CONTROLLING RADIATION FIELDS IN CANDU® REACTORS USING CHEMICAL DECONTAMINATION TECHNOLOGIES

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ABSTRACT

Radiation dose to personnel during major maintenance and reactor refurbishment of CANDU reactors can be controlled using chemical decontamination technologies. Technologies that have, and can be applied in CANDU reactors include; sub- and full-system decontaminations of the heat transport system using the CAN-DECON™, CAN-DEREM™ and CAN-DEREM Plus processes; and removal of Sb-122 and Sb-124 from the reactor core using hydrogen peroxide.

CAN-DECON™ is a dilute chemical decontamination process that employs ion-exchange technology to continuously remove dissolved metals and radionuclides and regenerate the components of the CAN-DECON™ formulation. Qualification of the CAN-DECON™ process, equipment requirements, process effectiveness, recent process improvements and future directions are discussed.

Radioantimony deposited on in-core surfaces can be released into the HTS coolant by air ingress during maintenance. At Gentilly-2, where large amounts of in-core antimony are present, these releases have resulted in increased radiation fields around the reactor, making outage dose planning difficult and contributing significantly to the radiation exposure of maintenance personnel. An antimony removal process developed by KWU for PWR's and adapted to meet CANDU specific conditions, has been successfully applied at Gentilly-2. Optimization of process conditions, and improvements in the in-core antimony removal process are described.

Introduction

Chemical decontamination technologies have been used to reduce radiation fields around the heat transport system (HTS) prior to major reactor refurbishment campaigns. In addition, chemical decontamination can be used to control radiation fields to minimize dose to personnel during reactor operation, routine maintenance and during unit shutdowns.

Technologies that have, and can be applied in CANDU reactors include:

- sub- and full-system decontaminations of the heat transport system using the CAN-DECON™, CAN-DEREM™ and CAN-DEREM Plus processes; and
- removal of Sb-122 and Sb-124 from the reactor core using hydrogen peroxide.

These technologies are discussed in this paper, with a focus on plant experience and on optimization to further minimize personnel dose, cost and application time.

In-core Antimony Removal

During reactor operation, antimony, present in many CANDU materials of construction as a trace impurity, is released and transported to the core, where it is activated. At Gentilly-2, the primary pump seals and bearings contain significant quantities of antimony, and constitute a source of antimony that is not present in other CANDU reactors. Releases of ^{122}Sb and ^{124}Sb after oxygen excursions during shutdown at Gentilly-2 have resulted in five-fold increases in out-of-core radiation fields (during the 1993 outage at Gentilly-2, the radiation fields at the steam generators increased from 50 to 250 mR/h). Unexpected increases in radiation fields have adversely affected maintenance procedures, to the degree where maintenance outage actitivties have been delayed or cancelled. To prevent these antimony excursions, and minimize personnel dose during maintenance outages, an antimony removal process for the CANDU HTS was developed. The antimony removal proces has been applied during mainteneance outages since 1994.

The key components for a successful antimony removal application are:

- mobilize the antimony in a form that can be readily removed on an ion exchange resin; and
- control the chemistry to minimize antimony deposition on other system surfaces.

The oxidizing antimony removal process applied at Gentilly-2, most recently in 1997 February [1], is a modification of the Siemens-KWU antimony removal process. This process had been applied several times at European and American nuclear generating stations, and was adapted for use in a CANDU HTS, taking into account the differences in chemistry and materials between a PWR and a CANDU [1]. The antimony removal process uses H_2O_2 to create oxidizing conditions in the HTS coolant at 85 °C during reactor shutdown. Addition of H_2O_2 results in the oxidation of antimony adsorbed or ion-exchanged on in-core surfaces, which is then rapidly released into solution. It is believed that the oxidation process involves the conversion of the reduced antimony to an Sb^V species. The anionic Sb^V species formed are then removed on an anion exchange resin.

