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**Application of KWU Antimony Removal Process
at Gentilly-2**

**Mise en application du procédé KWU d'élimination
de l'antimoine à Gentilly-2**

Y. Dundar, S. Odar, K. Streit, H. Allsop, D. Guzonas

To be presented at the 7th International Conference on Water Chemistry
of Nuclear Reactor Systems, British Nuclear Energy Society,
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by

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RÉSUMÉ

La présente étude décrit les travaux portant sur l'adaptation aux centrales CANDU^{MC} du procédé KWU d'élimination de l'antimoine, ainsi que sur la mise en application de ce procédé à la centrale Gentilly-2 de Hydro-Québec. On présente les résultats de la mise en application de ce procédé et on discute en détail des leçons que l'on a tirées de cette expérience.

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Application of KWU antimony removal process at Gentilly-2

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This paper describes the work performed to adapt the KWU PWR antimony removal process to CANDU™ plant conditions, and the application of the process at the Hydro Quebec unit, Gentilly-2. The results of the application will be presented and the "lessons learned" will be discussed in detail.

Introduction

Gentilly-2, a CANDU type Pressurized Heavy Water Reactor (PHWR), has experienced significant increases in radiation fields around the Primary Heat Transport System during unit shutdowns. During these excursions, significant quantities of radioactive antimony are released to the coolant when oxidizing conditions are created by air ingress. This results in increased radiation fields around the reactor, making outage dose planning difficult, and contributing significantly to the radiation exposure of maintenance personnel. Antimony removal from the Primary Heat Transport System at the beginning of the outage was seen as a solution to this problem.

In order to remove antimony from PWR primary systems, KWU developed a process for antimony removal, which was successfully applied in many PWR's. This process had to be adapted to CANDU plant conditions and requirements.

The KWU antimony removal process, modified using recommendations made by Hydro Quebec and AECL, was carried out at Gentilly-2 during the plant shut-down at the start of the April 1995 annual outage. The application followed a period of essentially continuous power operation since April 1994. Continuous operation was interrupted only by a brief shutdown in March 1995, where a trial antimony removal process was conducted in preparation for the full scale removal carried out during the planned outage in April. The process has recently been repeated during the 1996 annual outage, and preliminary results are also reported.

Principle of the Process

Practical experience, literature studies and laboratory investigations [1] have shown that Sb is present in reduced form under the reducing operating conditions of

a PWR plant and is only very slightly soluble under these conditions. The task is therefore to transform the Sb into a soluble, ionic compound, which can then be separated out in an ion exchange resin. This is achieved by oxidation of the Sb to its thermodynamically stable form, Sb(+5). The Siemens KWU process [2] is based on the addition of H₂O₂ in order to force this oxidation process and to define the point in time when conditions are optimum to achieve the best possible mobilization and hence the best separation. As a general rule, Siemens KWU recommends the use of fresh resins for Sb removal, as the efficiency and residence time are comparatively poor if previously loaded resins are used.

Process adaptation to special CANDU requirements

A CANDU-6 has approximately 3000 m² of carbon steel surfaces in its feeders and headers. As a result, the deposits found on the piping and in the steam generators are magnetite, rather than the nickel- and chromium-containing ferrites found in PWR's. Previous Siemens antimony removal applications have been performed at the typical PWR shutdown pH₂₅ of 5.5 to 6.0. CANDU reactors have a shutdown pD of 10.6-11.2 (equivalent to a pH of 9.7-10.2 in light water). The Pourbaix diagram [3] for antimony, and field and laboratory experience indicate that the chemistry of the antimony removal process should be the same at pH 10. However, antimony has been observed to plate-out on carbon steel feeders at the reactor face of a CANDU reactor during application of a CAN-DECON™ decontamination. This deposition has been attributed to the surface charge of the freshly cleaned carbon steel surface. Work carried out at AECL [4] indicated that antimony deposition on magnetite at 25 °C decreased as the pH increased above the point-of-zero-charge (pzc) of magnetite (pH =6.5). However, at 85 °C, antimony deposition increased even though the pzc of magnetite decreases as the temperature increases. This increased adsorption is probably a result of an increased specific interaction between the dissolved antimony species and the magnetite surface. It was therefore recommended that the antimony removal be carried out at a temperature of 45 °C.

