

Impact of Main Radiological Pollutants on Contamination Risks (ALARA) Optimisation of Physico Chemical Environment and Retention Technics during Operation and Shutdown

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1- Introduction

The goal of this paper is to precise the behaviour of different radiochemical species in the primary coolant of PWR plants. Managing these pollutants must lead to limit Reactor Coolant System (RCS) walls “over-contamination” to decrease the dose rates during the maintenance operations (ALARA).

In French Plants, Co 60, silver and antimony represent the major radiochemical pollutants which require a good knowledge of the different phenomena to ensure the lowest contamination risks. The stakes deal with the control and the optimization of collective and individual doses including waste treatment with low costs. These stakes represent primordial elements of nuclear acceptability.

2- Normal contamination of circuits

In French PWR plants :

- More than 90% of integrated doses are due to contaminated walls in contact with the primary coolant because of activated corrosion products.
- 80% of total dosimetry are integrated during outages.

In the absence of specific pollution, the mean contribution of out of core deposits to dose rates is as follows (results expressed as percentage equivalent dose rates in Sv/h) :

- Co 60 = 50% (the older the plant, the greater the Co 60 quantity);
- Co 58 = 30% (with a higher level in 1300 MW units);
- Ag 110m + Sb 124 + Cr 51 + ... = 10%.

Usual contaminants come mostly from materials/coolant interactions leading to soluble, particulate, colloidal products transport and corrosion products activation (table 1).

Nuclides / Half-life	Gamma energy keV (% emission)	Beta energy keV (% emission)
Co58 / 71 days	811 (100%)	
Co60 / 5.3 years	1173 (100%) 1333 (100%)	318 (100%)
Ag110m / 253 d	658 (100%) 885 (80%)	86 (55%)
Sb124 / 60 d	603 (98%)	610 (51%)
Sb122 / 2.7 d	564 (66%)	1400 (63%)

Table 1: Gamma and beta energies and emission percentage (> 50%) of major pollutant nuclides

The dose rates can increase in case of more important corrosion products transport [1] or of incidental pollution. In the latter case, the ratio of species contributing to dose rates is modified.

3 - Incidental over-contamination

The major pollutants responsible for over-contamination in EDF plants are :

- Co 60 coming from stellite degradation ;
- Ag 110 m coming from control rod perforation and probably from materials like seals ;
- Sb 122 / Sb 124 coming from pumps of auxiliary system.

Given the importance of over-contamination with respect to dosimetry, representing 10 to 30 % of outages dosimetry in the concerned units, a specific program is being set up in France, in the context of the ALARA project. The goal is to optimize diagnosis, surveillance, prevention and remedies to reduce pollutions even though priority is set on prevention.

3.1 – Cobalt 60 contamination – “hot spots”

3.1.1 – Hot spots sources

In most cases, hot spots are due to particles of cobalt activated by a neutron flux (Co 60) mainly from hard facing surfaces equipments (stellite, rich in cobalt) in the RCS (valves, pumps, internals, etc.).

3.1.2 – Impact on dosimetry

The contribution of hot spots to shutdown dosimetry may appear to be marginal in French PWR reactors (2 to 4 %), but becomes more significant (15 to 25 %) for the units affected. This excess dosimetry has to be taken into account, particularly for the most exposed workers. Approximately ten French PWR units have been affected by this phenomenon over the last 15 years [2].

3.1.3 – Hot spots behaviour - Indicators

Surveillance is designed to inform the site as early as possible, of the presence of hot spots (mapping) in order to take the appropriate measures to prevent their propagation and/or to eradicate them.

During unit operation, most hot spots will remain fixed to the fuel. Others may fall, by gravity, to the bottom of the pool or the low points of the primary coolant system or be trapped in the special devices.

The most common locations are as follows:

- Thermal sleeves of the pressuriser
- Steam generator packing glands
- Valves of the primary cooling system.
- etc.

