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# Experience with Dilute Chemical Decontamination in Indian Pressurized Heavy Water Reactors

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## Abstract

Dilute Chemical Decontamination (DCD) process has been used in several full system and components of nuclear coolant systems to effectively remove the radioactive contaminants that causes radiation field and consequent MANREM problem. The DCD process uses chemicals in very low concentrations (millimolar) and dissolves the oxide film along with the activity incorporated in the oxide film. In DCD process operated under the regenerative mode, the chemical formulation spent in the process of oxide dissolution is replenished by passing through cation exchange columns. Finally, after achieving sufficient decontamination of the system/component, the added decontamination chemicals along with the activities and metal ions released during the process are removed by mixed bed ion exchange columns and the system is restored to normal operating condition in a few days time. In PHWRs, the regenerative DCD process is applied for full primary coolant system decontamination. The chemicals are added directly to the heavy water coolant with the fuel in the core. In Indian PHWRs (MAPS#1&2, RAPS#1&2, NAPS#1&2 and KAPS#1), the process has been applied eleven times. A chemical formulation based on NTA, Citric acid and Ascorbic acid has been applied seven times with good results. Decontamination factors in the range 2-30 have been obtained in different components with good MANREM savings in the subsequent maintenance works.

Efforts are on to modify the process to take care of the challenges posed by antimony isotopes. An inhibitor (Rodine-92B) based process was successfully tested in NAPS#2 for removing antimony isotopes ( $^{122}\text{Sb}$  and  $^{124}\text{Sb}$ ). Further refining of the antimony removal process is being worked out. Similarly, the process is being modified to effectively remove the hotspot causing stellite particles in the moderator system of PHWRs. A permanganate based process has been developed and tested in several adjustor rod drive mechanisms in KAPS and NAPS. The experience of applying/testing the DCD process in the Indian nuclear reactors is described in this paper.

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## 1. Introduction

Build-up of radiation field in reactor coolant systems of nuclear power plants is inevitable.

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Radiation field build-up is attributed to the deposition of activated corrosion products and the fission products released from the fuel elements. The activities commonly observed in the nuclear reactor coolant systems are given in Table-1.

Table-1  $\gamma$ -Emitters observed in the reactor coolant systems

<i>Activated corrosion products</i>	<i>Fission products</i>
$^{60}\text{Co}$	$^{144}\text{Ce}$
$^{58}\text{Co}$	$^{141}\text{Ce}$
$^{54}\text{Mn}$	$^{103}\text{Ru}$
$^{59}\text{Fe}$	$^{106}\text{Ru}$
$^{51}\text{Cr}$	$^{95}\text{Zr}$
$^{124}\text{Sb}$	$^{95}\text{Nb}$

Out of these activities, the contribution of  $^{60}\text{Co}$  to radiation field is maximum because of its high half life (5.26 years) and high  $\gamma$ -energy. Of late the contribution of  $^{124}\text{Sb}$  is increasing in some plants. Increased radiation field causes exposure of plant operating personnel to radiation resulting in MANREM expenditure. Efforts are being made by all the plants to keep the radiation levels as low as reasonably achievable (ALARA). Proper choice of reactor structural materials, maintaining a good water chemistry regime, adoption of techniques such as Zn ion passivation are being followed to reduce the radiation field to the extent possible. Despite these preventive measures, many nuclear power plants report increased radiation field and MAN-REM expenditure. Under this condition, decontamination is the only option available to bring down the radiation field. Decontamination of nuclear coolant system components can be achieved either using mechanical methods or chemical methods. Where as, decontamination of full coolant system can be achieved only by chemical methods. Pressurized Heavy Water Reactors (PHWRs) are amenable to full system chemical decontamination. The primary heat transport systems of PHWRs were decontaminated by the dilute chemical decontamination (DCD) process operated in the regenerative mode<sup>(1)</sup>.

## 2. Description of primary heat transport system of PHWRs

The primary heat transport system of PHWRs is a closed circuit. The primary coolant (heavy water) circulated through the zircaloy pressure tubes containing the fuel, passes through carbon steel feeders, headers and then to the steam generators where the nuclear heat is transferred to the secondary coolant to generate steam. The tubes in the steam generators are made of monel-400/incoloy-800. The temperature of the coolant is in the range 250–292°C and pressure is maintained at 92kg/cm<sup>2</sup>. A feed and bleed system maintains the pressure and also feeds the purification system consisting of filters and ion exchangers.

