DECONTAMINATION OF THE DOUGLAS POINT REACTOR BY THE CAN-DECON PROCESS

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BACKGROUND

Douglas Point Nuclear Power Reactor is a 200 MWe CANDU-PHWR*. Figure 1 is a schematic diagram of the primary coolant circuit of the reactor. The boiler tubes are made of Monel-400 alloy (nominally 70 wt% Ni, 30 wt% Cu); the primary circuit pipes and valves are made of ferritic steels; the pressure tubes and fuel sheaths are made of zirconium alloys (Zircaloy-2 and -4).

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*CANDU - CANada Deuterium Uranium
PHWR - Pressurized Heavy Water Reactor

The reactor was declared "in-service" in mid-1967. Over the next four years the increasing radiation fields made maintenance more difficult to perform because of shielding required to protect workers and the limited duration that workers could remain in the radiation field. By August 1971, the average of the fields at eight standard locations on the boiler cabinets had risen to about 3.5 R/h.

Around this time considerable maintenance work was required in the boiler room, associated with blowdown lines, valves and mechanical joints. In order to reduce personnel radiation exposures a program was started to reduce the radiation emanating from the Monel-400 boiler tubes. Various coolant parameters were cycled at weekends when the reactor could be shut down at minimum inconvenience to the utility. The most effective technique, dubbed "Redox Cycling", involved alternate additions of hydrogen and oxygen to the primary coolant while passing a very large flow through the purification systems (filters and ion-exchange resins). This procedure effectively reduced the radiation fields in the boiler room at a relatively low cost. Figure 2 shows the reduction accomplished during 14 weekend shutdowns between October 1971 and April 1972. Subsequent operating procedures have kept the average boiler room field below 1 R/h. A full account of this cyclic decontamination procedure has been published [1].

Although the cycling technique was very effective in reducing radiation from the Monel-400 boiler tubes, it had little effect on the carbon steel of the rest of the circuit. A study was started to develop an alternative decontamination procedure which would be effective on carbon steel.

A decontamination process was known to be effective, the AP-Citrox method, was selected as a backup method in case the laboratory development program was unsuccessful. The AP-Citrox process involves the addition of an alkaline permanganate solution (AP) to oxidize the corrosion products in the system, followed by addition of a mixture of citric and oxalic acids (Citrox) to remove the radioactivity. The application of the AP-Citrox process to the Douglas Point reactor was designed, engineered and costed, but not applied.

Several disadvantages were identified as being inherent to the AP-Citrox process, such as:

- about 2 months reactor down time would be required.
- about 25% of the mechanical seals in the system would have to be replaced after the decontamination because of corrosion during decontamination.
- copper from the Monel-400 boiler tubes would plate out on the carbon steel pipes.

- considerable capital expenditures would be required for storage tanks, injection pumps, etc., to perform the decontamination.
- about one million litres of radioactive liquid waste would be generated.
- it would be necessary to displace the D_2O primary coolant with solutions made up in H_2O, with associated losses of D_2O.
- considerable downgrading of the D_2O used to refill the reactor would occur from the H_2O left behind in dead legs and adhering to metal surfaces.
- about 100 man-rem would be consumed in carrying out the decontamination and disposing of the radioactive waste solutions.

It was not fully established that the fuel could be left in the reactor during an AP-Citrox decontamination. If discharge of the whole core was required, considerable time and expense would be involved.

CAN-DECON

Evolution of the Concept

A collaborative development program proceeded between scientists and engineers at CRNL* and WNRE**, and including engineers from Ontario Hydro attached to CRNL. The objectives of the program were to overcome the deficiencies recognized in the AP-Citrox method and other published decontamination processes. At all stages of the program a complete exchange of data and ideas prevailed between the three groups involved.

A major criterion was to avoid having to drain the D_2O primary coolant from the reactor. This requirement led naturally to studying the addition of reagents which did not contribute any H_2O.