As oxidizing conditions were required for the antimony removal, it was recommended to degas the coolant to remove dissolved hydrogen after shutdown instead of stopping hydrogen addition before shutdown. A review of the literature suggested that some conversion of magnetite to hematite might occur during the application of the antimony removal procedure. To test this, X-ray diffraction was used to characterize the oxides on carbon steel exposed to simulated Sb removal conditions. No conversion of the magnetite to hematite was observed suggesting that no disruption of the oxide layer should result from the application of the antimony removal procedure [4].

Process application at Gentilly-2 in 1995

In preparation for the Sb removal program, two ion exchange columns were refilled using standard commercial mixed bed resins. These columns were not connected to the system under plant operating conditions in order to minimize loss of resin Sb capacity due to contact with a high (operating) concentration of H_2 or H_2O_2 (during dosing). After putting them in service, they were operated with the maximum technically feasible purification rate.

Initially the process was applied at 45°C, in order to prevent Sb deposition on carbon steel surfaces. Afterwards, in order to improve the Sb release from the system surfaces, the temperature was increased to between 85 and 90°C.

H_2O_2 was redosed several times during the operation to maintain a constant high coolant oxygen concentration. The large carbon steel surfaces consumed large amounts of oxygen, which had not been anticipated.

Application results

During the time period at 45°C the first Sb release peak (spiking factor of 400) was observed. The second Sb peak was caused by the temperature increase, which indicates that the increased temperature favors oxidation of the Sb (Fig.1).

Apart from these peaks, Sb release rates were relatively slow and long, indicating the presence of a source of Sb not immediately mobilized by the oxidant. This can be attributed either to a diffusion-controlled release mechanism from relatively thick corrosion product layers or to a competition reaction of the oxidant with corrosion product layers. In any case it is probable that an early temperature increase or performance of the process at higher temperatures would have mobilized larger amounts of Sb.

Sufficiently high decontamination factors were found during the entire operation indicating that the ion exchange columns exhibited good retention during the whole process. This is presumably due to the avoidance of any preloading with H_2 and the relatively low H_2O_2 coolant concentration.

The observed ratio of Sb-122 to Sb-124 (Fig. 2) indicates that Sb was first mobilized primarily from the areas near the core (increase of the ratio). The temperature increase led to Sb mobilization in areas further from the core (decrease of ratio). During the process application an overall removal of 774 Ci of

Sb-122 and 558 Ci of Sb-124 by the coolant purification system was achieved. A part of this Sb activity was mobilized right at the beginning of the process application by H_2O_2 injection. The rest was mobilized over the entire application time and fixed on the resins.

Even though significant amounts of Sb were removed from the Primary Heat Transport System, no change in Sb dose contribution was observed during the process application. This means that little Sb-124 was mobilized from out of core surfaces. Although after the temperature increase, "old" Sb was mobilized (indicated by the decreasing Sb-122 to Sb-124 ratio) it still was not from the system surfaces, which were monitored by the Room Dose Rate Measurements. These measurements increased only slightly after H_2O_2 injection, despite an increase in the soluble antimony concentration of at least a factor of 400.

As a process-determining parameter, the oxygen values were always in a sufficiently high range. Although there were some differences between the two loops, the oxygen consumption was very significant. In previous PWR applications a continuous consumption of oxygen to this extent was not observed. This can be explained as resulting from the different surface conditions of the magnetite covered carbon steel, not present in PWR plants.

Discussions of the 1995 application results

The observations made during the first Sb removal process in Gentilly-2 and the results achieved can be concluded as follows:

- * The April 1995 application only partially achieved the desired result. This is particularly true if a clear dose rate reduction was anticipated. It was possible to remove the usual amount Sb-124, but no reduction in room dose rates could be observed.
- * The Sb removal trial during the short shutdown in March 1995 contributed considerably to the later problem of room and component dose rates. In this

shutdown, the purification process was interrupted early and the plant was started up again with very high Sb-124 concentrations in the coolant, which then plated out on the out of core surfaces. Based on coolant crud sample analysis it appears that the entire system was contaminated with Sb-124 by this interrupted Sb removal. This plated out "old" Sb could not be mobilized by the oxidant within the application time of the 1995 April 17 Sb removal. Subsequent laboratory results at AECL have shown that Sb deposited on carbon steel surfaces rapidly becomes incorporated into the corrosion film and is then very difficult to remove.