The behaviour of radioantimony during the application of the process is illustrated in Figure 1, which shows the solution activity of ^{124}Sb and ^{122}Sb in both loops of the HTS during the course of the 1997 February antimony removal. After the addition of H_2O_2, the activity of antimony in solution rapidly rises, peaking within one to two hours of peroxide addition. The antimony concentration then decreases after the ion exchange resins are valved in. The rapid increase in solution antimony activity indicates that the release of antimony from in-core surfaces is a fast process.

The four applications at Gentilly-2 have shown that the three critical aspects of this process are:

- injection of the appropriate amount of H_2O_2;
- bringing the purification system on-line as soon as an increase of radioantimony is detected in the coolant; and
- maintaining oxidizing conditions ($[O_2] > 1$ ppm) until antimony removal is complete.

Since the purpose of the antimony removal process is to minimize increases in fields due to deposition of ^{122}Sb and ^{124}Sb on out-of-core surfaces during shutdown, the fields measured by the room monitors throughout the plant can be used to gauge the success of an application. As an example, the data from the room field measurements for the 1997 February antimony removal is plotted in Figure 2.

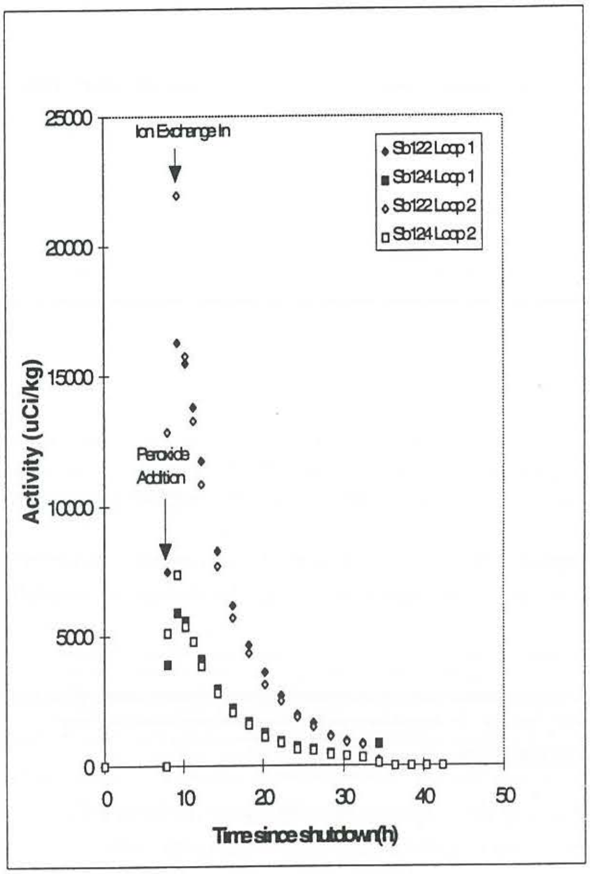

Figure 1: Behaviour of Radioantimony in the Coolant in Loops 1 and 2 of the Heat Transport System during the 1997 Antimony Removal at Gentilly-2.

In Figure 2, a rapid increase in room fields was observed due to the large antimony release after the initial H_2O_2 injection. The fields then dropped as the antimony was removed from solution by the purification system, leaving the final field levels similar to those measured prior to the start of the process. Between 14:00 and 16:00 hours on 1997 February 27, the oxygen level in the loops decreased below the threshold required to keep antimony in solution, and the remaining antimony (less than 5% of the original amount released) was deposited from solution.

The ion-exchange (IX) resins effectively remove antimony during the antimony removal process, although the capacity of the resin for antimony is low. Removal of roughly 10 grams of antimony (both active and inactive) requires about 2 m^3 of resin. This is likely a result of the low affinity of antimony for the anion exchange resin. Improving the capacity of the IX resins for antimony is the only major area for optimization of this process.

