SODIUM COOLANT: CHEMISTRY AND COOLANT QUALITY CONTROL, IN-SERVICE ONLINE MONITORING

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1 Introduction

Despite its attractive properties, the choice of sodium coolant induces challenges related to design, operation, maintenance and decommissioning phase particularly due to its well-known reactivity, radio-chemistry, and their consequences. It reacts with oxygen and can induce a sodium fire, in case of sodium leak or air ingress. It reacts also exothermically with water, and potentially with violence, depending of local conditions. Despite very strong care with regards the contact with air and water, sodium contains various non-radioactive impurities either present from the start or introduced during operation. Sodium can be activated and/or contaminated by activated impurities already present in the coolant or generated during operation of the reactor ie activated corrosion products (ACP) or by fuel cladding ruptures. Sodium radio-contamination and mass transfer created in the system, interaction between Na bulk and cover gas for liquid coolants induces relevant issues for radiological impact assessment, operation, including maintenance, inspection and handling, etc. Nevertheless, all these issues have been solved as it is underlined hereafter.

2 Main sources of impurities

There are three specific occurrences of pollution: reactor start-up, reactor operation in steady-state conditions and maintenance or incidental conditions among them water ingress from Steam Generator Unit (SGU), large air ingress and oil ingress. [1]

One source of discontinuous pollution by oxygen and hydrogen during reactor start-up or at the beginning of the cycle, is due to the metallic surfaces put in contact with the liquid sodium: structural material from vessel, pipes and components, fuel assemblies during handling phase… They provides metallic oxides, less thermodynamically stable than sodium oxide according to Ellingham diagram and oxygen and moisture, gaseous or adsorbed on material surfaces. A continuous hydrogen source comes from the aqueous corrosion of Steam Generator Units (SGU), diffusing through the pipes at relatively high temperature ie above about 400°C.

Oxygen contributes to corrosion of steel, mainly cladding due to highest temperatures (above 600°C) and the activated corrosion products are transported from the core towards the components and mainly to the Intermediate Heat Exchangers, leading to their contamination. All the steel elements (Fe, Cr, Ni, Mn, C) are susceptible to dissolve into sodium. Nevertheless, this phenomenon, which depends on diffusion near the interfaces, remains very weak because the diffusion coefficients of steel compounds are very low. Corrosion kinetics depends on sodium physical parameters (temperature and flow rate) and sodium chemistry (mainly oxygen activity). Even if it is generally considered, this "generalized" corrosion is only significant for high temperature and for oxygen contents above 5 ppm. It is generally considered that a SFR requires to be operated with an oxygen content below 3 ppm, in normal operation, to limit the corrosion and consequently the contamination and associated dosimetry during handling or repair operations.

In the primary circuit, it is generally considered that it is the oxygen content which determines the sodium quality control strategy, the low hydrogen content having no significant consequences on the operation and the behavior of structural materials.

In case of pin rupture, some gaseous fission products (caesium, iodine, xenon, krypton…) are released in the sodium and cover gas. In case of "open" rupture, some fuel particles can be released.Tritium, produced by boron carbide B_4C or by ternary fissions of ^{239}Pu, is continuously released in the primary sodium and can diffuse through walls to intermediate circuits, energy conversion system and finally into the environment. Tritium is trapped with hydrogen in cold traps.

In the intermediate circuit, the main event taken into account is the occurrence of a sodium-water reaction induced by a loss of tightness of one or more tubes in which liquid or steam water circulates under pressure. Main reaction involved is the following one:

$Na(l) + H_2O(l,g)$ ➔ $NaOH(l) + 1/2H_2$ (g) $\Delta H = -162$ kJ/mole
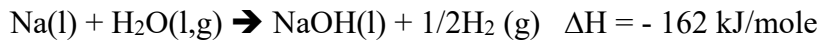
It is an almost instantaneous reaction in a liquid Na medium, whatever the temperature. Then the decomposition reaction of NaOH can occur with sodium excess:

$2\ Na(l) + NaOH(l)$ ⬅$^{2-1}$➔ $O^= + H^-$
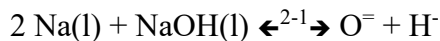
Another situation can generate the production of NaOH: it is about any task (inspection, repair, handling...) which generates an opening of circuit with potential ingress of humid air and reaction of water vapor with residual sodium present on the walls of the system, after Na draining. Afterwards, stress corrosion cracking (SCC) can be induced by residual caustic solution (NaOH-xH2O) during operation, after sodium filling and temperature rise.

