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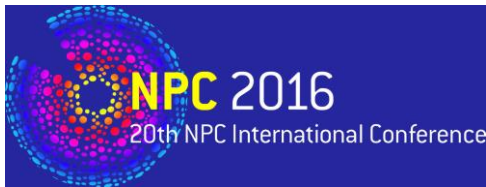
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^{110m}Ag behaviour in PWRs: Lessons learnt from the EMECC campaigns Paper Number: 81

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ABSTRACT

For 45 years, most of the time in collaboration with EDF, the CEA has measured the contamination of PWR circuits by gamma spectrometry using the so-called EMECC device. These measurements allow us to determine the surface activities accurately in order to study the behaviour of the activated corrosion products.

In case of pollution by ^{110m}Ag , the main lessons learnt from EMECC campaigns and primary coolant filtering campaigns as well are as follows:

- During oxygenation, ^{110m}Ag dissolves from the primary surfaces and precipitates on the cold parts of auxiliary systems before dissolving slowly from these cold parts. It leads to a sharp increase of dose rate in the vicinity of the cold parts of auxiliary systems.
- Because of the precipitation on the Nuclear Sampling System (NSS), ^{110m}Ag sampled via the NSS is not representative of the ^{110m}Ag volume activity of the Reactor Coolant System.
- Under oxidizing and acid conditions, Ag is trapped very well by cation exchange resins. On the other hand, silver is in an insoluble form (colloids) in a reducing medium and it is not trapped by ion exchangers.

INTRODUCTION

For 45 years, most of the time in collaboration with EDF, the CEA has measured the contamination of PWR circuits by gamma spectrometry using the so-called EMECC device. These measurements allow us to determine the surface activities accurately in order to study the behaviour of the activated corrosion products. According to the EMECC campaigns, two radioactive isotopes, ^{58}Co and ^{60}Co , contribute by over 80% to dose rates. Nevertheless in certain cases, ^{110m}Ag can be the major radio-contaminant. The most likely origins of silver leading to ^{110m}Ag pollution are the neutron-absorbing alloy Ag-In-Cd (AIC) contained in control rods, some silver coated seals (Bretelle et al., 2002) or the silver soldered connections of pressurizer heaters.

In the first part, based on EMECC campaigns and on primary coolant filtering campaigns as well, this paper mainly shows the typical variations of the ^{110m}Ag surface and volume activities during a cold shutdown. In the second part, the main lessons learnt from these measurements are presented.

EMECC AND FILTERING CAMPAIGNS

In order to study the behaviour of Activated Corrosion Products (ACPs) in the circuits of Pressurized Water Reactors (PWRs), two kinds of measurement campaigns are carried out by the CEA generally in collaboration with EDF:

- The EMECC campaigns which consist in measuring the activities deposited inside components (pipes, steam generator tubing, heat exchangers...) of the primary and auxiliary systems. The surface activities are measured by gamma spectrometry measurements using the so-called EMECC device designed by the CEA (Eimecke and Anthoni, 1988). The background noise and the volume activities are taken into account for each EMECC measurement in order to determine the surface activities only. Almost 400 EMECC campaigns in about 70 different PWRs have been carried out in France and abroad since 1971.
- The filtering campaigns which consist in measuring the activities trapped by ion exchange resins, the so-called mini-CVCS, or by ion exchange papers, the so-called micro-CVCS (both systems were designed by the CEA). The mini-CVCS has several lines in parallel composed of a particle filter paper and a resin pot which can be gamma monitored along its height with an EMECC device; it is connected to the PWR CVCS upstream from the particle filter. The micro-CVCS is composed of a multi-stage trapping paper system (particle filter paper, anion and cation exchange papers) and it is connected to the PWR Nuclear Sampling System in a glove box.

These campaigns are carried out during different reactor operation stages: during power operation, at the beginning of cold shutdown (before/after oxygenation) or at the end of outage.

Surface activity

Figure 1 presents the ^{110m}Ag surface activities inside the Reactor Coolant System (RCS - Hot Leg and cold side of steam generator tubes), the Chemical and Volume Control System (CVCS - Non regenerative heat exchanger, pipe upstream from the particle filter, pipe downstream from the particle filter and pipe downstream from the ion exchange resins) and the Nuclear Sampling System (NSS - heat exchanger and pipe downstream from the heat exchanger of the RCS sampling line and of the CVCS sampling line) in Reactor A measured at the beginning of the shutdown of cycle 1 before and after oxygenation by H_2O_2 injection at 80 °C. Reactor A is a 1450 MWe PWR (N4 standardized plant series) equipped with steam generator tubing in alloy 690TT. A boron-lithium coordinated chemistry at pH 7.2 at 300 °C was applied.