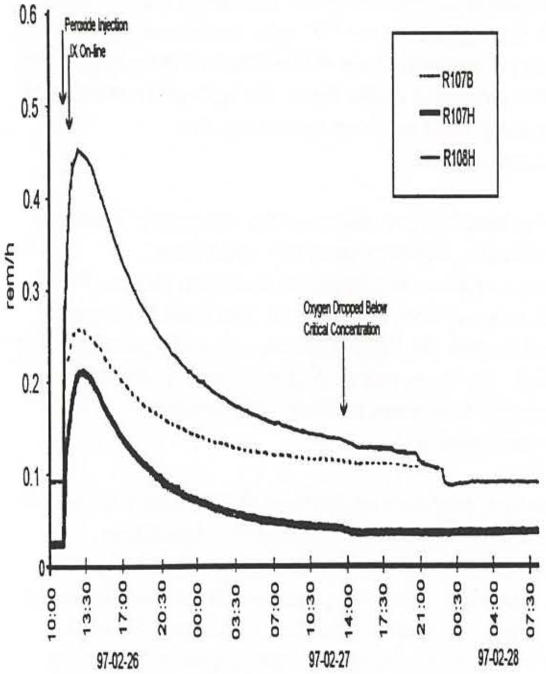

Figure 2: Fields measured by the room area monitors during the 1997 Antimony Removal at Gentilly-2.

Chemical Decontamination

Description of the CAN-DECON™ Process:

The CAN-DECON™ process was developed and qualified for application in CANDU reactors and has been applied in CANDU reactors from 1973 to 1991.

The CAN-DEREM™ process was developed and qualified in the mid 1980's for application in CANDUs and light water reactors. This process was applied in the first full-system decontamination of a power reactor in the U.S. (the Indian Point 2 PWR in 1995).

AECL has also developed the CAN-DEREM Plus process for decontamination of systems and components with high surface area/volume ratios and high deposit loadings. CAN-DEREM Plus was used in the decontamination of the Pickering Unit 1 steam generators in 1994.

CAN-DECON™, CAN-DEREM™ and CAN-DEREM Plus are dilute, regenerative chemical processes that employ ion-exchange technology to continuously remove dissolved metals and radionuclides and regenerate the components of the process formulation. At the completion of the decontamination, residual dissolved metals, radionuclides and reagents are removed on deuterated ion-exchange resin; the heavy water inventory is conserved and there is no need for rinsing the heat transport system following the process application.

The basic steps in the application of the CAN-DECON™ process during a full-system decontamination of a CANDU heat transport system include:

- lower reactor temperature to 85°C
- lower system pH; remove Li^+ from the heavy water coolant
- add corrosion inhibitor
- add CAN-DECON™ chemicals
- remove insoluble crud using filters and regenerate the CAN-DECON™ reagent using cation ion-exchange resin (all resins must be deuterated prior to use)
- add chemicals as required
- remove chemicals with mixed-bed ion-exchange resin
- restore HTS chemistry

Qualification of the CAN-DECON™ Process:

The CAN-DECON™ process has been extensively tested for use in CANDU reactors. The effectiveness of the process and the extent of corrosion of HTS materials has been evaluated in the qualification programs.

Heat transport system components such as irradiated fuel, defective irradiated fuel, valve packings, mechanical joints, gasketed joints, end closures, shield plugs, fuel channel rolled joints, cracked welds, and pump components have been evaluated in the qualification programs.

A key result from the component evaluation program was that full-system decontaminations of CANDU reactors, using the CAN-DECON™ process, could be carried out with a significant portion of the fuel in-place. The CAN-DECON™ reagent had no impact on the integrity of the fuel (fresh, irradiated, and irradiated, defective fuel).

Process Effectiveness:

To date twelve full-system decontaminations have been performed at Ontario Hydro's CANDU reactors, and two were performed at the Nuclear Power Demonstration (NPD) reactor. Process application times, decontamination factors, corrosion results and waste volumes produced during the decontamination of the Ontario Hydro reactors are listed in Table 1.

The effectiveness of the Pickering Unit 1 decontaminations performed in 1981 November and 1983 March were limited by the amount of ion-exchange resin available, the purification half-life of the system and precipitation of ferrous oxalate on heat transport system surfaces. An underestimate of the amount of iron oxides in the heat transport system, even with a contingency, resulted in insufficient ion-exchange capacity being available for the decontamination. An insufficient ion-exchange capacity leads to incomplete removal of oxide and radionuclides from the heat transport system.