After connection of the Residual Heat Removal System (RHRS), some hot spots may migrate into this circuit and be deposited or fixed. The most common locations are: the pumps, heat exchangers and valves of the circuit.

An underwater pool cleaner should pass through the pool out after discharging. In this case, particularly high equivalent dose rates, equal to or greater than 1 Sv per hour, measured in contact with the filters, represent the last indicator of the possible presence of hot spots, before draining of the pools.

Since no warning signs have been identified yet, to indicate the occurrence of hot spots, it was decided to concentrate on preventive filtering, trapping hot spots as close as possible to their source to eliminate them.

3.1.4 – Preventive strategy

Stellite limitation

It concerns all the units by performing the following actions:

- limiting the use of cobalt based components in contact with the primary coolant ;
- removing stellite particles produced during some maintenance operations (e.g. lapping).

Preventive filtration with specific devices

The simplified diagram below illustrates the principles of the preventive filtration methods which are proposed (Fig. 1). It consists on the filtration of all the effluents which could transport hot spots outside the Reactor Building.

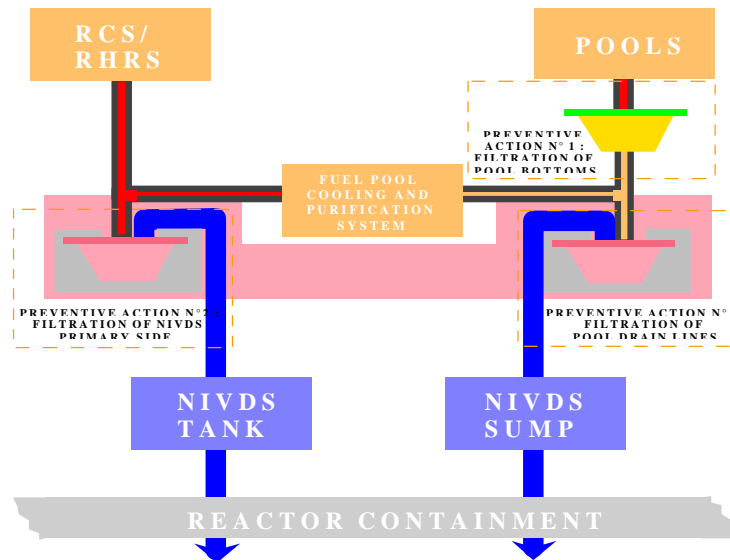


Fig. 1: Preventive filtration methods

The drains of pools are important routes for hot spots, before they spread through the systems. The installation of fine filters, an initial containment barrier, is proposed for the drain orifices of each pool :

- refuelling cavity located in the reactor building ;
- Spent fuel pit, located in the fuel building.

Appropriate filters are required :

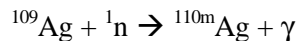
- Truncated sieves ;
- 50 µm mesh.

The drain lines of the primary cooling circuit represent the second main vector for the movement of hot spots. As a preventive measure, the installation of sleeves on the main migration channels enables sensitive systems to be filtered. This filtration prevents the spread of hot spots and ensures that they are eliminated. The filtration system is installed in the reactor building or the fuel building, depending on the shutdown phases, thus enabling all the pools to be treated with the same device.

3.2 - Metastable silver 110 contamination

3.3.1 – Silver sources

In some PWR units, the primary and auxiliary systems are subject to metastable silver 110 (Ag 110 m) contamination, due to silver 109 neutronic activation :



The most likely root causes for silver leading to the observed Ag 110m pollutions may be as follows :

- the neutron-absorbing alloy Ag-In-Cd contained in control rods ;
- some silver coated seals.

For French NPP, the major source for Ag110m is natural silver. Moreover, for the French plants polluted with Ag 110m, the quantity of metallic silver released in the primary circuit could be roughly estimated 1-10 grams.

3.2.2 - Impact on dosimetry

Ag 110 m systems contamination can be very penalising since it impacts :

- dosimetry integrated during maintenance operations ;
- shutdown schedule ;
- control rods management (examination and rejection).

