 500 MW_e (criticality foreseen in spring 2015) →

Experience in SFR Operation in WE (France)

Phénix (1973-2010)

Super-Phénix (1985-1998)

Rapsodie (1967-1983)

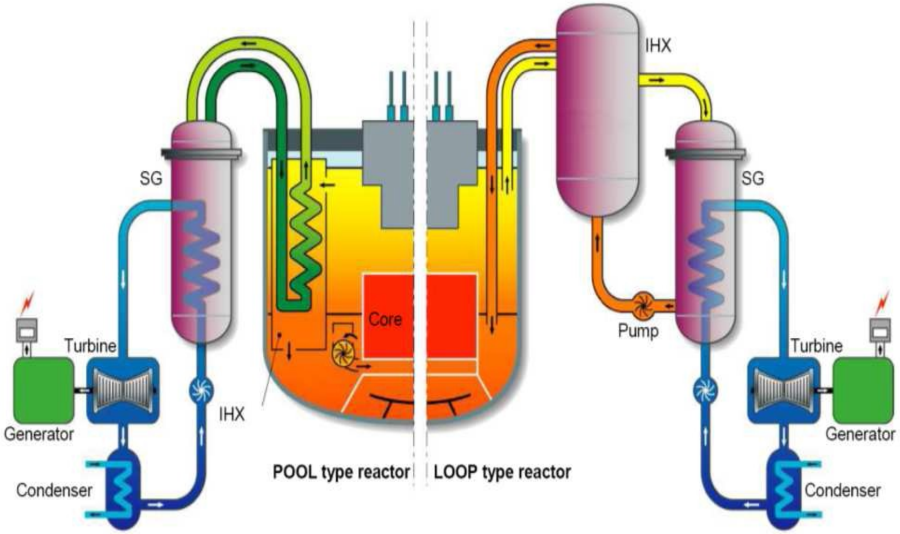
- Easy to operate: no pressurization of the primary coolant, high thermal inertia, control by single rod position, no xenon effect, no need of soluble neutron poison
- Radiation protection : higher level of protection than LWR
- Few effluents and little radioactive waste
- High thermal efficiency
- Large sodium boiling margin
- Natural convection
- Diversification of heat sink by using air

SFRs in Planning Phase

ASTRID - Preliminary design choices

Main features at the beginning of preconceptual design - mid 2010

- 1500 thMW - ~600 MW_e
- Pool-type reactor
- Intermediate sodium circuit
- High level expectations in terms of safety demonstration
- Preliminary strategy for severe accidents (core catcher…)
- Diversified decay heat removal systems
- Oxide fuel UO_2-PuO_2 for starting cores
- Transmutation capability
- ….



Why Sodium?

SFR as an option of GEN IV reactor concepts

Safety
- Level at least equivalent to GEN III systems (WENRA requirements)
- With significant improvements on Na reactors specificities issues
- Integrating *FUKUSHIMA* accident feedback

Operability
- Load factor of 80% or more after first “learning” years
- Significant improvements concerning In Service Inspection & Repair (ISIR)

Ultimate wastes transmutation
- Continue experimentation on minor actinides transmutation, up to large scales if decided)according to June 28, 2006 French Act on Waste Management)

Controllable investment costs

Why Sodium?

Sodium is a very attractive coolant for Fast Neutron Reactors

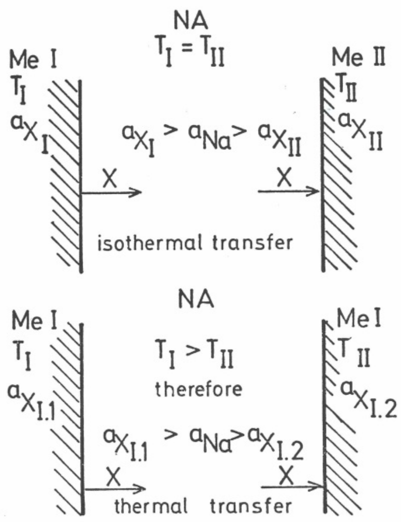
- Very good thermal conductivity.
- High thermal capacity.
- Liquid between 97.8 up to 880°C
- at dynamic pressure below 4 bars,
- Compatible neutron-physical properties.
- Viscosity comparable to that of water.
- Compatibility with metallic materials fairly satisfactory.
- No toxicity
- Low cost and sufficient availability, but very reactive with water!!

Corrosion Mechanisms

Na corrosion is based on dissolution!

The dissolution rate $\Delta S/\Delta t$ is ruled by the difference of the chemical activities in the solid phase, $a_{(s)}$, minus that in the liquid phase, $a_{(l)}$

- ☐ $\Delta S/\Delta t = ß\,[a_{(s)} - a_{(l)}]$ (1)
- ☐ Based on the work of Epstein and of Weeks



Mass transfer of the component X of the alloy Me I by sodium

Sodium Chemistry/Corrosion

- Corrosion in stagnant liquid sodium is characterized by the fact, that the difference of the activities, $a_{(s)} - a_{(l)}$, is dependent on time. The activity of the solute, $a_{(l)}$, increases from very low values at the beginning of the process to values close to that in the solid phase, $a_{(s)}$, thus, corrosion rate approaches zero
- Corrosion in turbulent liquid sodium flow is determined by equation (1)
- Flow and temperature gradients keep the difference of activities a_s and a_d on its level

Sodium Chemistry/Corrosion

- ☐ Chemical activity in the bulk stream in non-isothermal flowing systems is orders of magnitude lower than saturation.
- ☐ Its value can be neglected, when the temperature gradient is in the order of ≥100 K. The corrosion rate becomes proportional to the activity at saturation :
- ☐ $\Delta S/\Delta t = ß\ a_{sat}$, (2)
  ß is the corrosion constant, a_{sat} can be influenced by side reactions
- ☐ ß depends on the hydraulic parameters of the flow. Epstein and Weeks published equation (3):
- ☐ $ß = Sh \cdot D \cdot d_H^{-1}$ (3)
- ☐ Sh = Sherwood number, D = diffusion coefficient and d_H = hydraulic diameter of the test tube.
- ☐ The Sherwood number is related to the flow velocity via the Reynolds & Schmitt number:

$$Sh = 0.0481 \cdot Re^{0.75} \cdot Sc^{0.42} \quad (4)$$

- ☐ Re is the Reynolds number $Re = v \cdot d_H \cdot \nu^{-1}$ (v is the flow velocity and ν the viscosity)
- ☐ and Sc the Schmitt number $Sc = \nu \cdot D^{-1}$

Sodium Chemistry/Corrosion

- ß depends on temperature through viscosity ν and diffusion coefficient D. Corrosion rates are further related to temperature via the solubility of elements as a function of temperature.
- **With the knowledge of ß and a_{sat} one can estimate the Na corrosion rate** (using equs. 1-4)
- Confirmed by corrosion experiments with Ni in Na circuit and solubility data

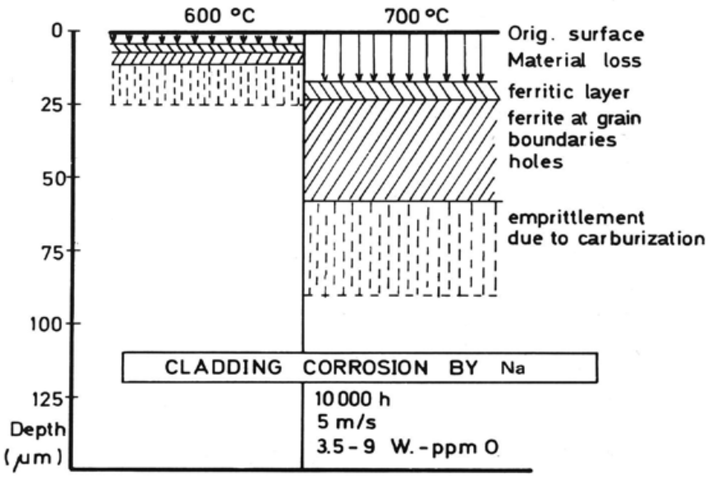
Saturation concentrations of steel components in liquid sodium at 500 and 700°C