Development work performed through the 1980's showed that the success of a decontamination in reducing fields can be improved by i) lowering the oxalic acid concentration in the CAN-DECON™ reagent, ii) having sufficient ion-exchange resin deuterated and loaded into the decontamination process system, and iii) ensuring that the purification half-life for the system is in the 50 to 75 minute range. Improvements in radiation field reductions in the full-system decontaminations performed from 1984 to 1991 were realized from lowering the oxalic concentration, better estimates of oxide inventories in the HTS and maintaining the purification half-life in the 50 to 75 minute range. The extent of field reduction following a CAN-DECON™ decontamination is best represented by the decontamination factor (DF = initial activity/final activity). The benefits of the decontamination will be realized in future maintenance outages, for emergency preparedness (unplanned events) and in minimizing personnel exposure during reactor maintenance under normal reactor operation.

Decontamination factors at the reactor face and in the steam generators ranged from 4 to 10, while DFs on the feeder and headers ranged from 3 to 13.5 in full-system decontaminations performed at Pickering "A" from 1984 to 1991 (Table 1).

Decreases in gamma radiation fields resulting from the full-system decontaminations performed at Pickering Unit 2 in 1984 January/April, and at Pickering Unit 3 in 1985 June and 1989 July/August are depicted in Figures 3 and 4.

The data for the Pickering Unit 2 decontaminations (Figure 3) show that the fields at Row "B" were reduced from 1400 mR/h to approximately 100 mR/h. The DF of 14 is consistent with the DF of 13.5 reported for the Pickering Unit 2 feeders (Table 1). The dose reduction observed at Row "B" reflects the contributions of the feeders to the radiation fields at the top of the reactor face. The radiation fields at Row "M" (the mid-point of the reactor face) decreased from 600 mR/h to 100 mR/h (a DF of 6), while the fields at Row "V" (the bottom of the reactor) decreased from 400 mR/h to 100 mR/h. Note that the radiation fields from the bottom to the top of the reactor were uniform following the decontamination.

Similar trends were observed for Pickering 3, taking the radiation fields prior to the 1985 June decontamination as the initial radiation fields. Fields were reduced from the 1000 to 2500 mR/h range to 75 mR/h after the decontamination performed in 1989 August. As observed in Figures 3 and 4, fields across the reactor face were uniform following the decontamination.

Reduction of radiation fields at the reactor face and in the feeder cabinets have resulted in significant reductions to personnel dose during the large-scale fuel channel replacements performed at the Pickering "A" Units. It is estimated that 1800 and 750 man-Rem were saved during the campaigns at Pickering Unit 3 and Pickering Unit 4, respectively. Note that the actual man-Rem saved is dependent on the radiation field prior to the decontamination.

Note that the waste volumes produced during the Pickering "A" decontaminations were in the 20 to 30 m^3 range. Waste volumes in decontaminations performed prior to 1984 were lower; however, this was due to under-estimation of the oxide inventory in the heat transport system.

Corrosion data, obtained from corrosion specimens installed in heat transport system autoclaves, indicate general corrosion rates for A106 Gr. B carbon steel in the 0.1 to 0.6 μm/h range. The general corrosion rates for 400-series stainless steel specimens (representative of the end-fitting and liner tubes) ranged from 0.004 to 0.1 μm/h. The 400-series stainless steels can exhibit active-passive behaviour during exposure to corrosion inhibitors.

