

Analysis on the Current Status of Chemical Decontamination Technology of Steam Generators in the Oversea Nuclear Power Plants (NPPs)

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1. Introduction

Since decommissioning of Kori Nuclear Power Plant (NPP) Unit 1 was determined on June 12, 2015 by the 12th National Energy Commission, the decontamination techniques regarding the major components and pipes in the nuclear facility have been emerged. Especially for the steam generators, it requires advanced technical skills to decontaminate due to its large volume and high radioactivity levels.

In domestic cases, the replacement of the steam generator was performed in Kori and Hanul NPPs. Additionally, the steam generators in Hanbit Unit 3 and 4 are scheduled to be replaced in 2018 and 2019, respectively. Nevertheless, the wastes from the dismantled steam generators are currently just on-site stored in the NPP because there are no disposal measures for the waste and lack of the decontamination techniques for large-sized metallic equipment.

In contrast, in the oversea NPPs, there are many practical cases of chemical decontamination not only for oversized components in the NPPs such as reactor pressure vessel and steam generator, but also for major pipes.

Chemical decontamination technique is more effective in decontaminating the components with complicated shape compared with mechanical one. Moreover, a high decontamination factor can be obtained by using strong solvent, and thereby most of radionuclides can be removed. Due to these advantages, the chemical decontamination has been used most frequently for operation of decontaminating the large-sized equipment. [1]

In this study, an analysis on the current status of chemical decontamination technique used for the steam generators of the foreign commercial NPPs was performed.

2. Chemical Decontamination Technique for Steam Generator

Various techniques were developed and applied to chemically decontaminating the steam generators around the world, such as CORD process of Germany, DfD process of United States and MEDOC process of Belgium. Each process is described in detail in the following subsections.

2.1 CORD Process

The process of CORD (Chemical Oxidation Reduction Decontamination) was developed in KWU in Germany and classified into three main sub-processes.

- Oxidation process between the permanganic acid (HMnO_4) and the metal surface
- Reduction process between the oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) and the oxide film on Fe-based metal
- Purification process between the hydrogen peroxide (H_2O_2) and the oxalic acid

The schematic diagram of CORD process is shown in Fig 1.

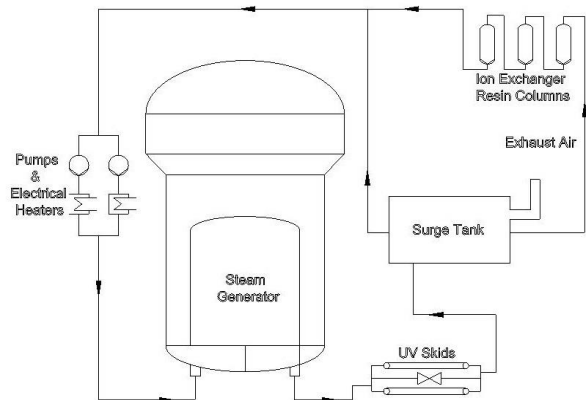


Fig.1. Process diagram of CORD

The process of CORD was used for decontaminating the steam generators of Obrigheim, Stade, Barsebäck NPPs in Germany and also for Trino one in Italy. Currently, many upgraded processes such as HP/CORD UV, HP/CORD and HP/CORD D UV etc. are used according to the types and materials of reactors.[2]

2.2 DfD Process

The process of DfD (Decontamination for Decommissioning) was developed at the EPRI in the United States and classified into three main sub-processes.

- Oxidation process between the tetrafluoroboric acid (HBF_4), potassium permanganate (KMnO_4) and the metal surface

- Reduction process between the oxalic acid ($C_2H_2O_4$) with the dissolved metal ion.
- Purification process with ion exchange resin

Oxidation and reduction process are iterated until the contamination level of the metal surface drops to less than the target value. Then, the circulating solution is filtered by using ion exchange resins. The schematic diagram of DfD process is shown in Fig.2.

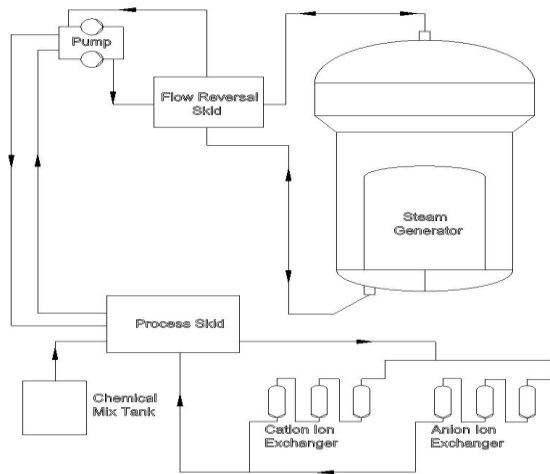


Fig.2. Process diagram of DfD

The DfD process was used for decontaminating the steam generator of the Big Rock Point, Maine Yankee and San Onofre NPPs in the United States. At present, the DfDX (Decontamination for Decommissioning, electro-chemical ion eXchange) process has been developed to improve the problem of the waste ion-exchange resin generation and used practically.[3]