During oxygenation, the ^{110m}Ag surface activity has a tendency to decrease by a factor of about 2 inside the RCS. On the other hand, it increases by a factor of about 2 to 7 inside the heat exchangers and the downstream pipes of the NSS and the CVCS, except inside the pipe downstream from the demineralizers where it decreases by a factor of about 2.

It is worth noting that the level of ^{110m}Ag contamination of the pipes upstream and downstream from the demineralizers is the same before oxygenation showing that silver is not trapped by ion exchange resins under reducing conditions.

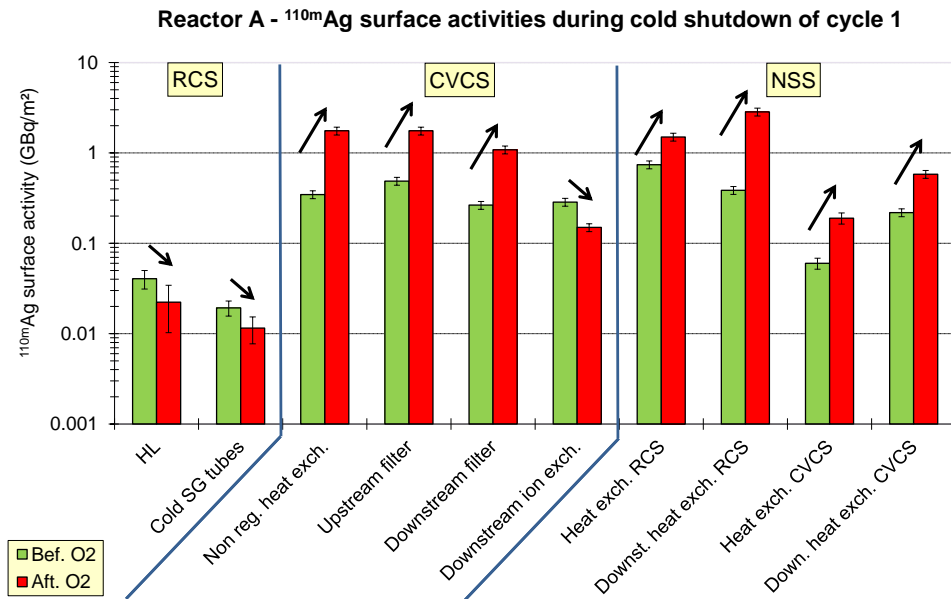


Figure 1. Reactor A – ^{110m}Ag surface activities of different components of the RCS, CVCS and NSS measured before and after oxygenation (Bef. O2/Aft. O2) during the cold shutdown at the end of cycle 1.

The ^{110m}Ag recontamination of the heat exchangers and the downstream pipes of the auxiliary systems during oxygenation is systematic in the French PWRs regardless of the shutdown case (unit and cycle). This is illustrated in Figure 2, which presents the ^{110m}Ag recontamination factor of the CVCS Non Regenerative Heat Exchanger (NRHE) due to oxygenation during different shutdowns of the EDF PWRs. The recontamination factor ranges from about 2 to 200 regardless of the type of PWR. It should be noted that the average ^{110m}Ag surface activity of the NRHE reached after oxygenation is 0.57 GBq/m² for the 900 MWe PWRs, 0.14 GBq/m² for the 1300 MWe PWRs and 1.1 GBq/m² for the 1450 MWe PWRs. The French 1300 MWe standardized plant series is less concerned by ^{110m}Ag pollution but the recontamination factor has the same levels as the other standardized plants.