Table 1: Summary of Decontamination Factors, Corrosion and IX Waste Volumes from CANDU Full System Decontaminations

Unit / Date	Duration (hours)	DF Reactor Face	DF Boilers	DF Piping	Carbon Steel Corrosion Rate (μm/h)	410 SS Corrosion Rate (μm/h)	IX Waste Volume (m^3)
DPt./75	12	5.0	1.5	5.0	0.14	0.058	3
DPt./83	20	6.0	1.8	4.0	0.25	0.020	4
P-1/81 (Nov.)	13	1.0	1.5	1.0	1.15	NA	6
P-1/83 (Mar.)	30	1.3	-	1.5	0.50	N/A	9
P-1/84 (May)	43	5.0	3.5	3.0	0.58	0.116	15
P-2/84 (Jan./Apr.)	62	7.5	3.8	13.5	0.52	0.061	26
P-3/85 (Jul.)	56	5.0	10	18	0.14	0.021	30
B-1/86 (Sept.)	65	1.6	2.0	1.6	0.22	0.062	18
P-3/89 (Jul./Aug.)	79	5.2	3.5	4.5	0.62	0.005	26
P-4/91 (Oct.)	75	3.8	3.2	10	0.65	0.004	28

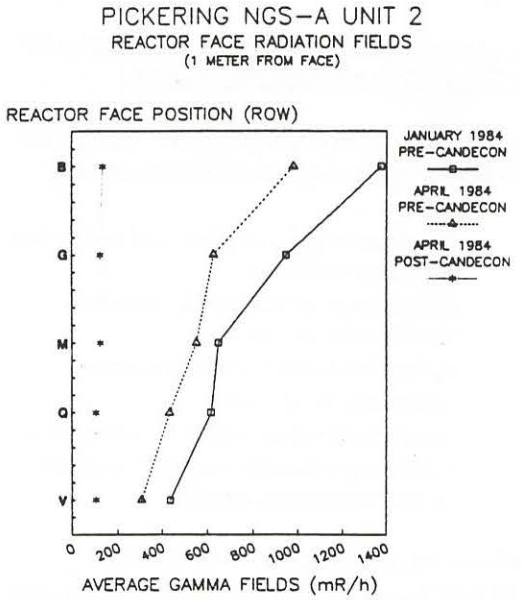

Figure 3: Radiation fields at the Pickering Unit 2 reactor face before and after CAN-DECON™ decontaminations.

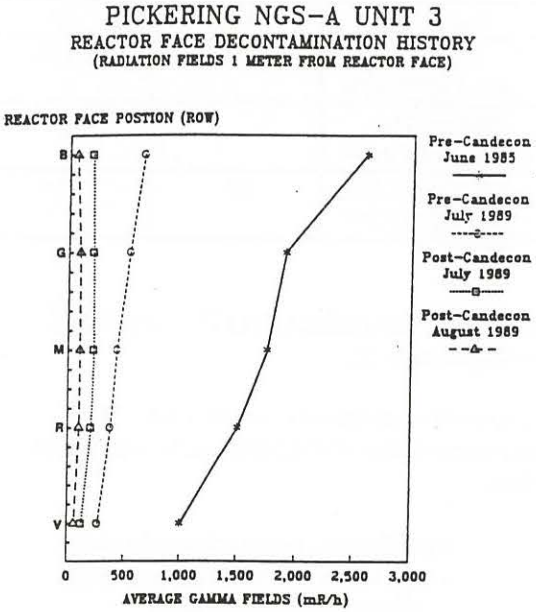

Figure 4: Radiation fields at the Pickering Unit 3 reactor face before and after CAN-DECON™ decontaminations.

Application of the Alkaline Permanganate (AP) Process in CANDU Reactors:

A three-step CAN-DECON™/AP/CAN-DECON process was applied at Pickering Unit 3 in 1989. The Alkaline Permanganate (AP) reagent is routinely applied during sub- and full-system decontaminations of light water reactors. The objective of applying the AP reagent was to reduce reactor face fields to levels as low as possible. In some cases the effectiveness of the CAN-DECON™ process in reducing reactor face fields is limited by the presence of oxides containing up to 40% Cr on outlet end-fittings and liner tubes (400-series stainless steel).

The oxidizing AP reagent conditions the Cr-rich oxide on system surfaces so that they can be easily removed during the subsequent CAN-DECON™ or CAN-DEREM™ step.

The radiation fields at the east and west faces of the reactor before the Pickering Unit 3 decontamination in 1989, after the first CAN-DECON™ step (1989 July) and after the AP and second CAN-DECON™ steps are listed in Table 2. The final fields at the east and west faces of the reactor were 85 and 75 mR/h, respectively. These were the lowest reactor face fields observed after a full system decontamination of a CANDU reactor.