2.3 MEDOC

The process of MEDOC (MEtal Decontamination by Oxidation with Cerium) was developed by SCK-CEN in Belgium, and it is classified into two main sub-processes as follows.[4]

- Decontamination of the contaminated metal using Ce^{4+}
- Regeneration of Ce^{4+} solution using oxidation reduction potential

The schematic diagram of MEDOC process is shown in Fig. 3.

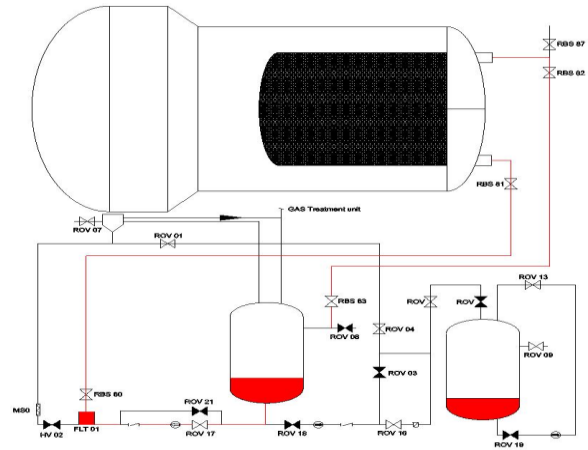


Fig. 3. Process diagram of MEDOC

MEDOC process was used for decontaminating the steam generator in BR-3 NPP in Belgium.

3. Conclusions

In this study, the three major chemical decontamination processes were reviewed, which are applied to the decommissioning process of the steam generators in the commercial NPPs of the United States, Germany, and Belgium. The three processes have the different features in aspect of solvent, while those are based in common on the oxidation and reduction between the target metal surface and solvents. In addition, they have the same goals for improving the decontamination efficiency and decreasing the amount of the secondary waste generation. Table 1 tabulates the comparative analysis results of the three chemical decontamination processes used in the decommissioning process of steam generator in commercial NPPs.

Table 1. Materials used, Advantages & Disadvantages of the three major chemical decontamination processes

	Materials used	Advantage	Disadvantage
C O R D	- $HMnO_4$	- High decontamination efficiency	- A large amount generated of the secondary waste liquid
	- $H_2C_2O_4$	- Stability of the system	- Complexity of the process
	- Higher efficiency though adding the ultrasonic process	- Required to heat to 70-100°C for the effective decontamination	
	- Ion exchanger	- Ineffective for decontamination of porous materials	
D f D	- HBF_4	- Higher decontamination effect by dissolving Cr-based oxide	- A large amount generated of the secondary waste liquid
	- $KMnO_4$	- Many cases of application	- Exposure to airborne contamination
	- $C_2H_2O_4$		- Necessity of using the high toxic solvent for higher decontamination factor
			- Generation of spent ion exchange resin

M E D O C	- Ce ⁴⁺	- High efficiency by combining advantages of Ce and ozone decontamination - A small amount generated of the secondary waste	- Hydrogen generation - Durability problem of electrolysis module
	- O ₃	- Possible to reduce the amount generated of the secondary waste through adding the sulfuric acid reaction	- Required to maintain electrode resistance for a long time

Based on the analysis results on component sub-processes and major advantages and disadvantages of each process, Table 2 shows the key fundamental technologies for decontamination of the steam generator in Korea and the major considerations in the development process of each technology.

Table 2. Component sub-processes and major consideration of the chemical decontamination processes

Component Process	Major Consideration
Oxidation	- A target metal for decontamination - Type and efficiency of oxidizing agent - Airborne contamination during process
Reduction	- Type and efficiency of reducing agent - Treatment of deposit generated - Air exhaust during process - Decontamination factor
Purification	- The toxicity of process waste liquid - Generation of the secondary radioactive waste - Purification efficiency of waste liquid generated

Apart from consideration of the chemical decontamination process shown in Table 2, researches on the decontamination techniques to treat the retired steam generators are required. Simultaneously, it is necessary to prepare disposal of the large-sized metallic equipment expected to be generated through developing the conditioning process and disposal options in consideration of the actual circumstances in our country.

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