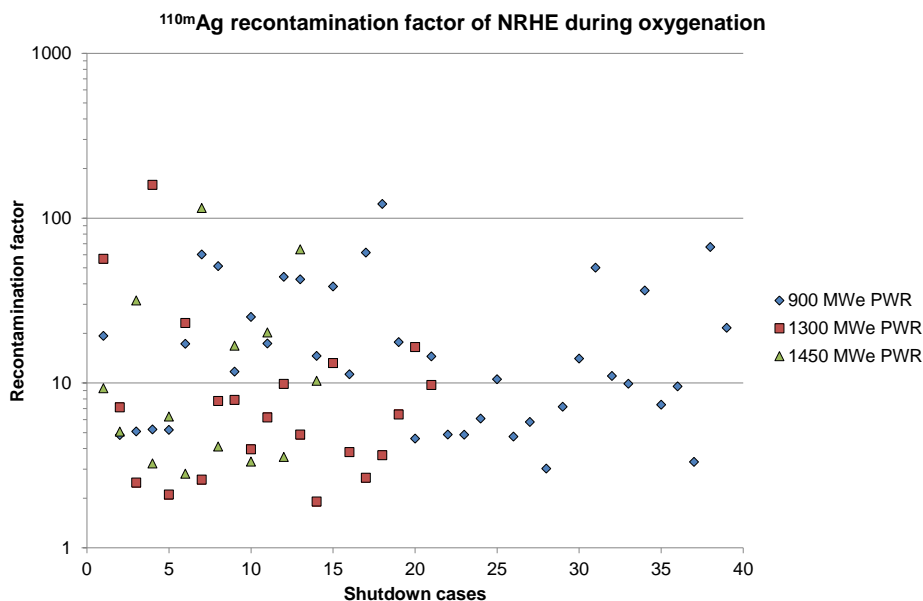


Figure 2. ^{110m}Ag recontamination factor of the CVCS NRHE due to oxygenation during different shutdowns of EDF PWRs.

During the cold shutdown at the end of cycle 1 of Reactor A, the variations of the surface activities inside the NSS heat exchanger of the RCS sampling line (first component of the NSS shown in Figure 1) were measured using an EMECC device. Figure 3 presents the variation of the ^{110m}Ag surface activity. One can observe that as soon as the primary system oxygenation occurs, the ^{110m}Ag surface activity inside this heat exchanger increases for several hours and then decreases.

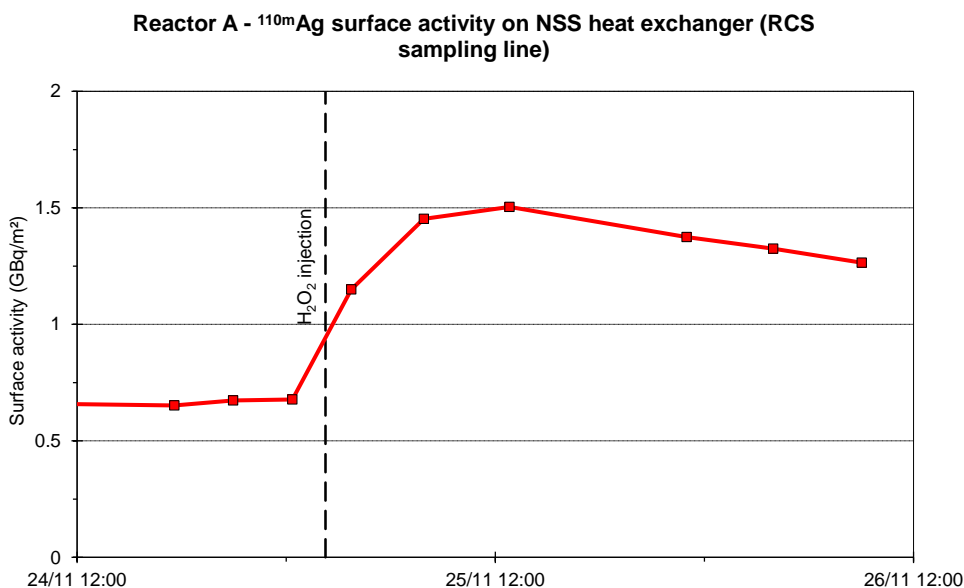


Figure 3. Reactor A – Variation of the ^{110m}Ag surface activities inside the NSS heat exchanger of the RCS sampling line during the cold shutdown at the end of cycle 1.

Dose rate

Figure 4 presents the dose rates measured in contact with the same components as those measured with the EMECC device during the cold shutdown (before and after oxygenation) at the end of cycle 1 of Reactor A.

During the cold shutdown procedure, the dose rates around the primary system do not change, whereas they increase by a factor of 1.5 to 7 around the NSS and the CVCS, except in the vicinity of the pipe downstream from the demineralizers where the dose rate decreases by a factor of 2.

