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FBR PRIMARY SODIUM CHEMISTRY CONTROL :

CONTROL APPROACH AND EXPERIENCE

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ABSTRACT

Primary sodium quality control ensures that the risk of plugging is avoided and thus, not only is corrosion limited, but also the contamination of the circuits and components. The objective of this note is to decribe the control approach that has been chosen for European reactors, to set down the information derived from the experience that was gained when the SPX primary sodium was polluted in 1990, and, lastly, to recall the main development lines as regards sodium quality control (R & D, instrumentation).

1 - INTRODUCTION

No primary circuit sodium of a European Fast Breeder Reactor had ever, while in operation, been subject to such extensive pollution as that of the Super-Phenix reactor at the beginning of summer, 1990. The purification system proved its efficiency in restoring satisfactory quality to the sodium as regards the operating specifications of the reactor within a reasonable period of time, without any danger of an active sodium leak, thanks to the concept of the integrated cold trap. Moreover, the corrosion of the structures and fuel element cladding induced by the polluted sodium (15 ppm) was limited to that produced by 3 months of normal operation ([O] < 3 ppm). However this incident did show :

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- the need for a very strict control of the cover gas quality, in order to avert pollution,
- the difficulty of interpreting plugging curves in terms of plugging temperature, especially when corrosion products are present in slight quantities. New interpretation rule have been proposed and adopted,
- some lack of knowledge in sodium physico-chemistry, despite the great number of studies that have been carried out in European and other laboratories.

The purpose of this paper, therefore, is to recall the approach for primary sodium quality control, to analyse the Super-Phenix pollution incident and its various consequences, and finally to deduce the main improvement lines of sodium quality surveillance, especially in the frame of the next European reactor, E.F.R.

2 - PRIMARY SODIUM QUALITY CONTROL APPROACH

The problems arising in sodium technology for reactor operation have been solved on a long term basis by the choice of the policy of maintaining the sodium at its "maximal" pUrity. This policy can be summed up by five essential recommendations :

a - supply high purity sodium of "nuclear" quality,
b - clean the primary circuit before filling (structures, gas),
c - carry out a purification campaign of the sodium supplied to the primary circuit during the first temperature rise (start-up purification),
d - ensure the continuous surveillance of sodium quality as regards oxygen by means of reliable devices, and maintain or not the purification systems in continuous operation,
c - limit the introduction of impurities (O_2, H_2O) into the cover gas by surveillance of the quality of this gas on one hand, and by controlling the containment and the quality of the gas during handling operations on the other hand.

Let us examine these five recommendations :

2.1 - Suplying nuclear quality sodium enables the number of disadvantages caused by the presence of certain elements [1] to be reduce. We can mention among these elements :

- calcium, barium and silicon, which can cause plugging,
- carbon, changes in the mechanical properties of the steels,
- uranium, boron and lithium, nuclear reactions,
- chlorine, bromine and sulphur, corrosion phenomena,
- potassium, activity in the cover gas (A_r),...

2.2 - Cleaning the primary circuit before filling by mechanical cleaning then by heating followed by sweeping with an inert gas, enables the elimination of any significant quantity of filings and the reduction of the quantity of oxygen available on the surface for the oxydation of sodium during primary circuit filling.

2.3 - Carrying out sodium purification during the first temperature rise enables the oxygen and hydrogen from the metal oxides - less stable than sodium oxide - to be removed from the system along with the gases adsorbed on the structure surfaces (O_2, H_2O).

The purification campaigns carried out on SNR300 and SPX have been described in [1]. The great volume of trapped impurities justified the choice of a high capacity cold trap for the start-up purification of these two reactors.

2.4 - During operation, primary sodium circuit purification must achieve an essential objective : limit the oxygen concentration to an acceptable value as regards corrosion. Corrosion actually increases the dissolving of metallic elements in the primary sodium whether these are oxidized or not, in particleS or dissolved form, some being active. These elements contaminate the structures by diffusion or depositing, especially those components that can be removed in case of failure, which means that cleaning and decontamination operations, necessary before any intervention, will be more difficult.

In France, it is considered that an oxygen concentration of up to 3 ppm allows the reactor to function without any risk of inacceptable contamination. On the other hand a concentration of over 5 ppm is undesirable. If these criteria are respected, when the sodium is cooled during a reactor shutdown, the risk of plugging of small openings by sodium oxide deposits (or hybrides when there is a high hydrogen concentration) is definitely averted.

UK view is that oxygen level can be in range up to 10 ppm. Corrosion allowances have assumed 10 ppm and it is expected improve friction/wear at oxygen levels in range of say 5-8 ppm.