The initial emphasis was on P_2O_5 additions, with a simultaneous investigation of a large number of organic acids and comercially available mixtures. Considerable effort was expended on the P_2O_5 study, both in laboratory tests and in supporting trials on actual reactor components. However, P_2O_5 was eventually abandoned because it was too corrosive towards some components, and because it did not prevent copper from the Monel-400 boiler tubes plating out on the carbon steel.*

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* CRNL - Chalk River Nuclear Laboratories of Atomic Energy of Canada Limited, Chalk River, Ontario, Canada

** WNRE - Whiteshell Nuclear Research Establishment of Atomic Energy of Canada Limited, Pinawa, Manitoba, Canada

During this study the idea of regenerating the reagent on ion-exchange resin was innovated and developed. This concept, using a low reagent concentration, minimizes corrosion while permitting extended periods of operation. In addition, there is no requirement to drain the system to remove exhausted reagent. Although P_2O_5 was dropped, the regenerative, dilute reagent concept was retained and further developed, until it evolved into the CAN-DECON process.

The CAN-DECON Process

The CAN-DECON process involves the addition of chemical reagents (typically to give 0.1 wt% concentration) directly to the coolant of a shutdown reactor. The reagent attacks the surface oxide layer and releases both particulate and dissolved material to the coolant. A continuous high flow of coolant is passed through filters and cation-exchange resin in the reactor purification circuit. The filters remove the insoluble matter while the resin removes dissolved metal ions and at the same time regenerates the reagents, which are recirculated back to the primary circuit where they again attack the contaminated surfaces. The process is continued as long as contaminants are being removed, until the ion-exchange resin is spent, or until the allotted time has expired. The reagents and dissolved corrosion products remaining are then removed by mixed-bed resin.

The process is applicable in D_2O without serious downgrading, since the reagents are added in a D_2O slurry and the primary system is neither drained nor flushed. Compared to conventional decontamination processes using strong reagents this process requires very little equipment.

The regeneration principle economizes on reagents while at the same time it concentrates wastes on the resin and filters. This simplifies disposal, since there are essentially no liquid wastes to deal with.

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* A commercial reagent, Nutek L-106, was eventually selected for use at Douglas Point, primarily because it prevented copper redeposition whilst giving adequate decontamination factors. It is formulated and marketed by The Nuclear Technology Corporation, Amston, Conn.

CAN-DECON AT DOUGLAS POINT

Procedure

The Douglas Point decontamination was directed primarily at the carbon steel header piping rather than at the Monel-400 boiler tubes. Accordingly, half of the boiler units were valved out of the circuit before starting the decontamination, thereby halving the area of Monel-400 exposed to the decontaminant. This arrangement also improved the flow distribution in the system. The reactor purification system did not have sufficient filtration and ion-exchange capacity to handle the decontamination which necessitated the temporary installation of a larger purification circuit.

Since the primary coolant at Douglas Point normally operate at a pH 25°C of between 10.3 and 10.7, attained by adding Li_2O dissolved in D_2O, the first phase of the decontamination ("preparation") involved the removal of this alkalinity on a mixed-bed ion-exchange column to give a conductivity of less than 0.2 mS/m. The mixed-bed column was then valved out, and a column filled with cation resin was valved in. A slurry of the reagent in D_2O was added to give a concentration in the primary coolant of approximately 0.1 wt%. The second phase ("regeneration") then commenced.

Corrosion products were released from the system surfaces and appeared both as undissolved particles and in solution in the decontaminant. By a continuous flow of a bleed stream through the large temporary purification circuit, particles were removed by sub-micron filters. Metallic ions in solution were removed by the cationic resin, thereby simultaneously regenerating the reagent.

Radioactivity associated with the corrosion products remained on the filters and cation-exchange resin. To monitor the progress of the decontamination, samples were taken frequently from three locations, viz., before the filters, before the ion-exchange column and after the ion-exchange column. Two supplementary additions of oxalic acid and one of citric acid were made during this phase.

After nine hours the regeneration phase was terminated by valving out the column containing cationic resin and valving in the column with mixed-bed resin, thus starting the "removal" phase. During the "removal" phase, which lasted for 10 hours, residual reagent, corrosion products and radioactivity were collected on filters and the mixed-bed resins.

The final phase, "restoration of normal chemistry", was accomplished by replacing the mixed-bed resin with columns of new resin in the Li-OD form, and by injecting Li_2O dissolved in D_2O.

The reactor was ready for startup 72 hours after shutting down to start the decontamination. (Actual startup was postponed 24 hours while maintenance work, unconnected with the decontamination but made easier because of it, was performed.) This 72-hour period included several hours required to interchange the permanent and temporary purification systems before and after the decontamination. It is considered that, with a suitable permanently installed purification system plus experience gained from the first decontamination, another CAN-DECON could be performed at Douglas Point within a 36-hour shutdown period.