These variations are due to the changes in the ^{110m}Ag surface activity during oxygenation. Indeed, the ^{110m}Ag contribution to the dose rates around the auxiliary systems is the major one or at least very high, whereas it is negligible around the primary system (see Figure 5).

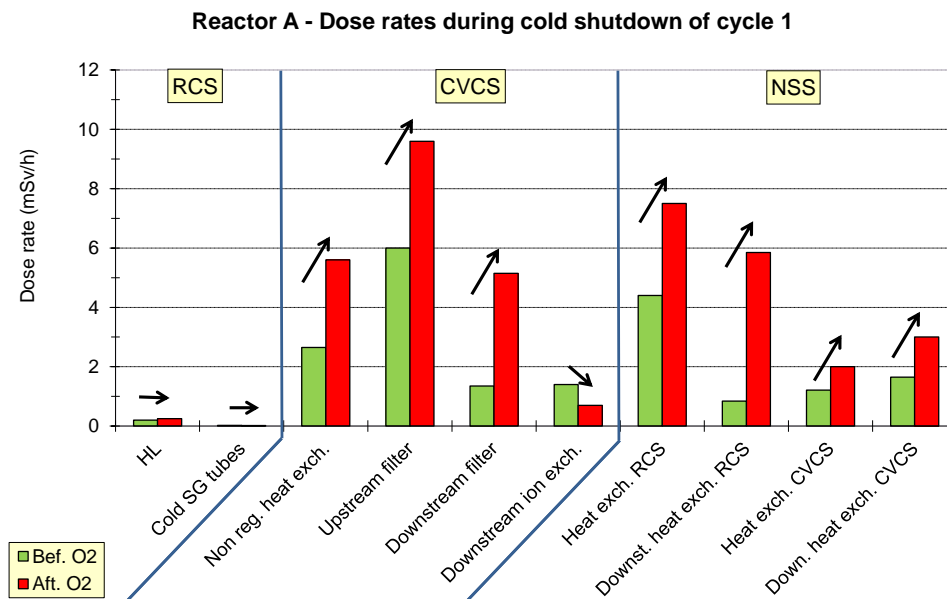


Figure 4. Reactor A – Dose rates in contact with different components of the RCS, CVCS and NSS measured before and after oxygenation (Bef. O2/Aft. O2) during the cold shutdown at the end of cycle 1.

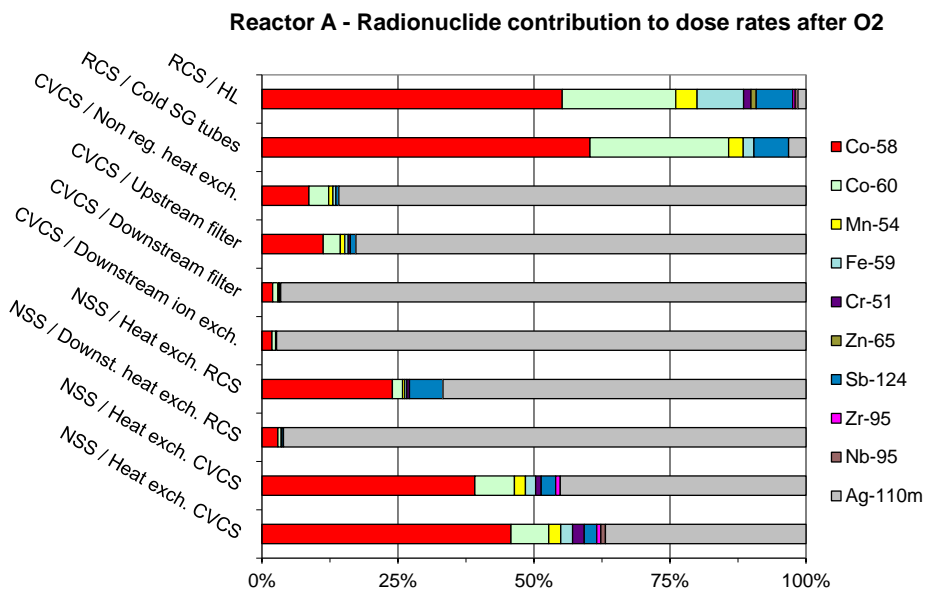


Figure 5. Reactor A – Radionuclide contribution to dose rates around the RCS, CVCS and NSS after oxygenation at the end of cycle 1.