Table 2: Reactor Face Radiation Fields during the Pickering Unit 3 Decontamination in 1989

	Reactor Face Fields (mR/h)	
	East Face	West Face
Pre-decon	450	437
After 1st CAN-DECON™	192	196
Before 2nd CAN-DECON™		180
After AP and 2nd CAN-DECON™	85	75

Equipment Requirements for CAN-DECON™ Decontaminations:

Equipment requirements for CAN-DECON™ decontaminations of CANDU reactors are listed below:

- a purification (ion-exchange) system;
- a high temperature filtration system;
- a chemical injection system;
- an ion-exchange resin deuteration/de-deuteration system;
- an ion-exchange resin loading system; and
- an ion-exchange column flow commissioning system.

The sizing of the equipment is primarily based on the volume of ion-exchange resin required. The ion-exchange requirements are, in turn, based on the estimated deposit loading in the heat transport system. Hence, obtaining an accurate estimate of the deposit loading prior to design of the decontamination process equipment is critical to the success of the decontamination. It is possible to slurry out the spent resin and load fresh, deuterated resin, but this increases the complexity of the decontamination operation.

Key features of decontamination process equipment design include:

- high reliability; through redundant components (maintain high flows through filters and IX while adding or removing chemicals);
- sufficient IX resin capacity to accommodate system oxide inventory;
- compatibility with station systems;
- minimal operational maintenance required;
- minimized station manpower to set-up, commission and operate equipment;
- decommissioning activities minimized; and
- high temperature and high flow filtration.

A block diagram of the equipment interfaces is shown in Figure 5.

Improvements in the CAN-DECON™ Process for CANDU Full-system Decontaminations:

Improvements in the CAN-DECON™ process for CANDU full-system decontaminations include:

- development of a sulphur- and halide-free corrosion inhibitor;
- optimization of the AP Cr-rich oxide conditioning process;
- optimized decontamination process equipment design; and
- specification of strategies to minimize waste volumes produced during sub- and full-system decontaminations.

Corrosion inhibitors are added to the CAN-DECON™ formulation to minimize waste volumes generated during a decontamination and to minimize corrosion of carbon steel surfaces during the decontamination.

Rodine 31A, a commercially available corrosion inhibitor containing sulphur, was used in the full-system and sub-system decontaminations at the Pickering NGS. However, residual sulphur and chloride can potentially induce localized corrosion in steam generator tubes with high nickel content (e.g. Alloy-600 in Bruce "A" and "B", and Alloy-800 in Darlington and CANDU-600 stations) during subsequent reactor operation. Hence, a sulphur- and halide-free inhibitor was required for application in sub- and full-system decontaminations of post-Pickering CANDUs.

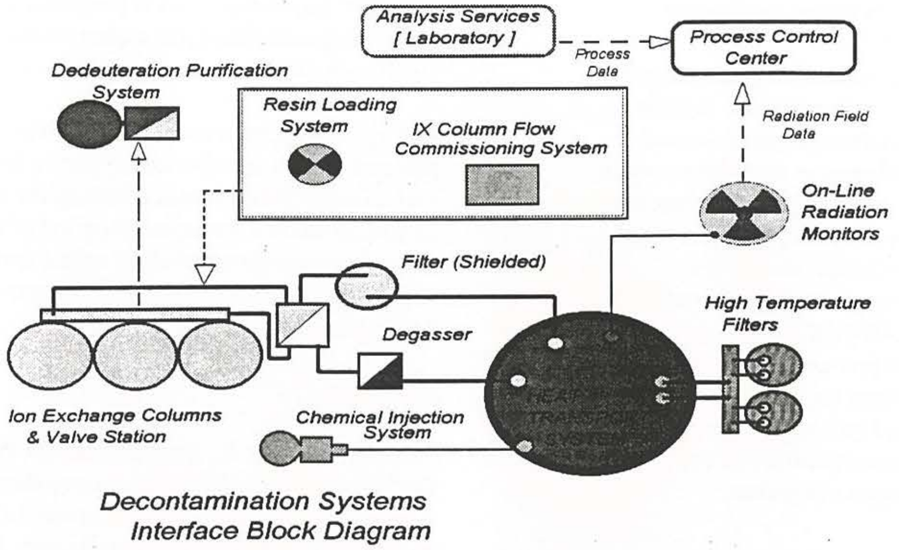

Figure 5: Process equipment required for a CAN-DECON™ decontamination.