It can represent 5 to 15 % of a shutdown total dosimetry.

Auxiliary systems most sensitive to silver contamination are :

- The Residual Heat Removal System (RHRS) heat exchangers and
- The Chemical and Volume Control System (CVCS) non regenerative heat exchangers ;
- The purification system downstream the CVCS demineralisers.

Ag 110m can contribute to more than 90 % of the dose rates around some parts of auxiliary systems.

3.2.3 - Silver behaviour - indicators

The volumic activity of Ag 110m in the primary coolant stays at a low level (1-10MBq/t) due to the low silver solubility in reducing medium. Activity increases higher than 10 MBq/t indicate a poor silver removal in the CVCS or an important silver source.

During the shutdown, in case of silver pollution, the observed levels of activity increase dramatically (several decade) during and after the oxygenation. This could be explained by :

- Changing from reducing to oxidising chemical conditions ;
- Simultaneously by temperature and pH changes.

At the opposite from other corrosion products for which dissolution is maximum at the “oxygenation peak”, silver dissolution shows a trend to go on after the effective oxygenation (dissolved oxygen concentration close to 1 mg/kg).

Generally, the silver peak activity appears 1 to 12 hours later after the Co 58 peak. The table 2 gives further data about silver peaks for the French plants in the year 2000 during shutdown.

Standardized plant series	Ag110m average	Ag110m maximum	Ag110m minimum
900 MWe	1.47 GBq/t	6.17 GBq/t	0.07 GBq/t
1300 MWe	0.16 GBq/t	0.48 GBq/t	0.04 GBq/t

Table 2: Ag 110m, 900 and 1300 MWe French Standardized plant series in 2000.

There is no clear correlation between the Ag 110m activity peak and the other corrosion products. A first level of assessment can lead to consider that RCS is polluted when Ag 110m peak during shutdown is higher than 0.5GBq/t on primary coolant sampled on the Nuclear Sampling System (NSS).

The observation of different and unpredictable behaviour of silver, mostly measured by gamma-spectroscopy and particularly during different cold shutdowns, even in a same plant, can be surprising when the operation schedule seems stable. Measurements demonstrated that it is possible to decrease a lot the steam generator channel head silver contamination and to increase the CVCS exchanger.

Depending on chemical environment and physical properties (pH, redox potential ...) silver would be :

- In ionic form in solution, Ag (I) cation;
- In metallic form, Ag (0), likely under colloidal form (200-600 Å).

Studies, conducted by EDF, demonstrated the essential simultaneous impact of redox potential, pH, and temperature on silver behaviour. In a large range of pH (corresponding to the nominal operating conditions or to the shutdown ones at 300°C, 80°C and 30°C) and in different locations of RCS, CVCS and RHR, Ag(0) and Ag⁺ can be simultaneously found on thermodynamic stability diagram and are very sensitive to the redox variation and the concentration. Actually, it seems that the physical and chemical conditions of the primary coolant set silver mostly on the limits of different existence areas on considering the corresponding pH-potential diagrams.

On the opposite, pH is determinant on colloids behaviour. Repulsion between them is the lowest at iso-electric point, meaning at pH for which the zeta potential is zero.

In an other hand, kinetic behaviour of silver in primary coolant conditions is not known well enough.

Thus, optimization of its removal is difficult, the preferential deposition of Ag 110m taking place in “cold points” of auxiliary systems exchangers, where thermal gradient is important. This also may elucidate the apparent unoperating conditions of the purification. The goal will become to manage the silver so as to transport it in the form able to be removed by the purification system.

3.2.4 - Preventive strategy

Control rods non destructive tests

Eddy current and ultrasonic non destructive control rod tests have been performed. Doubtful rods or rods with perforation indications are systematically replaced with either chromium or nitride coated rods.