Volume activity

In order to measure the volume activities of the primary system, the primary coolant can be sampled by using the RCS sampling line (sampling nozzle at a hot leg) or the CVCS sampling line (sampling nozzle at the pipe upstream from the particle filter). Figure 6 shows the impact of the sampling line (RCS vs. CVCS) on the ⁵⁸Co and ^{110m}Ag volume activities measured by EDF.

The measured ^{58}Co volume activity does not depend on the sampling nozzle. On the other hand, the $^{110\text{m}}\text{Ag}$ measured volume activity sampled via the RCS sampling line is generally different from the one sampled via the CVCS sampling line. Moreover, one can generally observe a delay of some hours for the increase in the $^{110\text{m}}\text{Ag}$ measured volume activity after oxygenation and then a plateau of volume activity for several hours or days.

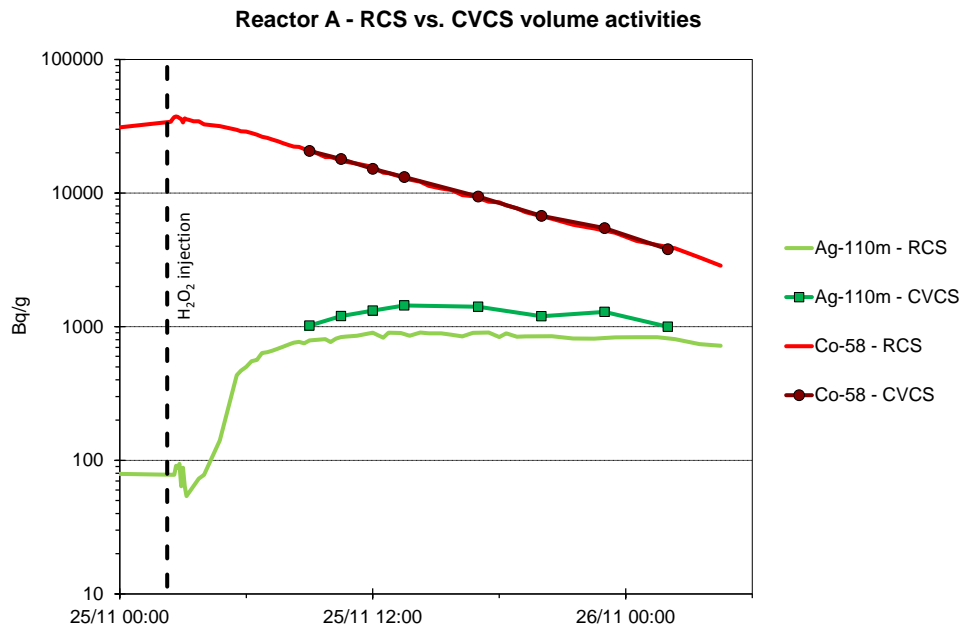


Figure 6. Reactor A – ^{58}Co and $^{110\text{m}}\text{Ag}$ volume activities sampled by using the RCS vs. CVCS sampling lines during the cold shutdown at the end of cycle 1.

Activity trapped by ion exchanger

During a cold shutdown of a 900 MWe PWR (Reactor B), the mini-CVCS was connected in order to study the trapping efficiency of each radionuclide by 4 types of resins. The gamma monitoring along the height of each resin pot showed that before oxygenation (reducing medium), silver is practically not trapped by resins. On the other hand after oxygenation (oxidizing and acid medium), silver is trapped very well by resins as $^{110\text{m}}\text{Ag}$ is trapped at the top of the pot by the first layers of resins (see Figure 7) and it is trapped even more than the other cations, especially ^{58}Co .