Steel component	C_{sat} [mol%] at 773 K	C_{sat} [mol%] at 973 K
Fe	$3.5\ 10^{-5}$	$2.7\ 10^{-4}$
Ni	$4.3\ 10^{-5}$	$1.1\ 10^{-4}$
Cr	$2.2\ 10^{-7}$	$5.6\ 10^{-4}$
Mo	$9.9\ 10^{-7}$	$4.0\ 10^{-4}$

Sodium Chemistry/Corrosion

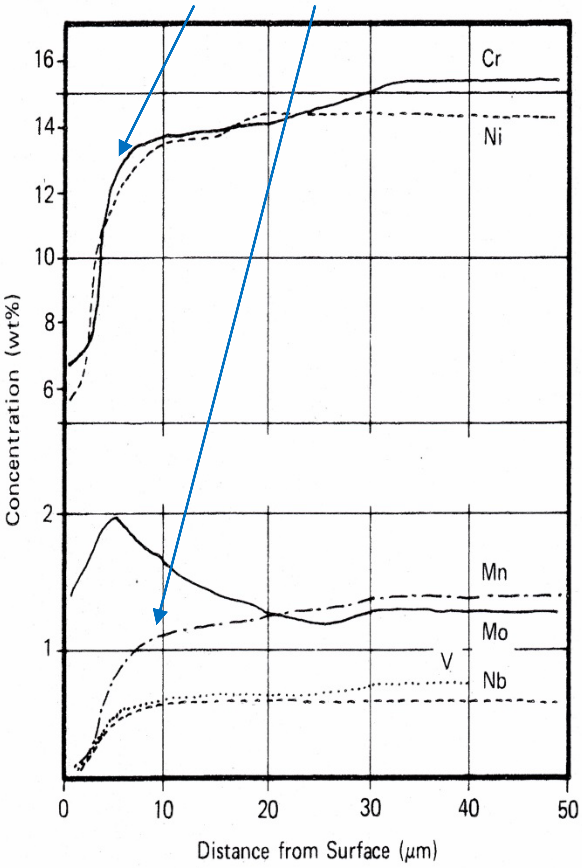
Selective leaching of alloy components

- Different apparent solubilities cause selective leaching of alloy components
- Stainless steels form surface layers depleted in Cr, Ni and Mn
- Fe and Mo are enriched in surface layers
- Austenitic structure is changed to ferritic one
- Grain boundaries are depleted to larger depth



Material 1.4988 (X8 CrNiMoVNb 16 13)

Surface layer depletion/reaction zone

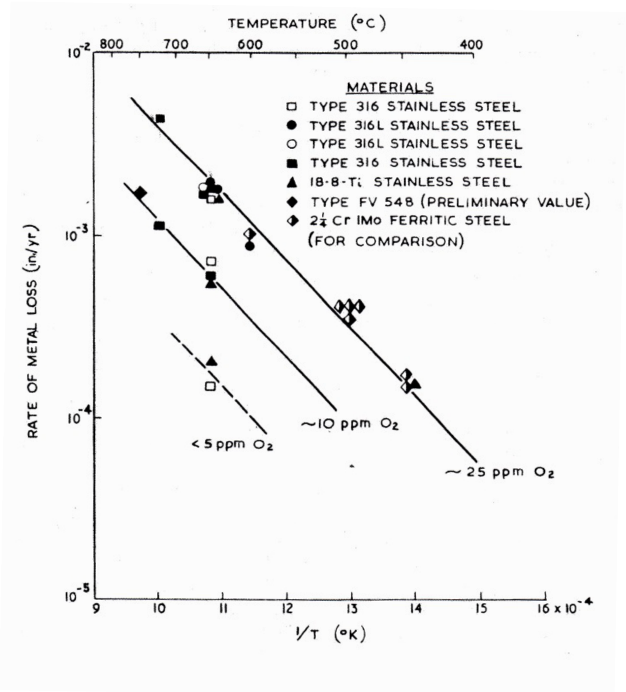


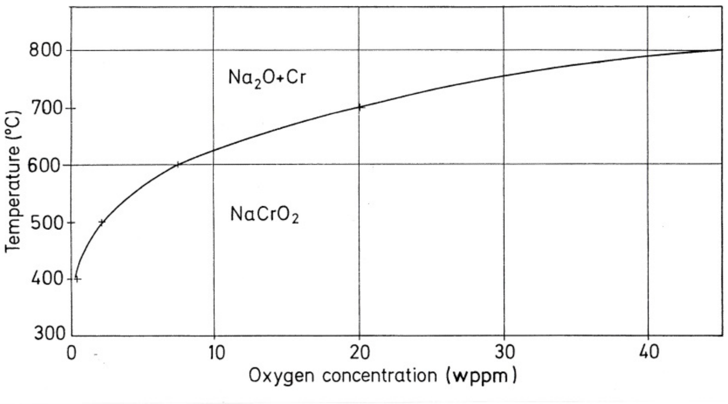
X8 Cr Ni Mo V Nb 16 13 (no. 1.4988)
Na; 5000 h, 973 K, 5 m/s, 5.5 ppm O.

Sodium Chemistry/Corrosion

Influence of impurities (non-metals) in liquid sodium

- Thorley and Tyzack exhibited the influence of oxygen on the Na corrosion of a group of steels in a systematic study
- $\log S = 2.44 + 1.5 \log c_O - 18000/2.3RT$ (with mass loss S in mils/y, c_O in ppm and T in K
- Na corrosion of stainless steels can be significally reduced by decreasing the oxygen content of sodium





Na chromite is only stable at moderately high temperature and high oxygen concentration in Na

General corrosion models

[O] < 5ppm, Baque's model

$R = 0$ $(T < 817{,}13\ K)$

$R = a \cdot V^{0.435} \cdot [O] \cdot \exp(-150.5/(T-817{,}13))$

R = rate of metal loss in kg/m^2 per year

a = coefficient function of the alloy

V = sodium velocity (m/s) (below 10 m/s)

$[O]$= oxygen content in ppm (Eichelberger law)