The purification system also enables the contamination level of the primary circuit to be acted upon directly, by retaining in the cold traps a part of the activated corrosion products (^{60}Co, ^{54}Mn, ...), fission products released during possible clad failures (^{137}Cs, ...), tritium, and thus reducing any release of the latter into the water circuits [2].

Thus, to maintain or not the primary purification in continuous operation has to be considered, taking into account :

- the specification on oxygen concentration,
- the cold trap efficiency in regard to corrosion products (and associated consequences as activity,...),
- the amount of hydride possibly trapped in the cold trap

(function of the cold point temperature) which reduces the capacity of the primary cold trap, although there is any specification on hydrogen on primary sodium.

As already said, an oxygen concentration higher than 5 ppm allows a better tribological behaviour to be obtained, but no mechanical problem has even been observed with low oxygen concentration sodium.

For all European fast breeder reactors, primary sodium chemistry control as regards oxygen (and also hydrogen) is ensured by a plugging indicator whose reference indication is plugging temperature. The indicators set up in PFR, KNK II and SNR 300 are equipped with a fast unplugging system by mechanical shifting which enlarges the passage cross-section area.

A periodical check of the metallic elements present in the sodium is carried out by sampling (cup or tube) [3].

2.5 - Limiting the introduction of impurities into the cover gas and controlling the latter's quality will, of course, limit sodium pollution by acting at its source. Oxygen reacts, in fact, with the sodium aerosols, thus fixing them on their place of deposit. It also reacts with the free surface of the sodium, or the existing sodium film, on the wetted surfaces, due to sodium volume variations.

Quality control is usually carried out by chromatography in the Phenix, PFR, SNR 300, and KNK II reactors. In SPX1, before the 1990 sodium pollution, the control was done by chromatography after sampling. It is, of course, the nitrogen that is controlled ; control specifications vary between 1000 ppm for PFR and 3000 ppm for SPX. The other gases that are controlled can be the hydrogen that can show a possible sodium-water reaction, the methane that can show a grease or oil reaction with the sodium, He, CO ...

3 - THE ACCIDENTAL POLLUTION OF THE SPX PRIMARY SODIUM

A considerable pollution had affected the primary circuit of SNR 300 [1] before its commissionning. This was caused by moisture entrainment in the cover gas from the radiation shield material (basalt) of the roof stab. Therefore, during the whole start-up purification stage, the primary plugging temperature depended on the moisture ingress which was a function of the sodium temperature. An estimation was made of the quantity of impurities trapped in the form of sodium oxide and hydride, produced by the above mentionned pollution and by the normal pollution, that was anticipated, during the purification campaign following the first sodium temperature rise [1] : approximately 930 kg of Na_2O and 100 kg of NaH.

The sodium of SPX was polluted during reactor operation in June 1990. The difference between the oxygen concentration between two sampling points on an argon line enabled the cause of the high oxygen pollution (air) to be identified : the failure of a compressor membrane of an activity measurement channel. During nominal power build-up, an evolution of the information given by the two plugging indicators (Figure n°1) was observed, expressing a rise of the impurity content in the sodium : a decrease of the low level temperature step duration Dpb (T = 110°C), rise of the low unplugging temperature Tdb, rise of the low plugging temperature Tb1, corresponding to Na_2O, and high Tb3 attributed to chromite content, appearance of an intermediate plugging temperature Tb2. On the 1st of July, the plugging temperature Tb1 reached the limit value of 150°C. The reactor was shut down on the 3rd of July. Difficulties in interpreting the plugging temperature and the inaccuracy of the readings made it difficult to assess the exceeding of the Tb > 150°C criterion (to shut down immediately the reactor). The temperature of the sodium was thus brought down to 250°C, in order to maintain the sodium temperature above the saturation temperature (~210°C) (T = 250°C : hot shut-down). The oxygen concentration in the sodium had reached the maximal value of 15.5 ppm, deduced from the low unplugging temperature by using the relation Tsat = Tdb - 5°C (established in test facilities) and Noden's solubility law [4]. This value was confirmed by the measurement of the saturation temperature Tsat, according to the partial plugging method [5].

An evaluation of the quantity of oxygen that was introduced, using the nitrogen balance, was carried out : 117 kg O, that is to say 453 kg Na_2O or 0.200 m^3. In terms of impurity volume, this pollution is pratically the same as that anticipated and eliminated during the start-up purification campaign [1], 248 kg Na_2O and 158 kg NaH, that is to say a volume of 0.225 m^3. The sodium was purified by means of the integrated purification system (Figure n°2) made up of 2 cold traps [6] : 6 cartridges were necessary to purify the sodium. The system fulfilled its function very satisfactorily, without any risk of active sodium leakage, despite the fact that cartridge handling had to be carried out [7].