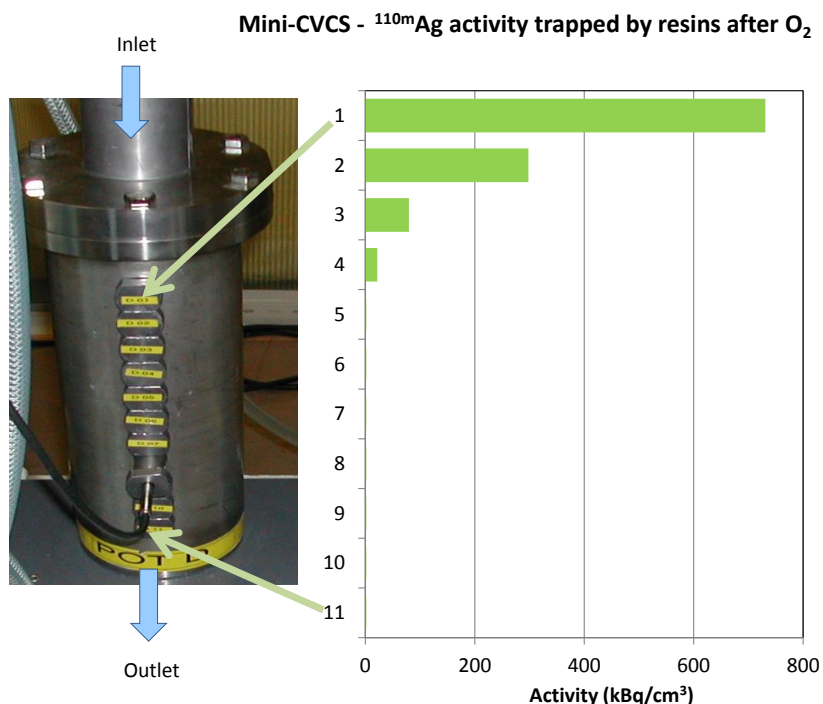


Figure 7. Reactor B - Mini-CVCS – ^{110m}Ag activity trapped by ion exchange resins in a pot gamma-monitored along its height after oxygenation.

DISCUSSION

Based on the experimental data and the comments presented in the previous part, one can conclude that:

- Silver is in an insoluble form (colloids) in a reducing medium and it is not trapped by ion exchangers (see section *Surface activity* and section *Activity trapped by ion exchanger*). On the other hand, silver is in a soluble form (cations) in an oxidizing and acid medium and it is trapped very well by ion exchangers (see section *Activity trapped by ion exchanger*).
- As soon as the primary system oxygenation occurs, silver dissolves from the primary system ($T = 80\text{ }^{\circ}\text{C}$) and precipitates on the cold parts ($T \cong 40\text{ }^{\circ}\text{C}$) of the auxiliary systems including the NSS (see section *Surface activity*). The silver dissolution from the hot parts and its precipitation on the cold parts could be due to the silver solubility which would increase with rising temperature as it is illustrated for Ag_2O in water in Figure 8.

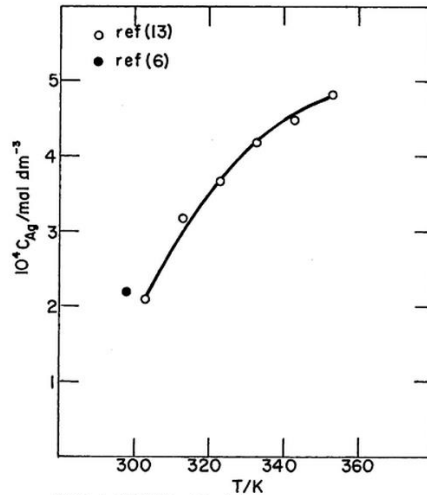


Figure 1. Solubility of Ag₂O in water.

Figure 8. Solubility of Ag₂O in water (Dirkse, 1986).

The fact that silver precipitates on the NSS results in an inaccurate estimation of the ^{110m}Ag volume activity of the primary coolant (see section *Volume activity*). It is generally underestimated and then overestimated (Dacquait et al., 2008). Thus, the measured ^{110m}Ag volume activity is generally not representative of the real ^{110m}Ag volume activity of the primary coolant and neither is the ^{110m}Ag volume activity downstream from demineralizers which may wrongly suggest that the efficiency of the CVCS purification system is poor. Thus, the CVCS decontamination factor for ^{110m}Ag cannot be determined accurately after oxygenation.

After the ^{110m}Ag recontamination of cold parts by precipitation for some hours just after oxygenation, there is a slow decontamination by dissolution (see Figure 3), the silver dissolution rate decreasing with falling temperature. This slow decontamination at low temperature continues throughout the outage as long as there is an oxidizing and acid medium as shown in Figure 9. The level of contamination at the end of the outage is of the same order of magnitude as the one at the beginning of the outage, whereas it has increased by a factor of 10 during the primary system oxygenation.