[O] > 5ppm, Thorley's model

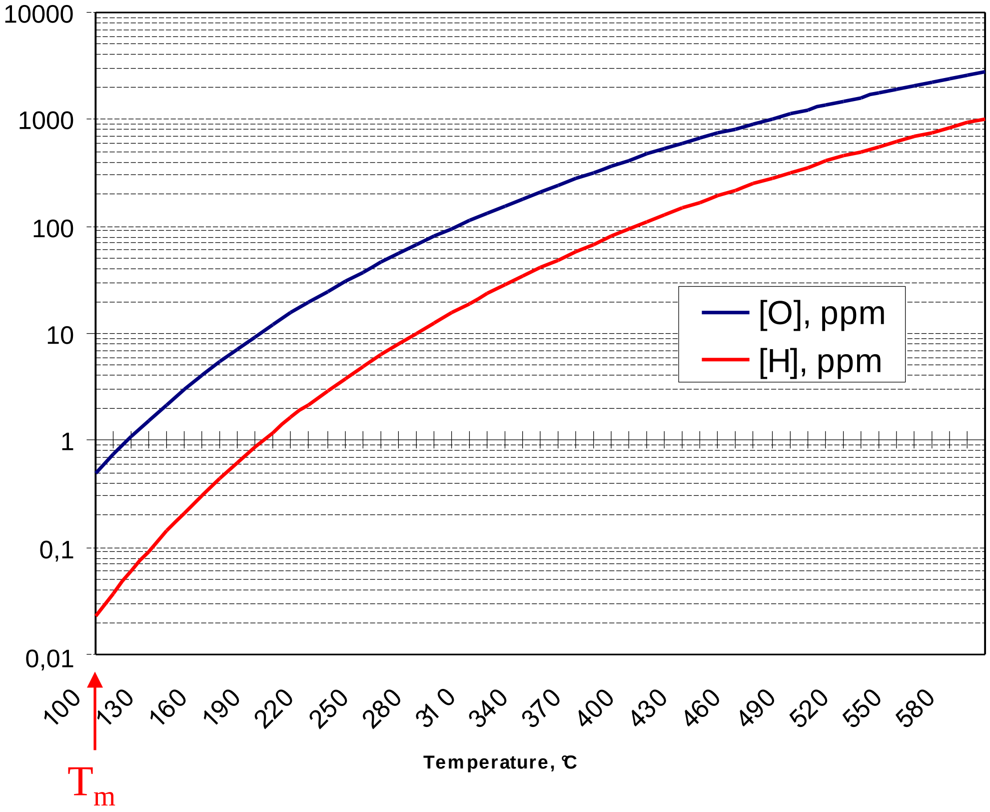
(given for [O] ranging from 0 ppm to high concentrations but used in France > 5 ppm and T>817,13 K)

If $V \leq 4$ m/s, $R = (V/4)^{0.435} \cdot 10^{4.724} + 1.106 \cdot \log_{10}[O] - 3913/(T)$

If $V > 4$ m/s, $R = 10^{4.724} + 1.106 . \log_{10}[O] - 3913/(T)$

Sodium Chemistry/Corrosion

Solubilities of oxygen and hydrogen in sodium



Noden

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

Wittingham

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

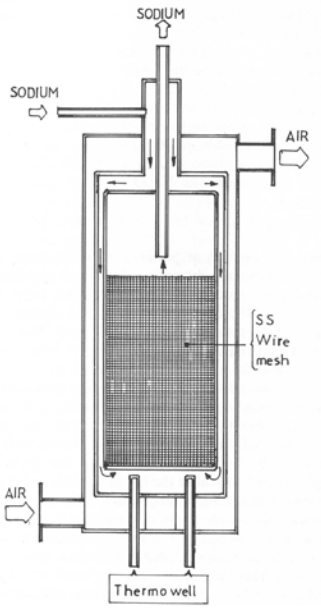
O and H solubilities are negligible close to T_m

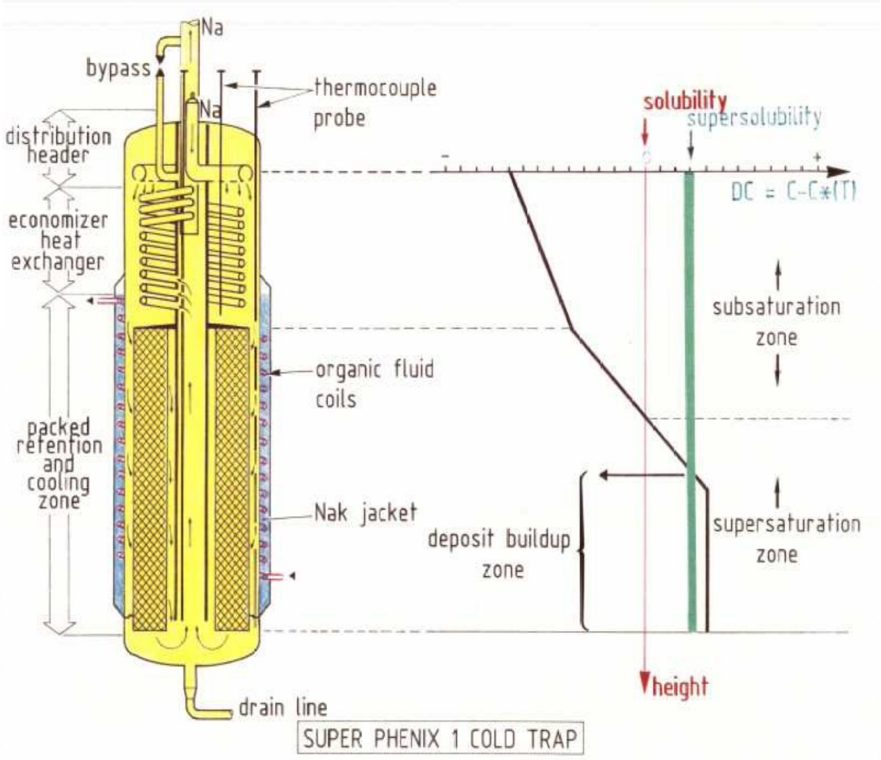
Consequences: Na can be purified by cooling down, leading to crystallization of O and H as Na_2O and NaH in a so-called "cold trap"

Sodium Chemistry/Corrosion

Cold trap for oxygen (and hydrogen)

- Na is cooled down in an integrated heat exchanger-economizer
- Then Na flows through a cooler where it reaches a temperature below the saturation temperature
- Precipitated crystals are retained on cold walls or stainless steel mesh packing
- The outlet flow of Na is then reheated in a heat exchanger-economizer before entering back into the main flow

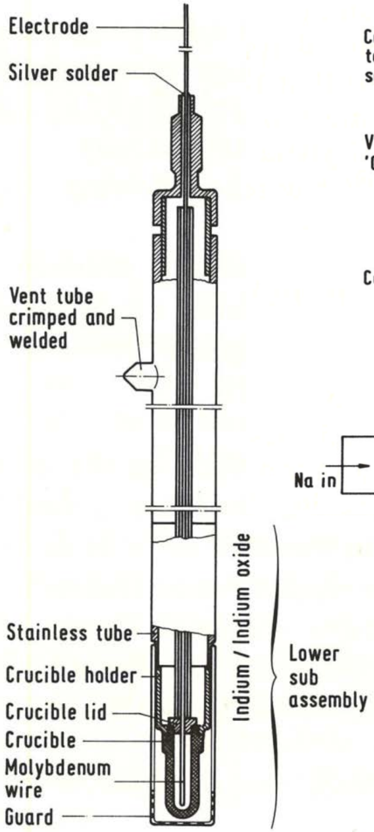


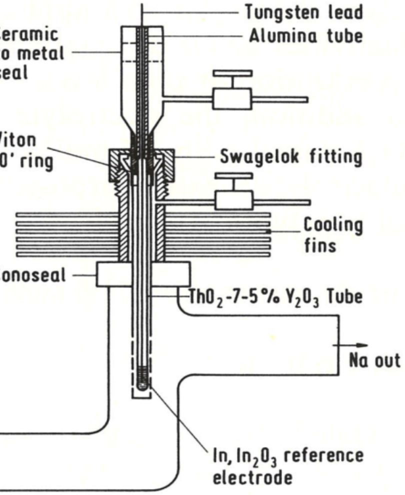


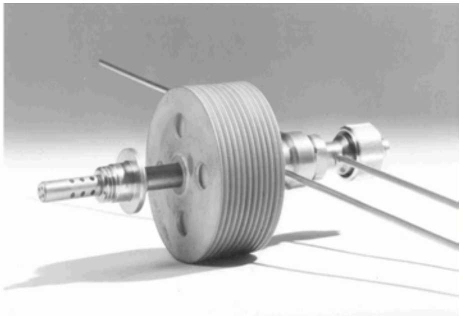
Oxygen levels in the order of 1 ppm can be achieved