The follow-up of pollution evolution, then of the purification campaigns allowed considerable information to be gathered concerning sodium quality surveillance, such as :

a - during the cooling of the sodium following the reactor shut-down, the disappearance of the intermediate plugging temperature Tb2 was observed ; it reappeared at each sodium temperature rise, over 350°C. Although Tb2 corresponds to an impurity of very low concentration, tests with its identification as objective were proposed and are being carried out by the CEA. If we refer back to corrosion studies that were made in the past, a compound (Fe, O, Na) could be involved, in a form to be determined [8] [9] [10] : a chelate that may be stabilized by another element, instable ternary oxide... The presence of this impurity complicated the interpretation of the plugging curves in terms of plugging temperatures.

b - The most reliable information provided by the plugging indicator concerns the low unplugging temperature and the duration of the low temperature level. In fact, the oxidation of the steel elements in the sodium made a classic interpretation of the curves in terms of plugging temperature very difficult. Only a more thorough analysis that integrated the events sequence enabled an evaluation to be made of the level and the nature of the pollution by oxygen.

c - An expert investigation of the cold trap cartridges was made by sampling and chemical analysis. It was ascertained that the cold trap has a low trapping efficiency as regards corrosion products, which are present in the sodium in dissolved and particle form. This is not an inconvenience insofar as we know that the maximum size of these particles is small (5 μ) and cannot lead to the plugging of reduced cross areas. In addition, we know that these products will settle preferentially on the intermediate heat exchanger walls during the next start-up when the reactor becomes anisothermal and therefore favours depositing on cold walls.

d - Finally, the quality of the cover gas must be controlled by means of a chromatograph that enables any pollution to be detected early and its nature to be defined : N_2 reveals pollution by air, H_2 pollution by water and wet air, CH_4 pollution by oil or by any other carbon product.

4 - DEVELOPMENTS IN SODIUM QUALITY CONTROL

Efforts have been made in Europe to improve sodium quality control. In addition to a progressive improvement in sodium and cover gas quality control policy, work has been carried our in the following domains :

a - Increase in cold trap availability and capacity by raising their filling rate thanks to a better knowledge of the crytallization mechanisms in cold traps [5] [11] [12] [14] and to the development of a computer simulation code, VICSEN [12].
The development of the PIRAMIDE concept [15] has made it possible, thanks to a modular cooling device, to significantly increase their filling capacity (Figure n° 3).

b - Improvement in plugging curve interpretation, notably of the length of the low temperature level [13] and of the estimation of the saturation temperature [5],

c - Improvement of specific instrumentation for the measurement of oxygen, hydrogen, tritium, and carbon content. Oxygen sensors with <u>thorine</u> with an addition of yttrium oxide (electrolyte of the electrochemical pile) have been successfully developed by HARWELL [16] and INTERATOM [17] : the use of a reference electrode in In/In_2O_3 enables a deviation in time of the signal to be avoided. Indicious mounting also enables the risk of a thermal shock leading to a break in the ceramic to be limited [16]. A tritium meter has been developed by INTERATOM [17] (Figure n°4) in order to determine the tritium content of the sodium (Figure n°5). A carbon meter, developed by HARWELL [16], set up in 1977 on PFR, is still in successful operation. Finally a diffusion hydrogen meter was mounted in 1985 on a primary circuit of Phenix [2] and the results obtained have contributed to acquire a better knowledge of the behaviour of hydrogen and tritium in the different circuits of a fast reactor.

d - Better knowledge is to be gained of sodium chemistry in the case of high pollution : this essentially means acquiring more thorough knowledge of the chemical form and the behaviour of corrosion products : solubility, thermodynamic stability according to the thermohydraulic characteristics of sodium. Endeavours will also be made to establish the dissolution kinetics of sodium oxide in sodium in the form of crystals within the sodium or in the form of an oxided film at the sodium-cover gas interface.

5 - CONCLUSIONS

In June 1990, a considerable quantity of air entered the cover gas of the SPX primary circuit, leading to a marked increase of the oxygen content in the hot sodium and consequently a noticeable increase of clad corrosion and the partial dissolving of these products, whose presence in the sodium made the interpretation of the plugging temperatures very complex. The extensive information provided by the treatment of this pollution incident, by the results of the laboratory studies it led to, by the thought given to this problem by the various European laboratories which are collaborating in order to supply the simplest and best-adapted solutions, should enable a policy to be perfected for the control and maintenance of sodium quality for primary circuits.

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