Purification during end of cycle shutdown

Ag 110 m purification is performed on a dedicated ion exchanger operating at the maximum possible flowrate [3].

During shutdown, when the filters are replaced, purification must not be suspended. Filters consistent with colloids removal are required (lower mesh with zeta polarised filtration medium). Thus, silver removal is improved and downstream resins pollution may be avoided (poisoning by colloids). If the upstream filter is not redundant, the filter replacement must lead to reduce by half the CVCS flowrate purification to minimize resins pollutions.

The background and the resin features show that macroporous mixed-bed would be the most adapted for soluble silver and silver colloids. The pressure drop must be specially monitored.

Until now, the feedback demonstrated that withdrawing lithium of the primary coolant with a non lithiated mixed bed ion exchanger during shutdown, giving the lower pH, improves the silver removal efficiency. Without fuel cladding failure, lithium can be eliminated starting from the rods drop.

3.3 - Antimony contamination

3.3.1 – Antimony sources

In some French PWRs, ^{122}Sb and ^{124}Sb volumic activity peaks have been observed. These peaks were higher than ^{58}Co peaks (table 3). They impacted dosimetry and waste management.

^{122}Sb and ^{124}Sb are two multi gamma emitters with radioactive half-life of 2.7 days and 60.2 days respectively. Thanks to its short radioactive half-life, ^{122}Sb has a low impact on health physics, but it allows to determine antimony sources.

Standardized plant series	Values	Sb 122 (GBq/t)	Sb 124 (GBq/t)
900 MWe first series	Mean	21	14
	Maximum	200	110
900 MWe	Mean	25	18
	Maximum	160	140
1300 MWe	Mean	14	11
	Maximum	70	55

Table 3: Mean and maximum volumic activities encountered at the oxygenation peak

Two major sources have been identified in French PWRs :

- 1 - Pumps bearing wear in the Boron Recycle System. These bearings are made with graphite impregnated with about 10 % of antimony ;
- 2 - Beryllium-Antimony source rod failure, but there are source rods only for the first reactor cycles.

A few activated antimony grams can explain such peaks of ^{122}Sb and ^{124}Sb . So, calculations demonstrate that about 7 grams can lead to a ^{124}Sb peak of 100 GBq/t.

3.3.2 - Impact on dosimetry

The important antimony released activity has an impact both on dosimetry and waste management.

^{124}Sb deposited activities on the out-of-core surfaces increase a lot as it is shown in table 4.

^{124}Sb (GBq/m ²)	Before H ₂ O ₂	After H ₂ O ₂ injection
Hot leg	0.29	1.02
SG tubing	0.32	0.95

Table 4: RCS recontamination after a ^{124}Sb peak of 70 GBq/t

Thus, ^{124}Sb contribution to the dose rates can reach 10 % in some parts of circuits. And the dosimetry for maintenance during a plant shutdown can increase to about 5 % because of the ^{124}Sb contamination.

3.3.3 – Antimony behaviour

EDF studies, elaborating pH-Potential diagrams at normal operating conditions (300°C) and at forced oxygenation conditions at 80°C confirmed the behaviour observed on plants.

It seems that, in nominal conditions at 300°C, metallic antimony is likely the more stable in aqueous reducing medium (fig 3).

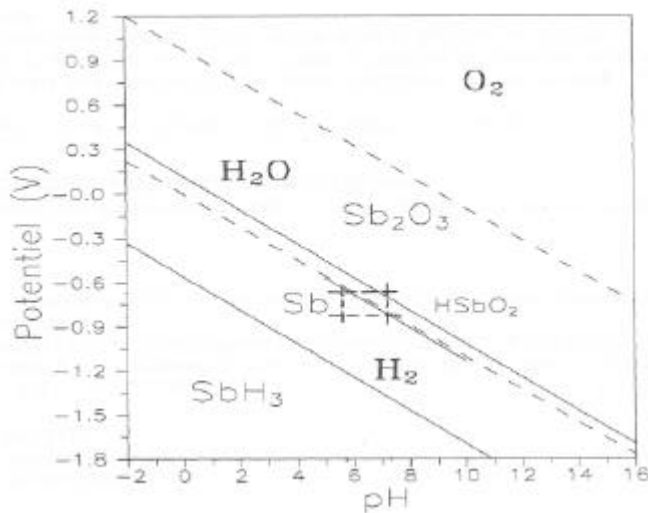


Fig 3: Simplified Pourbaix diagram for antimony at 300°C. The dotted line limits the RCS operating conditions