Oxygen measurement

Electrochemical Oxygen sensor



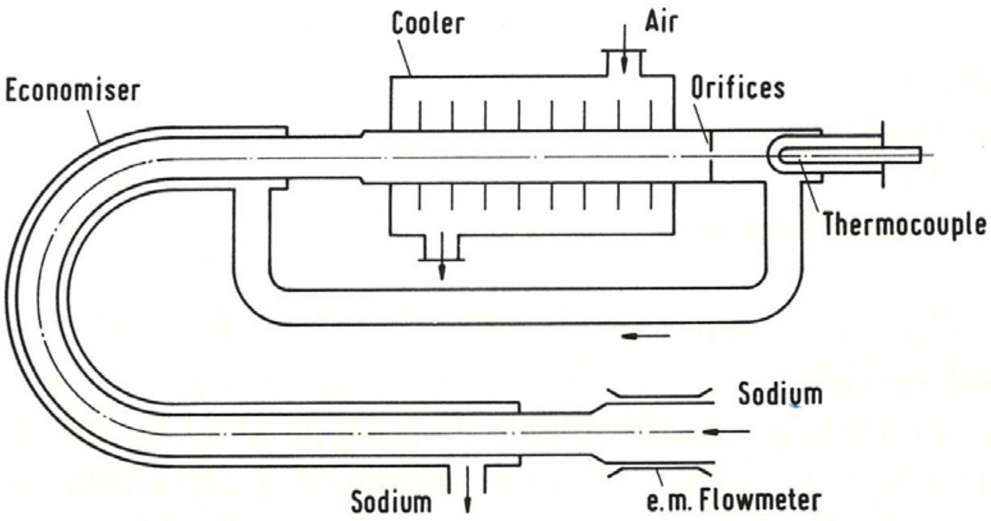




By Harwell Labs, UK

Plugging meter

- Widely used in sodium loops
- Simple and inexpensive
- Measures automated periodically the plugging temperature of the orifice T_{pl}
- The oxygen solubility at T_{pl} corresponds to the oxygen concentration in the Na loop
- Risk that more than one impurity contributes to plugging of orifice (e.g. H)

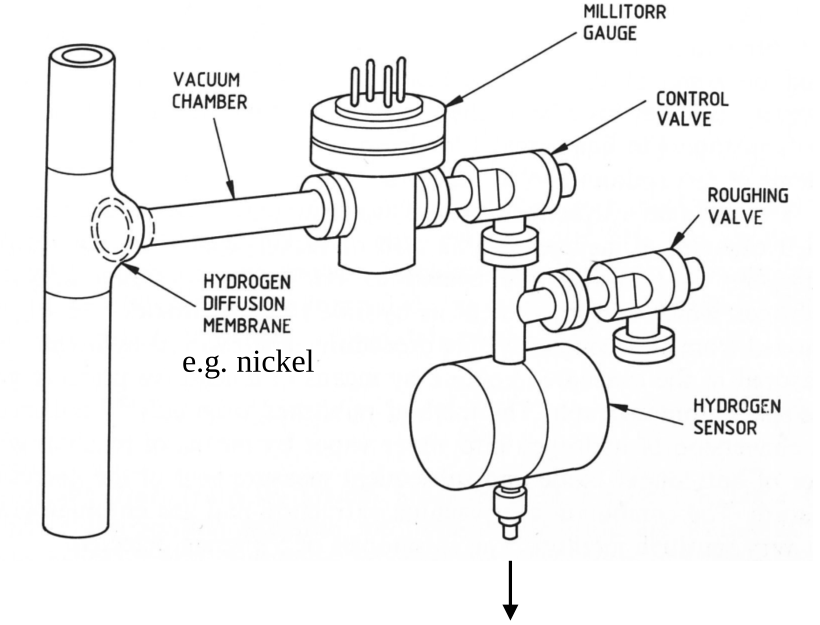


Hydrogen measurement

Main purpose of hydrogen measurement is the immediate detection of water leaks in the steam generator unit (SGU)

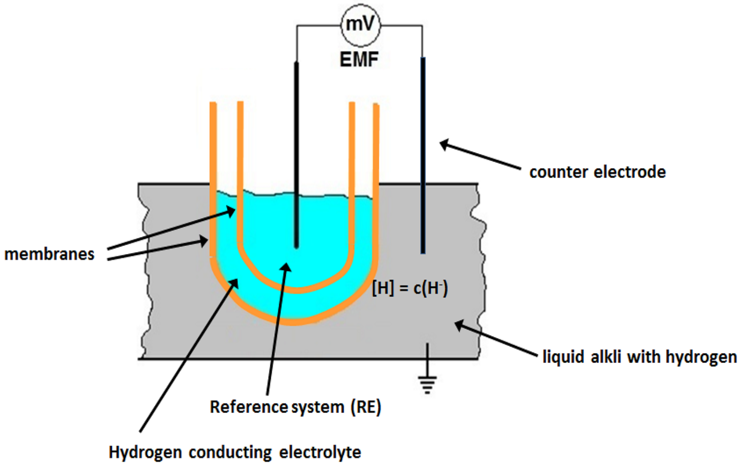
Principal methods are:

- Vacuum extraction
- Amalgamation
- Isotope dilution
- Electrochemical sensor
- Diffusion-type hydrogen meter



e.g. nickel

To gas chromatograph or mass spectrometer



Sodium Chemistry/Corrosion

Other impurities

- Tritium: from boron carbide or ternary fission products
- Activated corrosion products: mainly ^{60}Co, ^{54}Mn,…
- Sodium: ^{22}Na (2.6 years) → 3700 Bq/g, ^{24}Na (15 h), ^{23}Ne (cover gas)
- Na impurities: ^{110}Ag, ^{65}Zn, ^{113}Sn, ^{124}Sb (depending on Na purity)

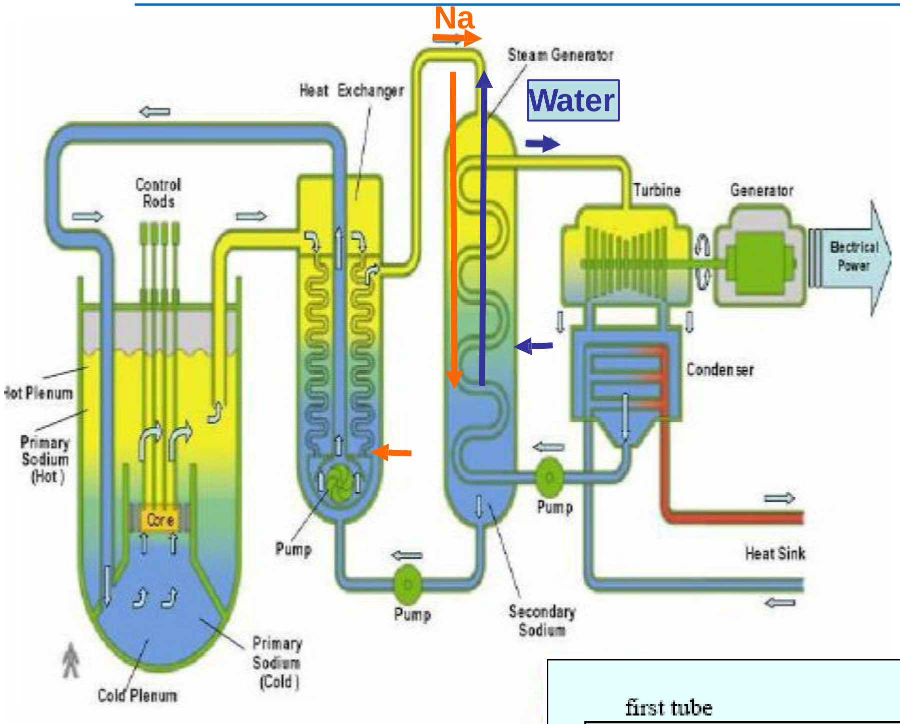
- Activation of components due to activated steel elements