Under the operating conditions of PHWRs and carbon steel being the main corroding surface, magnetite is the dominant corrosion product. In addition to magnetite, nickel ferrite, chromite and mixed ferrites are also observed. These oxides trap the radioactive nuclides and fission products, which leads to radiation exposure hazard.

## 3. The dilute chemical decontamination (DCD) process

The DCD process involves the addition of chemicals through a slurry addition pump to the PHT system and then the chemical decontamination formulation is allowed to circulate through the system. Simultaneously, the partially exhausted chemical formulation is passed through a cation exchange column to exchange the dissolved iron, other corrosion products and activities for H<sup>+</sup> thereby to regenerate the acids consumed in the oxide dissolution process. After achieving sufficient decontamination of the system/exhaustion of predetermined number of cation columns, the cation exchange columns are valved-out and the mixed bed consisting of anion and cation exchange resin is

valved-in to remove the added chemicals and the remaining metal ions and activities and thus to terminate the decontamination process. The schematic of the process is given in Figure-1.

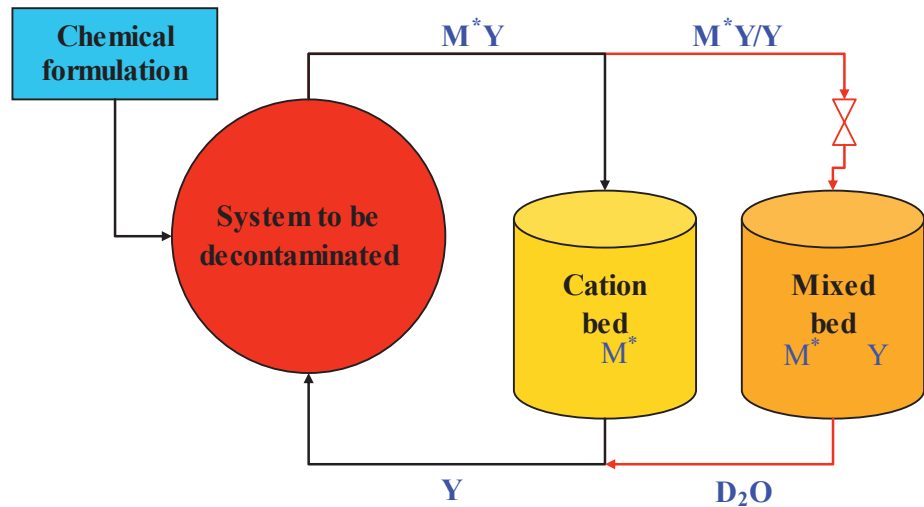


Fig.1. Schematic of the dilute chemical decontamination process

Subsequent to the decontamination, the system is hot conditioned and brought to normal operating condition. The salient features of this process are:

- The process uses mild organic acids (EDTA or NTA, Citric acid etc..) in dilute form (0.1 g/l)
- The chemicals can be added directly to heavy water (D<sub>2</sub>O) coolant without significant down grading
- The process is carried out anytime after one week of shut down and with the fuel in place
- The process takes hardly two days
- It generates only solid radioactive waste in the form of ion exchange resins.

#### 4. Experience of application of DCD process in Indian PHWRs with NTA based chemical formulation

The full primary coolant systems of PHWRs in India were decontaminated by the DCD process. The hardware required for implementing the process in the primary system was designed in house. Ion exchange columns of 500 litre capacity with adequate shielding, chemical addition facility with slurry pump and on-line gamma monitoring facility were lined up before starting the process. Initially EDTA based chemical decontamination process was applied. During the application of EDTA based chemical formulation, the following difficulties were experienced <sup>(2)-(4)</sup>

- The EDTA was removed by cation IX and its concentration varied during DCD
- Low DFs on surfaces other than carbon steel
- Elution of <sup>60</sup>Co activity from IX
- Poor ion exchange capacity for Cu<sup>2+</sup> and Ni<sup>2+</sup>