- * The laboratory observation that Sb plates out on carbon steel surfaces at temperatures over 80°C could not be verified in Gentilly-2. On the contrary, above this temperature Sb mobilization increased.

Recent Application at Gentilly-2:

During the annual outage in May 1996 the Sb removal process was repeated at Gentilly-2. Based on the "lessons learned" from the first Sb removal the following application conditions were recommended and followed:

- * A higher process temperature, 85 °C, was selected; this was maintained during the entire Sb mobilization and purification phase of the process. Because the surfaces outside of the core in Gentilly-2 are contaminated, it must be ensured that the Sb at these locations is mobilized
- * The resins used have performed well. The resins should not be put into operation until the H₂O₂ concentration has decreased. This protects the resins and stabilizes their efficiency.

The preliminary results of the 1996 May application can be summarized as follows:

- * A large amount of antimony was mobilized from the core areas (Fig. 3)
- * The antimony mobilized was successfully removed by the ion exchange purification system without any increases in fields. There was no Sb plate-out problem (Fig. 4).
- * The total amounts of antimony removed were:
Sb-122: 1158 Ci, and Sb-124: 563 Ci

Conclusions

The results of the May 1996 process application at Gentilly-2 demonstrated that the Siemens/KWU Antimony removal process could be successfully used in CANDU plants.

Acknowledgement

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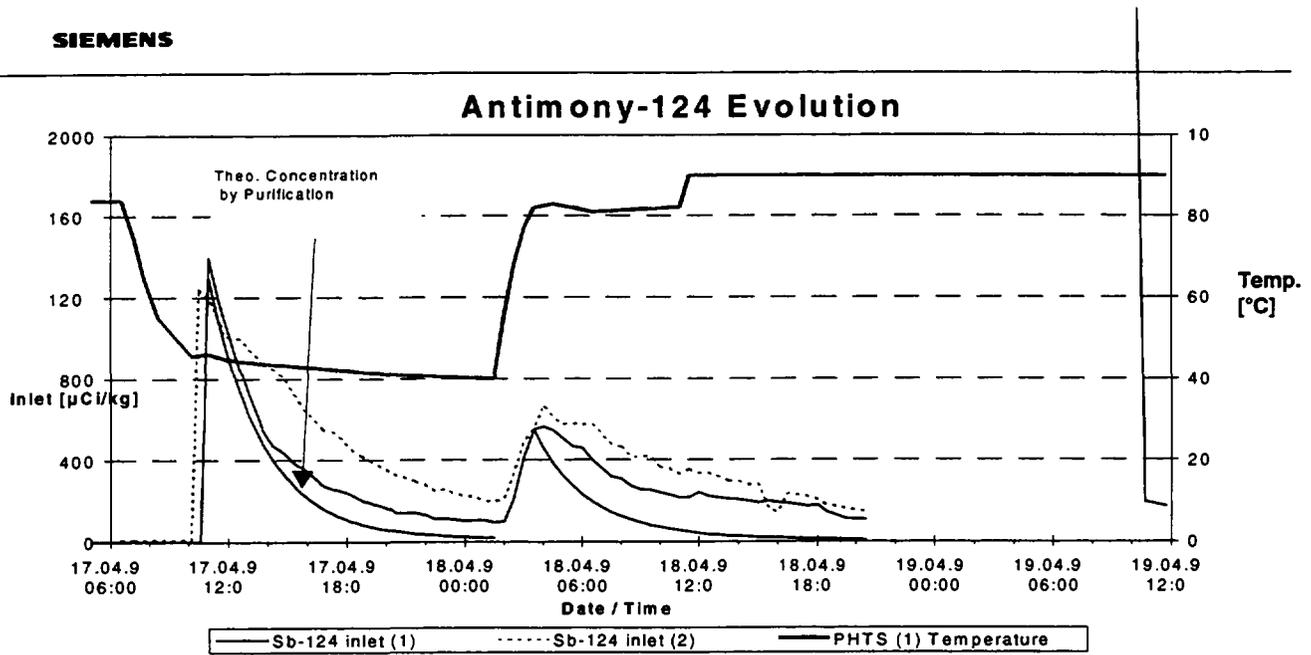


Figure 1: Sb-124 activity concentrations in the Primary Heat Transport System.