In all circuits, some events can introduce carbon products: lubricating oil for pumps (PFR 1991, Phenix), or grease for mechanisms. In case of contact of oil with sodium, the chemical reactions produce gases (H2, CH4, C2H6, C2H4, traces of heavier hydrocarbons…), tar-type heavy hydrocarbons, which can adhere to the walls and coke-type carbon suspension mainly at the surface of the sodium. Particles and aggregates of carbon and tars can plug narrow gaps. Part of this pollution can be trapped on filters. In KNK-2 (Germany), some metal shavings have been also detected, due to repair operation.

3 Impurities monitoring

With regards sodium quality control, the main elements of interest to be monitored by the operators are oxygen $O^=$ (for monitoring the corrosion of structures and the core), hydrogen H^- (for detecting the reaction between sodium and water) and carbon (for assessing the risk of carburization/ decarburization of structural materials. Oxygen and hydrogen contents can be roughly estimated together with a plugging-meter or measured specifically with dedicated sensors or sampled in dedicated crucibles then analysed at Laboratory.
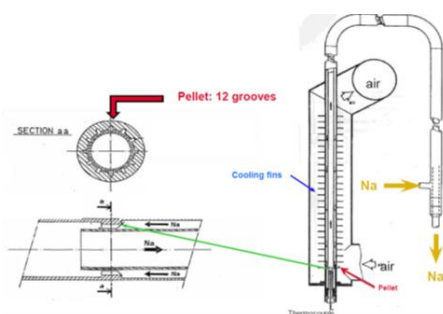
3-1 Plugging-meter

The purity of both primary and intermediate sodium is continuously assessed on reactors by plugging-meters able to quantify impurities as a whole (Fig:1). Their operating principle consists in cooling a continuous flow rate of sodium by-passed from a sodium main line, which then flows into a flow restriction area referred to as grooved "pellet", placed at the coldest point. When sodium temperature at the "pellet" is decreased down to a certain value, a solid phase is formed by crystallization of impurities on the walls of grooves, which generates a flow restriction, and so a decrease in the flow rate. This temperature is referred to as the "plugging temperature" (Tp), and indicates the temperature below which crystals are formed by heterogeneous nucleation. The plugging temperature (Tp) makes it possible to assess impurity concentration, and so to check compliance with operating rules, ie to maintain oxygen content below 3 $\mu g.g^{-1}$(ppm). In addition, it helps control the operation of the purification device, *i.e.* the "cold trap" (see hereafter). Plugging meters are devices easy to operate, but requires

sometimes a specialized personnel for reading and interpreting measurement results. During SUPERPHÉNIX operation, new operating rules for Plugging Meters have been suggested, using the so-called "un-plugging temperature" Tup, a more accurate data, very close to the saturation temperature Tsat, and used after 1991.

3-2 Electrochemical measurements

Electrochemical measurements using potentiometric probes have been studied to monitor the chemistry of sodium: each of these probes is specific to measuring the concentration of a chemical element (O, H, C) in sodium, and provides a continuous response over a wide range of contents. Although early tested in reactors such as EBR-II (O-meter), their use has remained essentially limited to the experimental facilities. However, given their specificity and the increased speed and accuracy of measurement compared to plugging meters, new developments have been taking place since about twenty years in several countries. The principle is that of a chemical potential measurement between liquid sodium and a reference integrated in the probe, of which the chemical potential of the element to be measured is fixed. The potential measurement responds to Nernst's law. Development of electrochemical sensors requires satisfying 4 main criteria: accuracy, low temperature coefficient ($\Delta E/\Delta T$), low signal time drift and high resistance to thermal shocks (for electrolyte made of ceramic).