Hence, studies were carried out to find a substitute for EDTA. It was found that Nitrilo tri acetic Acid (NTA) is a better alternative to EDTA <sup>(5)-(6)</sup>. A chemical formulation consisting of 300 mg/l each of NTA, Citric acid and Ascorbic acid (termed as NAC) was used in subsequent chemical decontamination campaigns. The fluctuations observed in the concentration of EDTA were not observed with NTA. The radiolytic decomposition rate of NTA was found to be lower than EDTA. Hence, extra addition of chelating agent to make up the loss due to radiolysis and ion exchange removal was less. The removal of copper and nickel ions by the cation exchange resin improved. Also, the elution of <sup>60</sup>Co just before

the exhaustion of cation column was considerably less. The performance of the NTA based chemical decontamination process when it was applied to PHWRs is given in the Table-2.

Table-2 Field data of various decontamination campaigns carried out with NTA based formulation

	<i>MAPS#2</i>	<i>RAPS#1</i>	<i>MAPS#1</i>	<i>NAPS#1</i>	<i>NAPS#2</i>	<i>KAPS#1</i>
Date	Jan'02	May'02	Oct'03	Nov'05	Jan'08	Jul'08
Formulation	NAC	NAC	NAC	NAC	NC(Sb) and NAC	NC(Sb) and NAC
<sup>60</sup> Co(Ci)	12.9	40	30.3	8.3	2.1	20
<sup>124</sup> Sb(Ci)	--	--	0.1	1.0	39.6	6
Total activities Removed (Ci)	35.8	50.8	46.3	46	59	34
Radioactive resin waste (Tons)	7.0	7.0	7.0	7.0	6.8	6.5
Iron(kg)	222	232	305	262	84	219
Inhibitor	Yes	Yes	Yes	No	Only during NC(Sb)	Only during NC(Sb)
Decontamination Factor (DF) on feeders	2 – 7	4 -5	4 - 12	1 -2	--	--
DF on boilers	2 – 12.5	1 – 2.5	1.6- 4	1 – 2.5	--	--

\*NC (Sb) – Modified process to remove antimony activity

In each decontamination campaign, 200-300 kg of iron along with 35-200 curies of total activity was removed from the system. Decontamination factors varied from 2-15. Carbon steel feeders and headers showed higher decontamination factors, whereas steam generators and components made of stainless steel such as end fittings exhibited lower decontamination factors. In each decontamination campaign, 7m<sup>3</sup> of solid radioactive waste in the form of ion exchange resin was generated. After each campaign, the plants reported significant MANREM savings due to decontamination.

Antimony isotopes (<sup>124</sup>Sb, <sup>122</sup>Sb) were found to give problems in Narora and Kakrapar Atomic Power Stations (NAPS & KAPS). As soon as the chemicals were added to the PHT system, antimony activities were released from the in-core zircaloy surfaces and remained in solution without getting removed over cation exchange resin. Besides, the antimony activities so released get deposited on the out-of-core surfaces thereby offsetting the reduction achieved in radiation field by the removal of <sup>60</sup>Co and other activities. In fact many components in the PHT system showed higher radiation field than the field observed before decontamination. The process was modified by introducing an antimony removal step [NC(Sb) followed by NAC] in which the antimony released by the formulation chemicals were quickly removed by the mixed bed without allowing the antimony activities to deposit. The corrosion inhibitor Rodine 92 B also helped to prevent the deposition of antimony over carbon steel metal<sup>(7)</sup>.

## 5. Chemical decontamination of hotspots

In NAPS and KAPS moderator systems a unique problem was observed. There were localized areas of high activity. These hotspots were attributed to  $^{60}\text{Co}$  originating from the ball screw mechanisms of adjustor rod drive mechanism. The hard facing alloy viz. stellite was found to be released in particulate form from these components and activated by the neutron flux inside the core and deposited in low flow regions in the out of core surfaces of moderator coolant system. Experiments were carried out with permanganate under acidic and alkaline conditions<sup>(8)</sup>. It was found that permanganic acid has superior dissolution capability as compared to other permanganate based reagents. The combination of permanganic acid and EDTA based formulation was evaluated in adjustor rod drive mechanisms and was found to give good decontamination factors.

## 6. Conclusion

Good radiation field reduction can be achieved by carrying out full primary heat transport system chemical decontamination in PHWRs. Process modification is being carried out to take care of the problems being faced by antimony.

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