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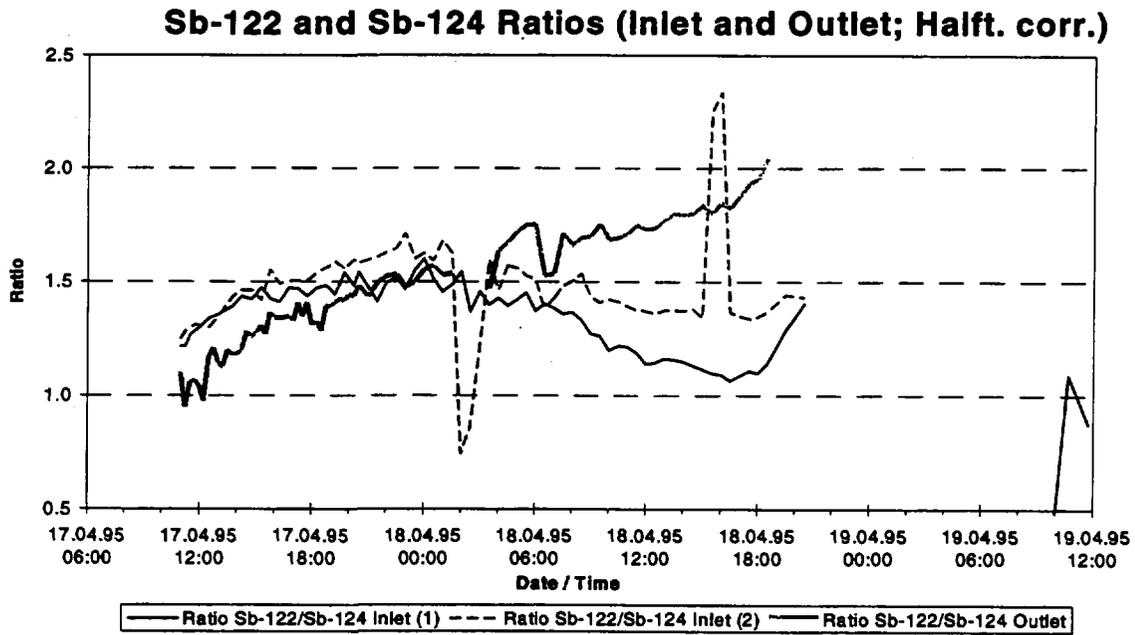


Figure 2: Sb-122 to Sb-124 ratio observed during the process application.