Effectiveness of the Process

Before starting the decontamination, a survey was made of radiation fields in a large number of areas around the reactor circuit. These areas were surveyed immediately after the decontamination, and again at a shutdown after two months of reactor operation. A further survey was made after about a year's operation at high capacity factor (greater than 80%). A summary of the results is shown in Table 1.

From the table it is evident that very useful radiation field reductions occurred in most areas around the reactor, but particularly adjacent to the feeder cabinets which were the primary target of this decontamination. It is also evident from Table 1 that the rate of growth of fields is very slow following the decontamination. This point is illustrated in Figures 2 and 3.

A second measure of the effectiveness of the process is the amount of radioactivity removed. To estimate corrosion product activity in-core, representative fuel bundles discharged from various channels in the reactor were immersed in hot 6N HCl to dissolve all the contamination from their surfaces. The resulting solutions were analyzed for metals and for radionuclides. Other bundles were treated similarly after the decontamination. The Co-60 results are summarized in Table 2 and indicate an average decontamination factor of about 20.

The amount of Co-60 removed from the primary circuit was estimated from analysis of water samples collected before and after the filters and ion-exchange resin columns during the regeneration and removal phases of the decontamination. Table 3 summarizes the amount of Co-60 estimated to have been collected in the purification system.

Because the fuel remained in position during the decontamination, activity removed from fuel surfaces was not available for subsequent redistribution around the circuit. In addition, the removal of Co-59 reduced the subsequent rate of production of Co-60. These factors contributed significantly to the low rate of growth of radiation fields following the decontaminations (Figures 2 and 3).

Corrosion Considerations

Corrosion evaluation played a prominent part throughout the development program. Laboratory trials were conducted on coupons, and the corrosion of actual reactor components was evaluated in a series of trials in a Components Test Loop.

Corrosion which occurred during the Douglas Point decontamination was assessed in four ways:

(i) by analyses of iron and other metals in solution, assessing total metal loss from the system,

(ii) by Corrosometer* probes, measuring instantaneous corrosion rates by change in electrical resistance of metallic wires inserted in the circuit,

(iii) by evaluation of corrosion coupons, some of which had been exposed in the heat transport system before the decontamination,

(iv) by inserting new units of some components, eg, pressure tube closure seals, immediately before the decontamination and removing them for examination as soon as convenient afterwards.

A summary of corrosion incurred by various materials during the decontamination is presented in Table 4. The results were as expected.

Effects on Component Reliability

In the two years since the decontamination, no failures or malfunctions of equipment have been attributable to the decontamination. The amount of maintenance work required on equipment has not increased at all.

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* A commercially available Magna Corrosometer Model L-3 was used.

Effect on Heavy Water Leakage

Over the period since the decontamination, the average leak rate of D_2O from the primary system during operation has been the lowest in the history of Douglas Point. The decontamination certainly did not increase the leak rate of coolant from the system.

Effect on Crud Concentration and Specific Activity

Before decontamination, the concentration of insoluble particles ("crud") in the coolant was normally less than 0.01 mg/kg. Following the decontamination, crud levels of about 0.05 mg/kg were commonly observed. It was suspected that these higher values, which are well within the allowable specification, were the result of contamination of the sample lines during the decontamination. When a new sample line was installed the measured values fell to 0.01 mg/kg, which is believed to have been the true value over most of the period since the decontamination.

Before the decontamination the specific activity of crud varied in the range 2 to 5 *Ci Co-60/kg crud. Since the decontamination, specific activities have been much lower, with an average value of 0.7 *Ci Co-60/kg being found on recent samples. This reflects the removal of Co-59 generated during early operation.

DOSE SAVED BY DECONTAMINATION

A total of 10 man-rem was expended in conducting the decontamination. About half of this was attributable to the temporary nature of the installation; a permanently installed and well shielded injection and cleanup system would have required less radiation exposure from the operators.

It is estimated that between 150 and 180 man-rem were saved during a scheduled maintenance outage in November 1975, because of the decontamination in August. The estimate is obtained by multiplying the actual exposure recorded for each job by the decontamination factor for the area in which the job was done, and then summing the savings for all of the jobs performed. This estimate should be considered a minimum since many additional jobs were done for which the dose was not identified. The lower radiation fields and lower total man-rem required for the shutdown work permitted additional desirable jobs, which had been postponed at previous shut

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* 1 Ci = 3.7×10^{10} Bq

downs, to be performed. The lower fields and their low rate of growth following the decontamination are continuing to benefit the station.