For shutdown conditions at forced oxygenation, it seems that the more stable species is at the limit of the SbO_3^- area in aqueous solution. Eliminating antimony as well as possible becomes easier in this zone (fig 4).

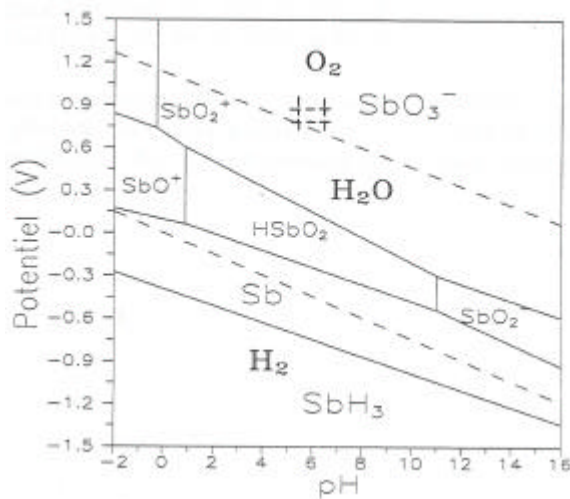


Fig 4: Simplified Pourbaix diagram for antimony at 80°C. The dotted line limits the RCS shutdown conditions at forced oxygenation.

3.3.4 – Preventive strategy

Pumps bearing replacement

To avoid antimony pollution, the incriminated pump bearings have been replaced by antimony free pump bearings . As indicated in the table below (table 5), this allows to make the ^{124}Sb peaks decrease.

Cycles	13	14*	15
^{124}Sb (GBq/t)	100	60	20

Table 5: Bearing replacement consequence during the 14th cycle

Shutdown purification

During oxygenation, antimony seems to be on a soluble form ($< 0.45 \mu\text{m}$). When an antimony pollution occurs, to improve purification by the ion exchange resins, reactor coolant lithium content has to be lower than 1 ppm [4]. In order to obtain acidic conditions, purification can be carried out thanks to non-saturated lithium cation bed demineralizers of the Boron Recycle System. Nevertheless, it should be noted that an acidic reactor coolant seems to increase antimony deposition on the primary circuit surfaces [4].

As for silver behaviour, to manage an antimony pollution, the operators face some difficulties linked to the different physical and chemical conditions of the RCS and the auxiliary systems. Except for removing the root cause, the objective consists in the optimization of the form of the antimony to enable the purification line to remove the pollution.

4 - Conclusion

EDF plants faces radioactive pollutions (i.e. Co 60, Ag 110m and antimony) leading to significant increases of shutdown dosimetry in affected units (10 – 30%) or increasing the contamination risk for personnel. Early detection in operation as well as during shutdown requires a good knowledge of their behaviour to set up appropriate solutions.

Replacing critical materials as soon as it will be possible should limit the source term. Limiting pollution in circuits need to implement chemistry and shutdown procedure to minimize over-contamination..

It is obvious that implementing specific chemistry and optimizing purification features (filters, resins and flowrate) warrant limiting the effects of this type of pollutions.

That's why studies are yet in progress to propose operators a chemical policy and adapted procedures for each type of radioactive pollution able to reduce the impact on dosimetry.

On other hand, a new specific gamma spectrometer - able to characterize on the field the nature of radioactive deposits, in order to improve diagnostic, is being developed.

References

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