- Corrosion products, dissolved in the sodium, then exposed to the neutron flux in the core
  - ^{54}Mn (312 d) by (n,p) of ^{54}Fe
  - ^{60}Co (5.3 y) by (n,g) of ^{59}Co
  - ^{58}Co (71 d) by (n,p) of ^{58}Ni
  - ^{51}Cr (28 d) by (n,g) of ^{50}Cr

- The main contamination of the core components is coming from that activation (primary pump, IHX)

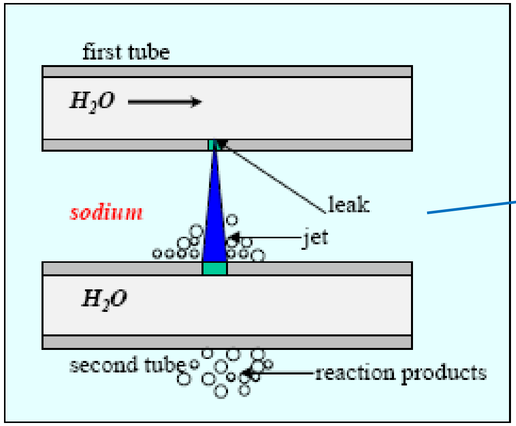
- Deposition of activation products on steel surfaces, depending on flow rate and ΔT

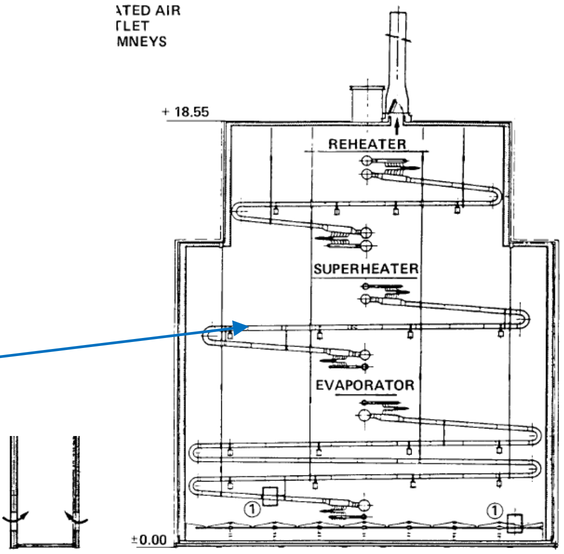
Sodium Chemistry/Corrosion



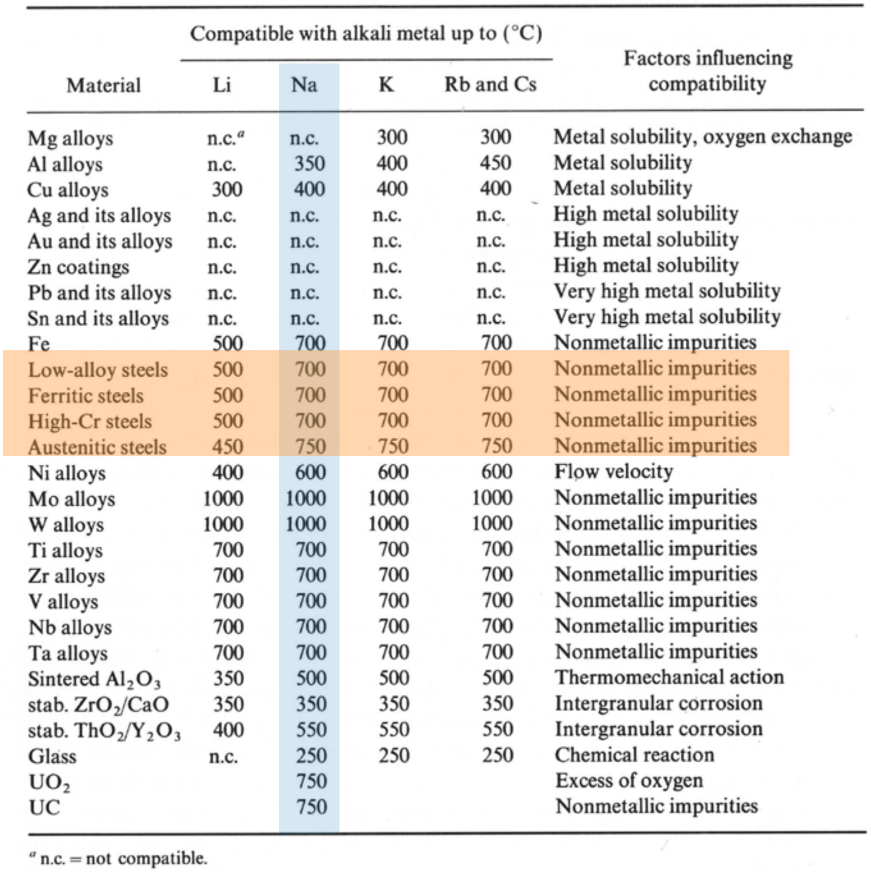
Sodium water reactions!!

$$\underbrace{Na + H_2O \rightarrow \overset{\substack{\text{decomposes into } Na_2O \text{ and NaH} \\ \downarrow}}{NaOH} + \tfrac{1}{2} H_2 \quad - 145\ kJ/mol_{Na}}_{\text{pressure and temperature increase of Na!!}}$$





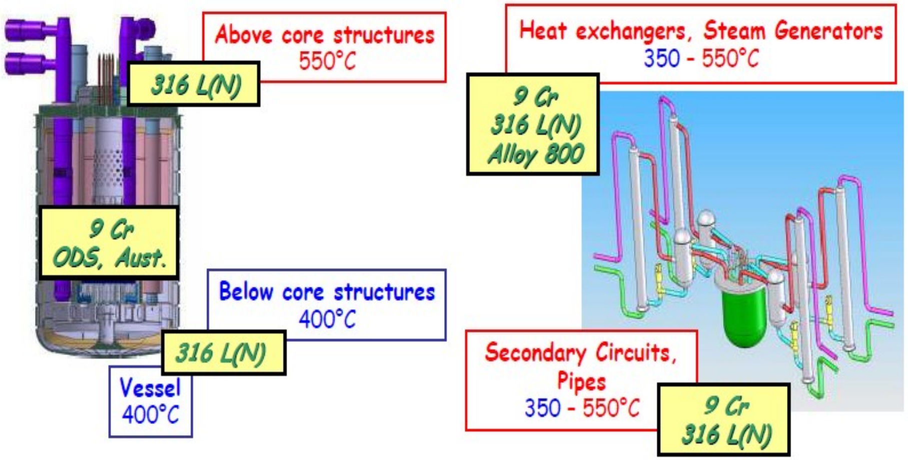
Sodium compatibility of materials



Material	Compatible with alkali metal up to (°C) Li	Na	K	Rb and Cs	Factors influencing compatibility
Mg alloys	n.c.[a]	n.c.	300	300	Metal solubility, oxygen exchange
Al alloys	n.c.	350	400	450	Metal solubility
Cu alloys	300	400	400	400	Metal solubility
Ag and its alloys	n.c.	n.c.	n.c.	n.c.	High metal solubility
Au and its alloys	n.c.	n.c.	n.c.	n.c.	High metal solubility
Zn coatings	n.c.	n.c.	n.c.	n.c.	High metal solubility
Pb and its alloys	n.c.	n.c.	n.c.	n.c.	Very high metal solubility
Sn and its alloys	n.c.	n.c.	n.c.	n.c.	Very high metal solubility
Fe	500	700	700	700	Nonmetallic impurities
Low-alloy steels	500	700	700	700	Nonmetallic impurities
Ferritic steels	500	700	700	700	Nonmetallic impurities
High-Cr steels	500	700	700	700	Nonmetallic impurities
Austenitic steels	450	750	750	750	Nonmetallic impurities
Ni alloys	400	600	600	600	Flow velocity
Mo alloys	1000	1000	1000	1000	Nonmetallic impurities
W alloys	1000	1000	1000	1000	Nonmetallic impurities
Ti alloys	700	700	700	700	Nonmetallic impurities
Zr alloys	700	700	700	700	Nonmetallic impurities
V alloys	700	700	700	700	Nonmetallic impurities
Nb alloys	700	700	700	700	Nonmetallic impurities
Ta alloys	700	700	700	700	Nonmetallic impurities
Sintered Al_2O_3	350	500	500	500	Thermomechanical action
stab. ZrO_2/CaO	350	350	350	350	Intergranular corrosion
stab. ThO_2/Y_2O_3	400	550	550	550	Intergranular corrosion
Glass	n.c.	250	250	250	Chemical reaction
UO_2		750			Excess of oxygen
UC		750			Nonmetallic impurities

[a] n.c. = not compatible.