The total dose recorded at Douglas Point has decreased steadily since it peaked in 1971. In the last two years improvement is due to several factors which include efforts in radiation exposure control by many methods [2] of which decontamination is one which has achieved identifiable benefits.

CURRENT SITUATION

The CAN-DECON process has proven its value at Douglas Point, following full-scale trials in the 25 MWe NPD CANDU-PHW reactor and the 250 MWe Gentilly-1 CANDU-BLW* reactor. Ontario Hydro intends to apply it when required to their Pickering nuclear generating station (four 540 MWe CANDU-PHW reactors operating; another four similar reactors under construction). CAN-DECON capability has been designed into CANDU-600 stations and provision will be made for its use in Darlington NGS and future Ontario Hydro stations.

A development program is in progress to optimize the application of CAN-DECON to the stainless steel moderator circuits of CANDU reactors, and to the Inconel-600 and Incoloy-800 tubes used in the steam generators of recent CANDU-PHW reactors.

The CAN-DECON concept is to employ at regular intervals a mild, regenerated decontaminant producing only solid waste. This contrasts with the more conventional approach of using strong reagents infrequently to produce a high decontamination factor but causing considerable circuit corrosion and producing several reactor circuit volumes of liquid waste. The CAN-DECON concept is receiving considerable interest from utilities operating light water reactors in various parts of the world. AECL is a Federal Crown Corporation and Ontario Hydro is a provincial Crown Corporation, both dedicated to the use of CANDU reactors to produce electricity. Accordingly, a commerical Canadian company, W.P. London and Associates Limited of Niagara Falls, Ontario, has been licensed by AECL to apply the CAN-DECON process to other reactor systems on a world-wide basis.

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* BLW - Boiling Light Water

SUMMARY

The CAN-DECON decontamination of Douglas Point NGS has demonstrated that the procedure is essentially fully developed:

- it effectively reduces radiation fields
- it is economically viable
- it has no apparent adverse side effects.

AECL and Ontario Hydro will continue to refine the process to enhance its future flexibity and effectiveness. Provision for CAN-DECON decontamination is being incorporated in the designs of future CANDU reactors. This will permit decontaminations to be performed routinely by station staff during a 30-hour outage.

ACKNOWLEDGEMENTS

Very many people in AECL and Ontario Hydro contributed to the development of the CAN-DECON process and its successful application at Douglas Point. The list includes scientists, engineers, designers, operators and health physicists. The authors are grateful to them all.

REFERENCES

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2. J.E. LeSurf, D.A. Watson, R. Wilson, G.A. Vivian, "Radiation Dose Reduction Programs for CANDU Nuclear Power Stations". Paper presented at the 10th World Energy Conference, Istanbul, Sept. 1977. (Reproduced in the Conference Proceedings.)

TABLE 1

SUMMARY OF RADIATION FIELD MEASUREMENTS

Location	Before CAN-DECON mR/h	Immediately After CAN-DECON mR/h	1 Year After CAN-DECON mR/H
Walkway at Feeder Cabinets	2000 - 3000	300 - 500	285 - 700
East Fuelling Machine Vault*	1900 - 7900	650 - 850	685 - 1470
West Fuelling Machine Vault*	1600 - 5800	420 - 970	515 - 1045
Lower Main Circulating Pump Area (Affected by Fields from Monel Boilers)	800 - 4000	500 - 1400	500 - 1750
Contact With Boiler Cabinets (Average)	520 - 1300 (810)	320 - 875 (540)	300 - 850 (530)

* Measurements taken vertically up the center of the reactor face at 1.2 meters from the end-fittings. Fields increase with height as the feeder cabinet region is approached.

TABLE 2

DECRUDDED FUEL BUNDLE DATA

Bundle Location		Activity on Surface*
Channel Number	Position in Channel	Co-60 $\mu Ci/m^2$ †
BEFORE CAN-DECON		
C17	10	5.3×10^4**
HO4	10	1.6×10^4
N13	10	6.3×10^3
B9	6	4.7×10^3
AFTER CAN-DECON		
H12	10	8.4×10^2
MO4	10	3.6×10^2
P11	10	3.4×10^3
K13	10	5.0×10^2
BO7	10	5.2×10^2
G11	10	3.8×10^3
H12	6	2.4×10^2
M4	6	3.3×10^1
P11	6	1.8×10^2

* For simplicity, only the results of Co-60, the most significant isotope in radiation field generation, are shown. Similar results were obtained for Cr-51, Co-58, Zr-95 and Fe-59.