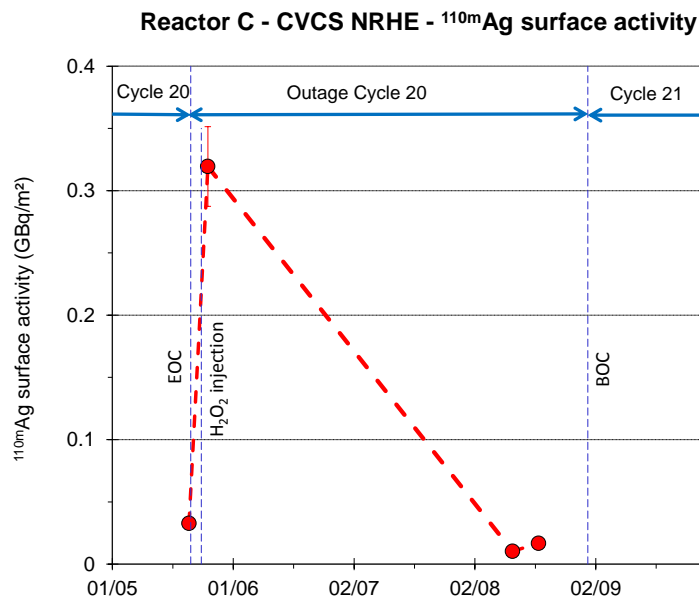


Figure 9. Reactor C - Variation of the ^{110m}Ag surface activity inside the CVCS Non Regenerative Heat Exchanger during the outage at the end of cycle 20.

In case of ^{110m}Ag pollution, the dose rates around the components (heat exchangers, pipes, valves...) of the cold parts of auxiliary systems can rise strongly during the primary system oxygenation (see section *Dose rate*) and therefore the occupational exposure as well. To reduce the latter in case of ^{110m}Ag pollution, based on the lessons learnt from the EMECC and filtration campaigns, we may suggest:

- Under reducing conditions during a cycle:
 - Use macro-porous mixed bed resins throughout the power operation cycle in order to trap colloidal silver.
- Under oxidizing conditions during an outage:
 - Decrease temperature as fast as possible during the cold shutdown in order to mitigate ^{110m}Ag activity transfer from the primary system surfaces (^{110m}Ag minor contributor to dose rates) to the cold parts of auxiliary systems (^{110m}Ag major contributor to dose rates). Nevertheless, with the aim to enhance silver dissolution in the primary system, a temperature plateau of 80 °C during oxygenation is recommended, but with an increased risk of a high ^{110m}Ag recontamination of the cold parts of auxiliary systems.
 - Remove lithium to favour an acid medium and use cation exchange resins in order to trap silver (soluble form for silver in these conditions).
 - If possible, postpone works on the cold parts of auxiliary systems as late as possible during the outage in order to have lower dose rates (Ag dissolution during outage in acid and oxidizing medium).

CONCLUSION

In case of pollution by ^{110m}Ag , the main lessons learnt from EMECC campaigns and primary coolant filtering campaigns are as follows:

- During oxygenation, ^{110m}Ag dissolves from the primary surfaces and precipitates on the cold parts of auxiliary systems before dissolving slowly from these cold parts. It leads to a sharp increase of dose rate in the vicinity of the cold parts of auxiliary systems.
- Because of the precipitation on the NSS, ^{110m}Ag sampled via the NSS is not representative of the ^{110m}Ag volume activity of the RCS.
- Under oxidizing and acid conditions, Ag is trapped very well by cation exchange resins. On the other hand, silver is in an insoluble form (colloids) in a reducing medium and it is not trapped by ion exchangers.

NOMENCLATURE

ACP	Activated Corrosion Product
AIC	Ag In Cd
BOC	Beginning Of Cycle
CEA	Commissariat à l'Énergie Atomique et aux énergies alternatives
CVCS	Chemical and Volume Control System
EDF	Electricité De France
EMECC	Ensemble de Mesure et d'Étude de la Contamination des Circuits

EOC	End Of Cycle
HL	Hot Leg
NRHE	Non Regenerative Heat Exchanger
NSS	Nuclear Sampling System
PWR	Pressurized Water Reactor
RCS	Reactor Coolant System
SG	Steam Generator
TT	Thermally Treated

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