A custom formulated corrosion inhibitor free of sulphur and halides was identified and evaluated for use with CAN-DECON™ decontamination solutions. Development work has demonstrated that this sulphur- and halide-free inhibitor is as effective as Rodine 31A for inhibiting general corrosion and protection against pitting corrosion.

The performance of the corrosion inhibitor was demonstrated in a pilot-scale decontamination of NPD feeder pipes. The results of the R&D program and the pilot scale test have been used to specify the application conditions for the sulphur- and halide-free inhibitor. The presence of the inhibitor did not alter the effectiveness of the decontamination process as high decontamination factors were achieved. In addition, the inhibitor formulation did not affect the performance of the cationic and mixed-bed ion-exchange resins used in the CAN-DECON™ decontamination process.

Although application of the AP reagent in Pickering Unit 3 was successful in reducing radiation fields to low levels, its application posed some challenges. Due to the combination of materials of construction in the heat transport system, decomposition of the AP reagent was significant. Decomposition of the AP reagent increases the waste volumes produced (although still small in comparison with the volume of waste from removal of oxide from the heat transport system) and makes process control more difficult. Furthermore, the production of particulate manganese dioxide (MnO_2) may limit the effectiveness of the following CAN-DECON™ step. Particulate MnO_2 settles in low-flow and stagnant areas during the AP and AP destruction steps, blocking access of the CAN-DECON ™ reagents to system surfaces.

In addition, the AP reagent is difficult to destroy. Typically, oxalic acid is used to reduce the AP reagent to soluble Mn(II). However, addition of a significant amount of oxalic acid to the heat transport system results in precipitation of ferrous oxalate on system surfaces. The presence of ferrous oxalate on system surfaces may also limit oxide and activity removal during the subsequent CAN-DECON™ step.

Process conditions to minimize decomposition of the reagent and alternate approaches for the destruction of the AP reagent have been identified and are undergoing evaluation in the COG-funded Decontamination Process Development program.

The effectiveness of some of the earlier full-system decontaminations at Pickering "A" were limited by the amount of ion-exchange resin loaded in to the decontamination process equipment (due to physical size limitations). Incorporation of on-line slurrying of ion-exchange resin into the decontamination process equipment design ensures that sufficient ion-exchange resin would be available for the decontamination. The ion-exchange system could be designed so that resin could be deuterated and de-deuterated, and slurried in and out of the ion-exchange column while other columns are valved-in. In addition, on-line slurrying of resin would significantly reduce the number and size of ion-exchange columns required, the overall size of the process equipment, and the heavy water hold-up in the process circuit.

Strategies to minimize waste volumes generated during full-system decontaminations include performing two-stage decontaminations and implementing technologies to consolidate waste resulting from oxide removal from the heat transport system. A two-stage decontamination process, consisting of mechanical (or chemical) decontamination of the steam generators followed by application of the CAN-DECON™ process leads to significantly reduced process application time, minimized ion-exchange resin and heavy water requirements, reduced corrosion of heat transport system materials of construction and smaller decontamination process equipment.

Summary

The in-core antimony removal and chemical decontamination technologies have served to significantly reduce personnel dose during major reactor refurbishment campaigns and during scheduled maintenance outages. The in-core antimony removal process is particularly suited to controlling radiation fields at stations having significant radioantimony inventories in-core.

Full-system decontaminations have significantly reduced total dose to personnel during large-scale fuel channel replacements, enabling the operation to be performed in a manageable period of time. The technology is well established, with a history of successful reactor operation following the decontamination.

Reference

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