Oxygen-meters using Yttria-doped thoria (YDT)-based electrolyte, with a reference electrode ie In-In_2O_3 and sometimes air reference, have been developped successfully for measuring oxygen in liquid sodium, since 1970's. (Fig 2) In CEA and IGCAR (India), yttria-doped thoria electrolyte, with a reference electrode In-In_2O_3, is currently under development. However, operational feedback has underlined this electrolyte, as any other ceramic, had a low thermal shock resistance leading to short lifetimes, if some protecting devices and dedicated operating procedures are not implemented to protect the cell. More recently, the low dosimetry due to thorium has motivated in different countries new studies with innovative electrolytes.

Fig F1 Plugging-meter   Figure F2: Oxygen-meter (AERE HARWELL)

Main function of Hydrogen-meters is to detect sodium-water reactions, which generate production of H_2 and its partial dissolution in sodium. [2]. Two devices based on different principles have been developed: a first measuring method lies in hydrogen property of diffusing through a nickel membrane 300 µm thick. It is set-up on a by-pass line in which sodium is flowing (so called "conventional device"); behind this membrane an ultra-vacuum circuit is maintained by ionic pumping; a mass spectrometer then measures the hydrogen concentration

in vacuum (Fig 3). These diffusion type H-meters were implemented in all SFRs in China, France, India, Russia, UK, USA…
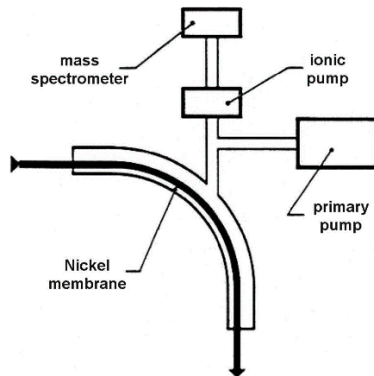

Fig 3: H-meter with Ni membrane (CEA))   Fig 4: Electrochemical H-meter IGCAR

A different hydrogen meter based on measuring the electrochemical potential was developed beginning of the eighties in UK then more recently by IGCAR (India) (Fig 4). It consists of a probe containing two electrodes in a thimble made of pure iron, and immersed in secondary sodium. Hydrogen diffusing through the thimble generates a potential difference between the measuring electrode ($CaBr_2$-CaHBr) and the reference electrode. So this potential difference is correlated with the hydrogen content. This device was successfully tested in India in FBTR then in France on Phenix reactor [3] and on Na facility in CEA Cadarache. Hydrogen-meters can be also set-up on cover gas.

Electro-chemical carbon-meters, developed initially by BNL (USA) then AERE Harwell [4] then more recently by IGCAR (India) [5] can be used for detecting any oil leak into sodium and more generally for surveillance of the purity of the coolant with regards carbon. It uses a molten electrolyte ie Li2CO3-Na2CO3 with graphite reference electrode. A carbon-meter has been set up on PFR (UK).

3-3 Sampling systems

Two sampling systems were used on PHÉNIX in order to carry out discontinuous measurements for the follow-up of primary sodium quality. TASTENA (Fig. 5) was a cup immersed in the free surface of (primary or secondary system, or storage drum) sodium, and ACTINA consisted of test tubes used for sampling primary sodium flowing in a pipe, that are very quickly frozen. TASTENA was also used on Superphenix. Measurements were later carried out in a radiochemistry laboratory, for measuring of activation products (^{22}Na, ^{24}Na …), activated corrosion products (^{54}Mn, ^{60}Co…), fission products (^{134}Cs, ^{137}Cs ^{131}I, ^{3}H…), impurities (Ca, K, C…), and inactive metallic elements (Fe, Cr, Ni…).
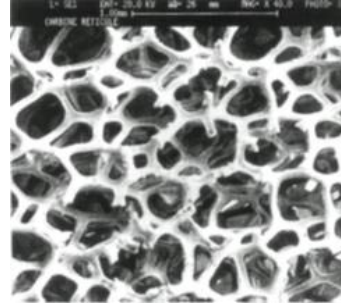
Fig. 5 TASTENA device. *Fig. 7 Reticulated vitreous carbon*

4 Sodium purification processes

Several main sodium purification processes are implemented among them two with regards to oxygen and hydrogen control:

- cold trapping based on the crystallization of Na_2O and NaH, by lowering the Na temperature below the saturation temperature and thus creating the conditions for Na_2O and NaH nucleation and growth on a steel packing or cooled walls (for NaH) distributed in an auxiliary cooled vessel., as shown in Figure 6.a-b-c

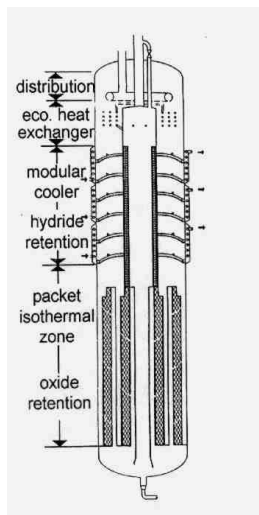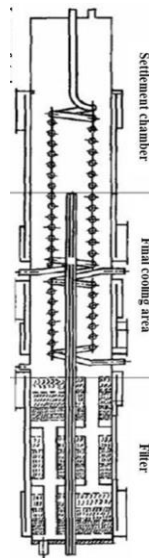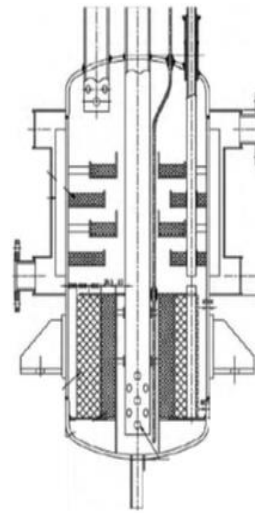*FIG. 6-a Cold trap (CEA)* *Fig 6-b IPPE* *Fig 6-c (IGCAR)*

This process is efficient because the respective solubility's of oxygen and hydrogen are very low [1]; the solubility reaching a value around nil, near the melting temperature i.e. 97.8°C (this is a property specific to sodium, in comparison with other liquid metals, used as coolants). The highest purification rate and loading capacity can be also obtained with optimized designs of cold traps, (capacity: maximum amount of impurities trapped in the cold trap). A computer tool has been developed by CEA in order to support the cold trap designer and later on the operator; this tool has integrated kinetics, thermal exchanges, pressure drops…

- Hot trapping or "getter" operation based on the capacity of the selected material (i.e. zirconium-titanium alloy for oxygen) to oxidize when it is placed in the presence of sodium containing some amount of dissolved oxygen. This last process is selected for small sodium volumes to be purified and when the risk of Na_2O dissolution by loss of cooling function in the cold trap is unacceptable. As example, the $Zr_{0.87}$-$Ti_{0.13}$ alloy has been qualified for hot trapping in an irradiation loop for Phenix [6]. For hydrogen trapping, "hydride" traps (ie yttrium foils) could be also be set-up.

- Filtering: Filtration makes it possible to extract the particles present in the sodium. A staggering of filters makes it possible to retain particles of extended particle size range, during the first sodium filling, from the storage tanks to the reactor itself. Then a dummy core equipped with dummy filtering assemblies (wire meshes) is installed to reproduce the core pressure drop and perform qualification tests of various components and systems. In steady-state operation, it is considered that sodium chromite particles can be present in liquid sodium, with limited low size range (about 1 to 50 μm): in SFRs, no filters were generally installed in sodium, except in the pumps ie for PFR.

- Adsorption for activated corrosion products: EBR2 operators used traps with Ni foils for ^{54}Mn, set up in a fuel assembly above pins ; this process seemed less efficient for ^{60}Co [7]. This process has been investigated also in Germany for KNK-2 and in France in SILOE.

- Adsorption for cesium, released by fuel cladding ruptures: Foam of reticulated vitreous carbon (RVC) (Fig 7) is used to trap cesium, at temperature around 200°C : it is possible to reduce contamination by a factor 10 for each transfert through the trap. It was applied successfully at EBR2, FFTF [8], BOR60, RAPSODIE, …

5 Conclusion

The quality control of sodium and its purification is performed satisfactorily thanks mainly to cold traps. Several innovative options have been developed in order to satisfy new requirements: high purification rate, optimized capacity and reduced heat losses. It is also possible to get a very high purity thanks to getters. Most of the Na processes developed in CEA can be adapted to various non-nuclear applications using sodium, without significant changes.

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