Typical materials selection of a SFR



SFR structures requirements :

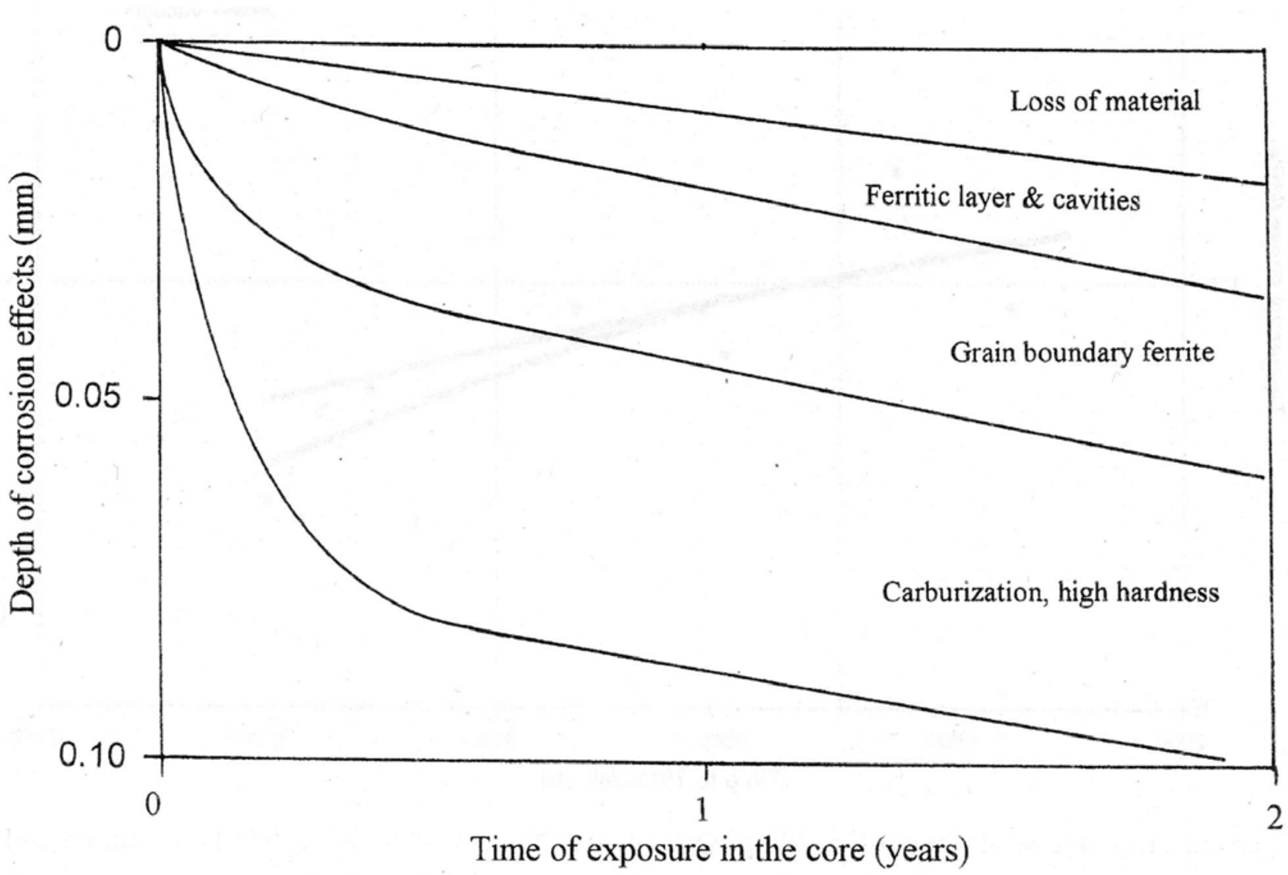
- High temperatures ⇒ creep, creep-fatigue domain
- Low pressures but high thermal gradients
- Sodium / water environments
- Low irradiation
- 60 years life at conception

Na Corrosion of Reactor Materials

- Core materials have to withstand sodium at highest temperature and flow velocity
- Life time of these materials is limited to about 2-3 years
- Cladding materials are stabilized or unstabilized austenitic stainless steels
- Structural materials are exposed to sodium of lower temperature and flow velocity
- Life time is in the order of more than 30 years
- Austenitic steels 304 and 316 are used