** High activity is due to bundle being part of original fuel charge. At decontamination time <4% of the bundles in the core were from the original loading.

†1 $\mu Ci = 3.7 \times 10^4$ Bq

TABLE 3

ESTIMATES OF Co-60 ACTIVITY REMOVED BY CAN-DECON

	Ci Co-60*
Removed by IX	190 - 210
Removed by filters	30 - 40
TOTAL	220 - 250

* 1 Ci = 3.7×10^{10} Bq

TABLE 4

CORROSION DURING CAN-DECON

Material	Average Penetration Rate, µm/h	Total Pentration µm
Carbon Steel	0.28	2.5
410 SS	0.08	0.7
316 SS	0.02	0.2
Monel-400	0.03	0.3
Nickel	0.02	0.2

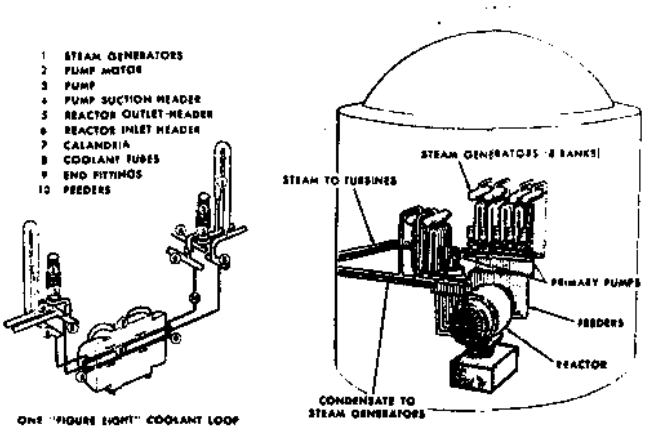

Figure 1

Sketch of Douglas Point Primary Circuit

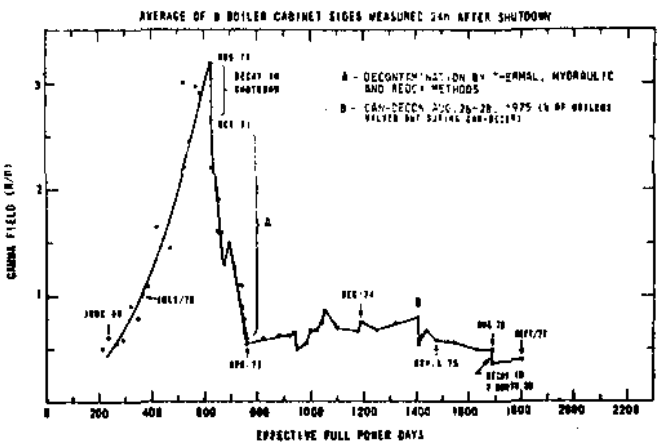

Figure 2

Douglas Point Nuclear Generating Station Boiler Room Fields

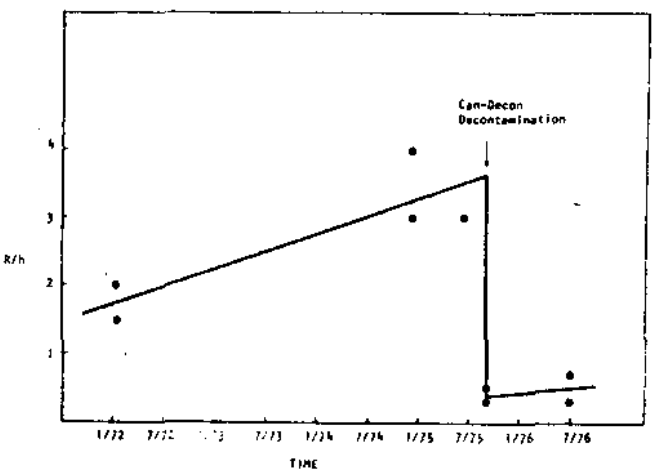

Figure 3

Radiation Fields From Douglas Point Feeders