Antimony-122 and 124

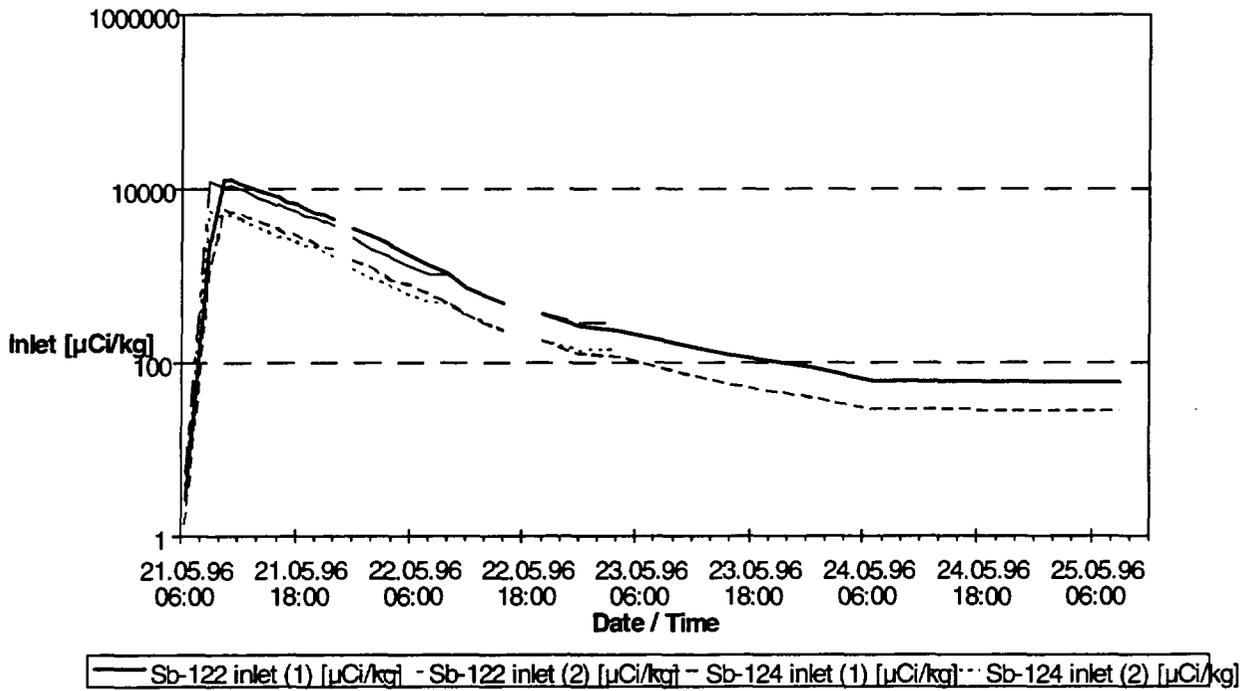


Figure 3: Sb activity concentrations in the Primary Heat Transport System.

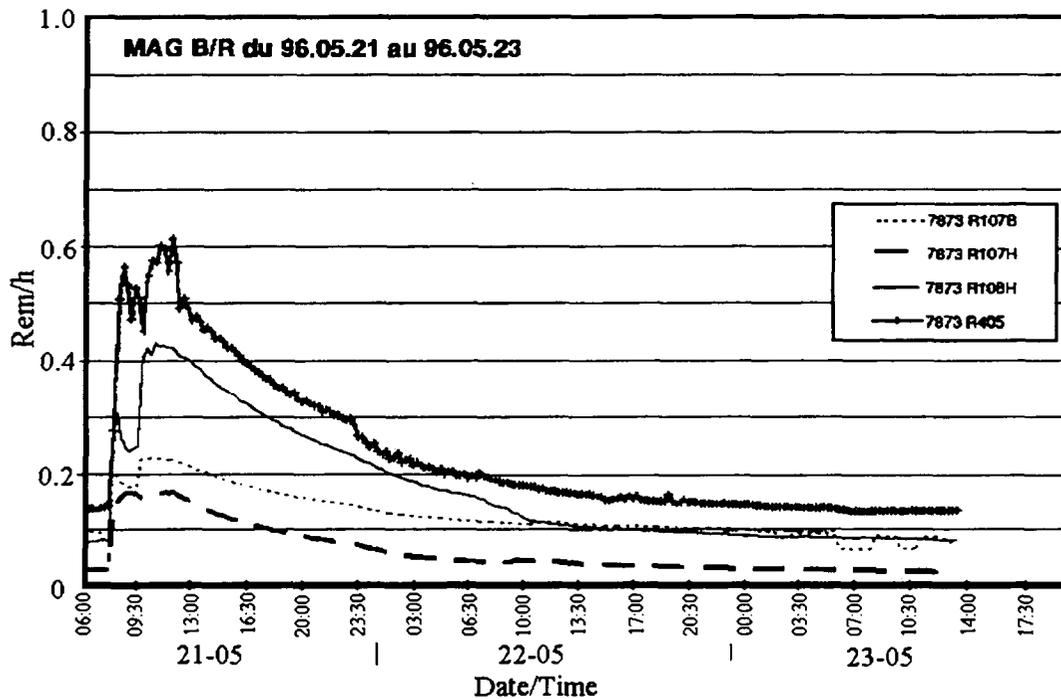


Figure 4: Field dose rate evolution.

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