Schematic view on corrosion effects of cladding tubes

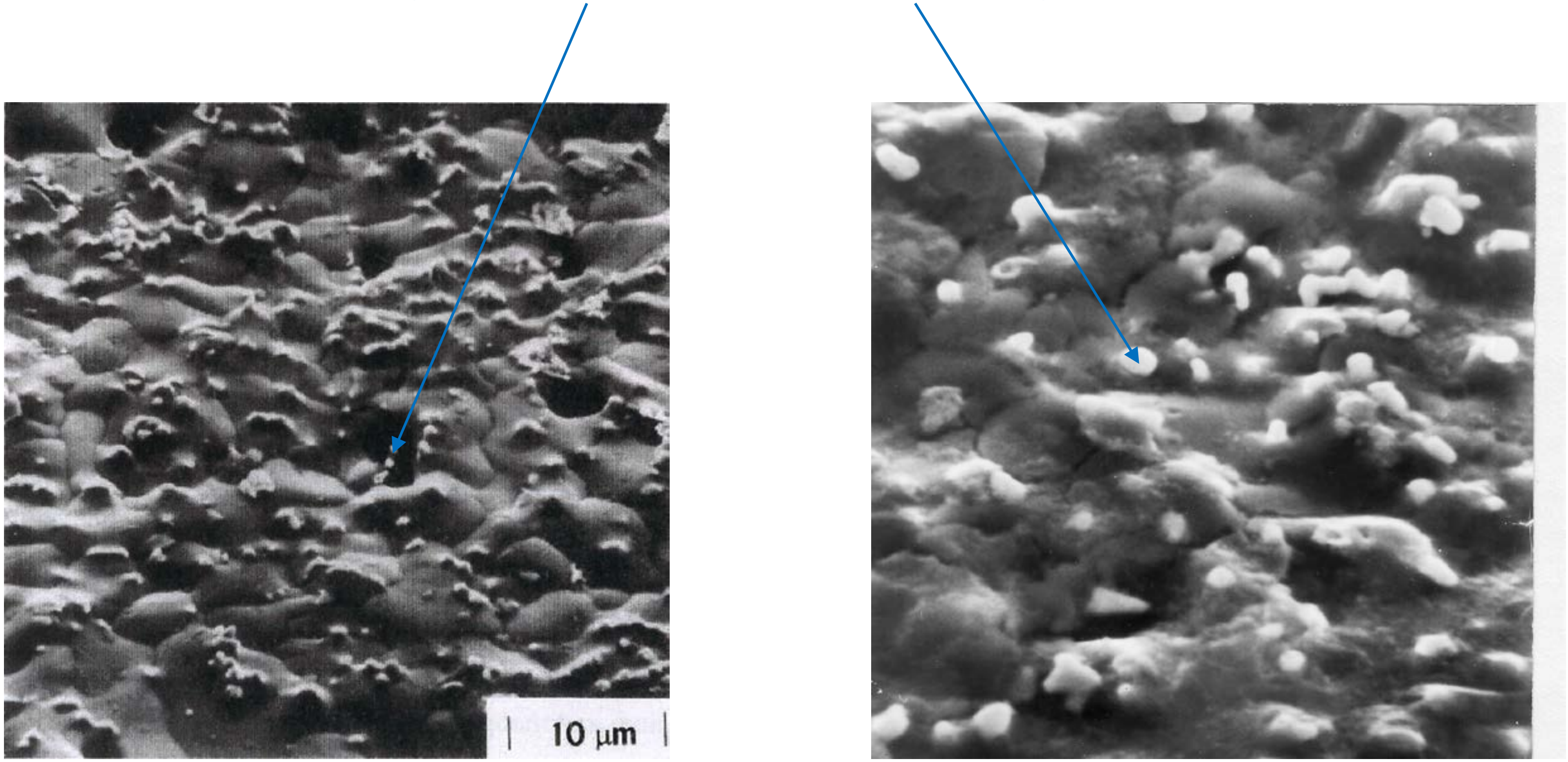
15 15 Cr-Ni steel (1.4970), T = 700°C



Materials corrosion in sodium

Corroded surface of 15 15 Cr-Ni steel 1.4970, 5000h at 700°C

Bright spots are Mo-rich particles on ferritic surface grains



Creep-rupture life of austenitic steels in sodium

- The creep-rupture life of type 316L(N) steel is longer in air than in Na at 550°C, whereas this trend gets reversed at 600°C ▶

- At lower stresses (typical level of service loading), no environmental effect of sodium is visible

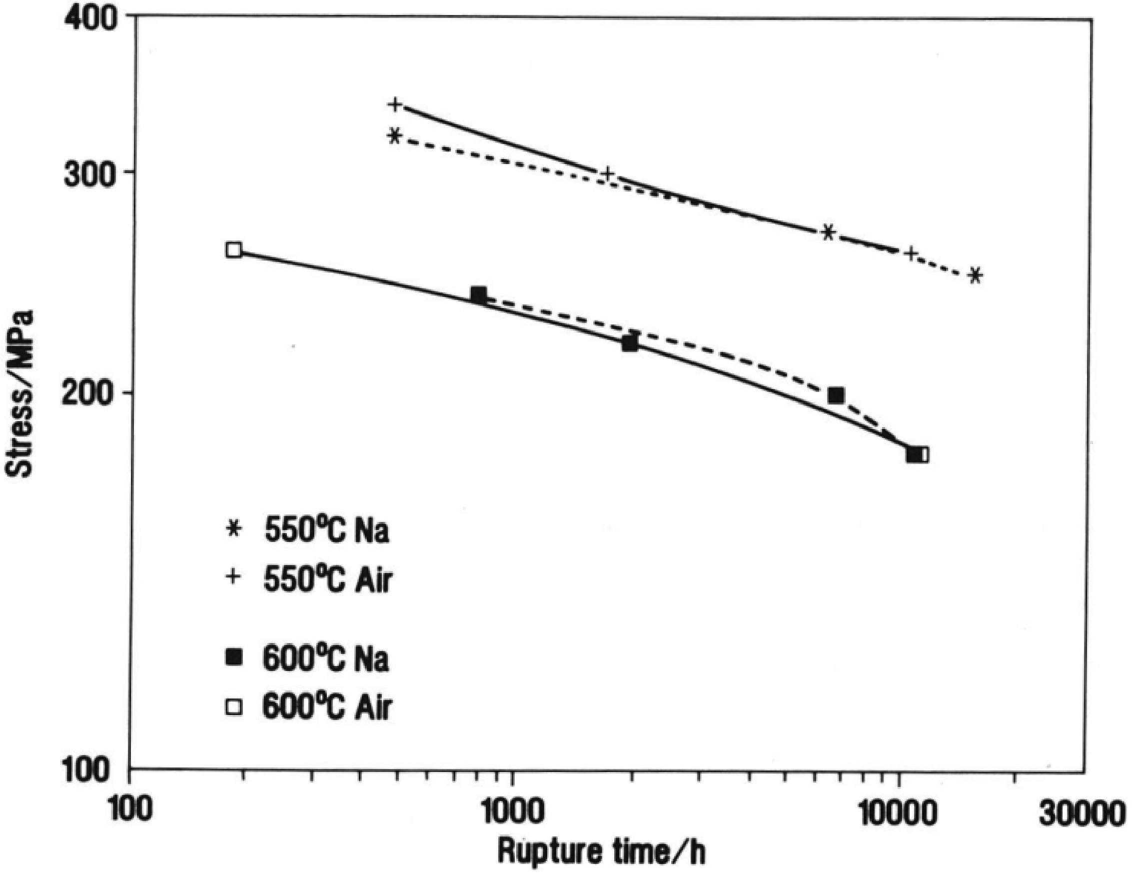
- The effect of sodium environment on creep and creep-rupture properties of type 316L(N) is less pronounced than in the case of 304 steel (Mo effect?)

- The earlier onset of tertiary creep and tertiary creep embrittlement (comp. to air) was not seen for type 316L(N) as seen for type 304 steel ▶

- The rupture life of type 316L(N) steel in Na environment at SFR operating stress and temperature conditions is comparable to basline data in air ▶

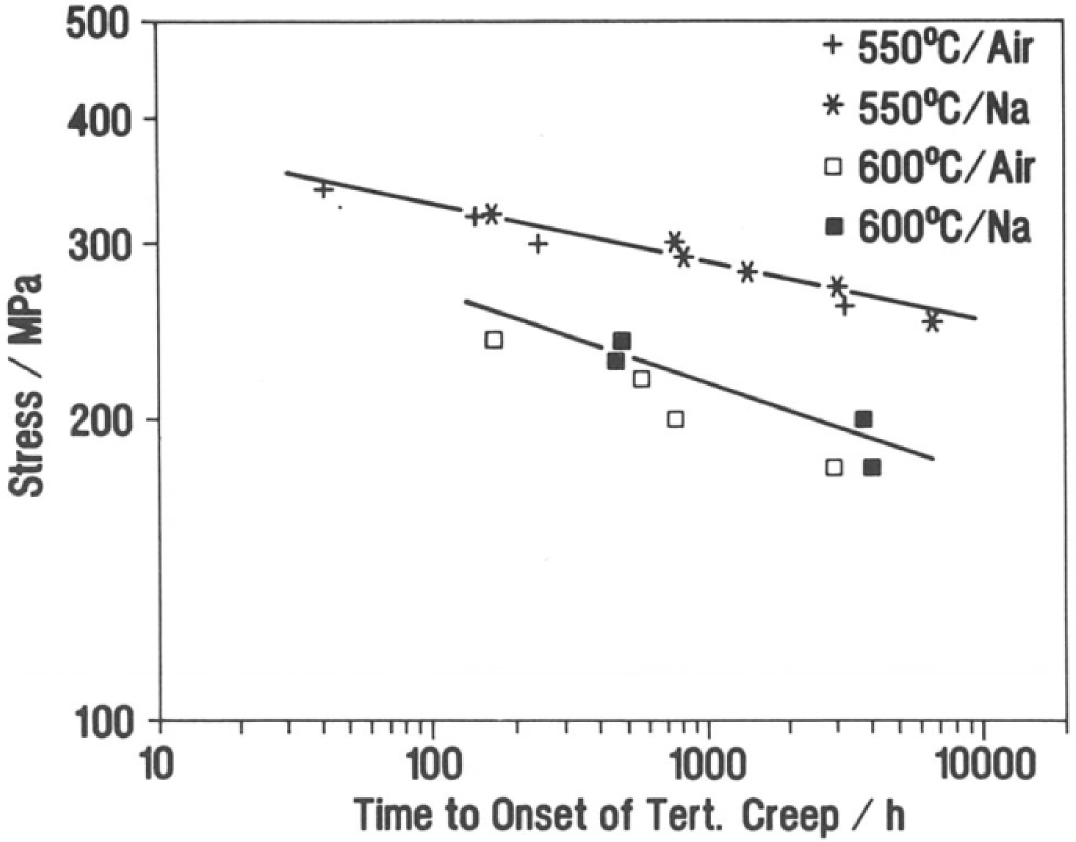
Materials corrosion in sodium

Stress-rupture time curves of type 316L(N) in air and sodium



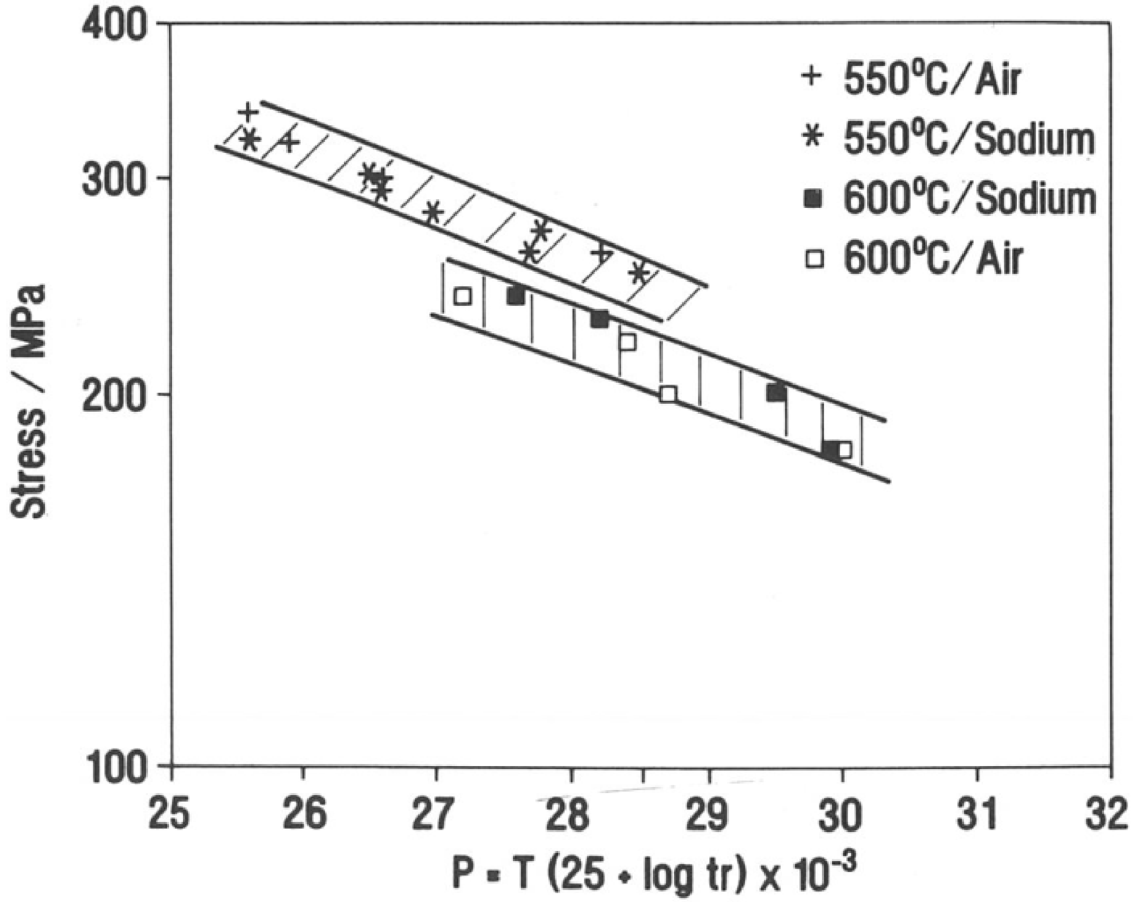
Materials corrosion in sodium

Stress versus time to onset of tertiary creep of type 316L(N) in air and sodium



Materials corrosion in sodium

Correlation of rupture data of type 316L(N) in air and sodium using Larson-Miller parameter P



Sodium corrosion of nickel base alloys

- Inconel 600 and Nimonic as nickel-based alloys were already studied by Thorley and Tyzack (1967)
- Ni-based alloys do not form layers of changed structures as Cr-Ni steels typically do
- Corrosion rates at 650°C were 3 times higher than with steel AISI 316
- There was no influence of the oxygen activity on corrosion rates
- Increasing flow velocity of sodium increased corrosion rates significantly
- Surface layers were not changed in their composition
- Austenitic structure remains, but losses of substitutional elements causes growth of cavities in the micro structure

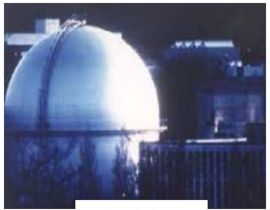
Corrosion of group IV, V and VI/VII metals/alloys

- Alloys from group IV and V metals such as Ti, Zr, V, Nb or Ta do not suffer from leaching of substitutional elements. Main corrosion is the exchange of non-metals, e.g. oxygen uptake/oxidation
- Zr forms stable surface oxide including α-Zr(O) phase underneath
- Ti does not form surface oxide layers due to high oxide solubility in Na
- Group VI/VII metals like Mo, W, and Re have extremely low solubility in Na and therefore excellent corrosion resistance, e.g. TZM (Mo-0.5Ti-0.1Zr) suffers only very little intergranular attack at 1300°C.
- Alloys based on these metals are well compatible with Na
- But Mo alloys are sensitive to oxidation in Na with oxygen concentrations close to saturation
- Such alloys may be used for particular high temperature applications

Corrosion of some ceramic materials

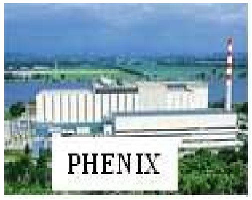
- ☐ Materials satisfying the thermodynamic stability criterion for sodium compatibility:
- ☐ Alumina, beryllia, magnesia, thoria, zirconia are compatible oxides
- ☐ Compatibility depends on the purity of the ceramic materials
- ☐ Unsufficient purity causes intercrystalline corrosion and desintegration of samples
- ☐ Basalt and concrete that are proposed as core catcher materials are poorly compatible
- ☐ Their humidity causes violent reactions
- ☐ Functional ceramics as ThO_2-Y_2O_3 are compatible up to 400 °C
- ☐ Graphite as getter material for radioactive cesium is compatible to high temperatures

Thank you for your attention



RAPSODIE

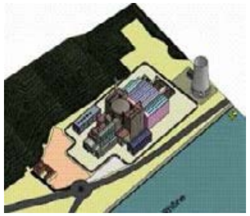
1967 - 1983



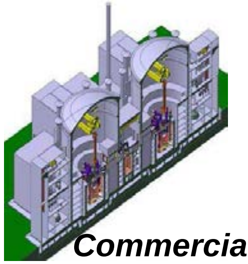
1973 - 2010

1985 - 1998

1988-1998



ASTRID



Commercial reactor

Many thanks to Christian Latgé from CEA for his help and valuable contribution to this presentation