

Technical requirements of the chemical decontamination for the PHWRs system

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1. Introduction

In all kind of nuclear reactors, radioactive field build up around the primary coolant system due to the deposition of radioactive isotopes on the corrosion oxide of the surface. With long term operation of nuclear power plants (NPPs), there are deposited radioisotopes, mainly cobalt and small amount of fission products throughout the reactor coolant system. Especially in early operation stage of a plant, cobalt-58 is produced from (n-p) reaction of nickel-58 with fast neutron, and after about 10 years operation, cobalt-60 forms as a result of (n- γ) reaction of Co-59, which seems impurity of base material, with thermal neutron [1]. These radionuclides cause the main sources to occupational exposure during maintenance or decommissioning of NPPs. Therefore, decontamination is necessary for achieving sufficiently reduced radioactivity during the routine maintenance or for decommissioning. The removal of radionuclides from the primary coolant system traditionally was applied to chemical decontamination which is the dissolution of corrosion metal oxide layers such as magnetite, nickel ferrite, and chromites, which are deposited with the radionuclides.

Current chemical decontamination technologies for system were focused on the Pressurized Water Reactors (PWRs), which were very thin corrosion oxide film of 2~3 μ m. Radioactive corrosion products generated from the reactor coolant system of PWRs were known to be composed of the magnetite (Fe₃O₄) and nickel ferrite (NiFe₂O₄) including various chromium oxides (FeCr₂O₄, Fe₂CrO₄, NiCr₂O₄). Chemical decontamination for PWRs should be repeated by oxidative and reductive dissolution process to reach target radiation level. However, Pressurized Heavy Water Reactors (PHWRs), have been informed to form very thick corrosion oxide film up to 75~100 μ m on the reactor coolant system due to the different structural materials and system operation. Conventional technologies like CAN-DECON, CAN-DEREM were generated secondary waste due to use of chelating agents such as EDTA, citric acid, and oxalic acid [2].

In this point of view, a new chemical decontamination technology for PHWRs system should be capable of dissolving very thick oxide and minimizing secondary wastes. In this work, we investigated the current status of conventional technologies and proposed the technical requirements of

chemical decontamination for the PHWRs in developing future eco-friendly technology.

2. Current chemical decontamination technologies for reactor system of NPPs

The reactor coolant system of the PWRs are operating in a closed cycle at a pressure of about 15 MPa and a temperature of 270~310°C. The main components of the system are consisted of zirconium alloy as fuel cladding material and inconel alloy for steam generator tube and other major components are made of stainless steel with excellent corrosion resistance. As the operation of a nuclear power plants were increased, radioactive corrosion oxide film formed to the surface of the reactor coolant system. It has known the two types of oxides that was attached outside impregnated on the system surface another oxides grown inside the metal. It is reported that the ratio of the radioactivity from these two oxides is almost the same.

These radioactive oxides have been identified with the magnetite (Fe₃O₄) and nickel ferrite (NiFe₂O₄) including various chromium oxides (FeCr₂O₄, Fe₂CrO₄, NiCr₂O₄) of 2~3 μ m. The composition of these oxide films are similar to that of nickel ferrite and is expressed as a non-stoichiometric mixed oxide of spinel structure (Fe)_{3-x}(Ni)_x(Cr)_yO₄. [1~3] The major chemical decontamination method that has been developed so far is the reduction and dissolution of Fe oxide film by a reducing agent. The chromium oxide in the corrosion oxide is oxidized to Cr (III) \rightarrow Cr (IV) and the iron oxides dissolve when reduced to Fe (III) \rightarrow Fe (II). In most commercial reductive decontamination processes, organic chelates are used to prevent the precipitation of dissolved metal ions by forming metal-organic acid chelation. The use of organic chelates results in improved decontamination efficiency. However, it was found that the organic acids and chelates used in those processes had detrimental effects on disposal safety due to the formation of stable and soluble complexes with radionuclides. For oxidation decontamination, typical permanganate processes such as NP, AP, and HP have been developed to dissolve chromium oxides by oxidation reaction. In reductive decontamination process to dissolve magnetite, CAN-DEREM, CITROX, LOMI, DfD and CORD processes have commercially applied up to now [4]. Nowadays KAERI has developed a chemical decontamination process called "HyBRID" (Hydrazine-Based Reductive metal Ion Decontamination) that does not use organic acids or

organic chelating agents at all [3]. A solution containing sulfuric acid (H₂SO₄), hydrazine (N₂H₄), and copper sulfate (CuSO₄) provides the acidic and reductive dissolution of transition metal ions from the corrosion metal oxides (Figure 1).

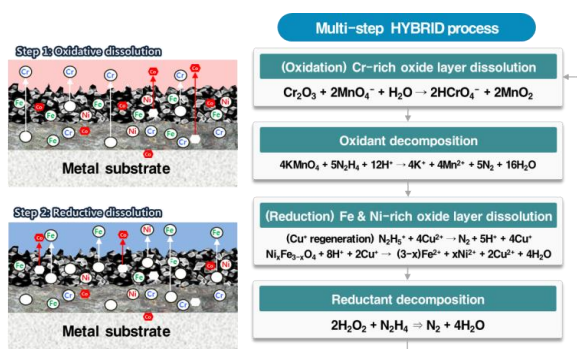


Figure 1. The schematic diagrams and flowsheet of HYBRID decontamination process

The primary system of PHWR shown in Figure 2 are operating in a closed cycle at a pressure of about 12 MPa and a temperature of 265~310°C. The primary heat transport system consists mainly of the in-core fuel channels connected to the steam generators by a system of feeder pipes and headers. The fuel channel components in contact with the heavy water primary coolant comprise the pressure tubes of Zr-2.5%Nb, the end-fittings of type 403 stainless steel, the liner tubes of type 410 stainless steel, the shield plugs of ductile iron and the seal plugs of Cr-Fe stainless steel. The fuel bundles are of elements sheathed with Zircaloy-4 that are separated by spacers of Zircaloy-4 that are resistance-welded to the end-plates.

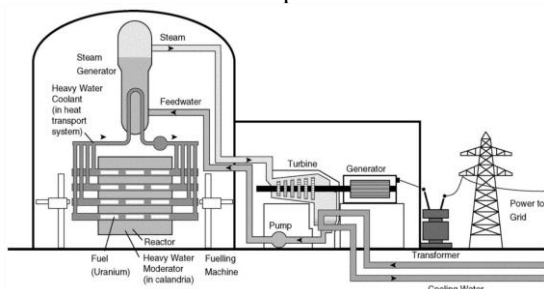


Figure 2. Schematic diagram of PHWR system

Compared to PWRs, PHWRs have been informed to form very thick corrosion oxide film up to 75~100µm on the reactor coolant system due to the different structural materials and system operation. Conventional technologies like CAN-DECON, CAN-DEREM for the decontamination of CANDU-reactors were generated secondary waste due to use of chelating agents such as EDTA, citric acid, and oxalic acid. The solution is continuously recycled through filters and ion-exchangers which fix the radionuclides and regenerate the chemicals. The CAN-DECON process has been applied to the Chalk River Nuclear Power Demonstration (NPD) reactor and the Gentilly-1 and

Douglas Point power reactors. A similar process with higher temperature and a greater concentration of chemicals could be applied for light-water moderated reactors. DFs of 50 would then be attainable. However, there were several disadvantages in applying CAN-DECON technology. Ferrous oxalate was precipitated on system surface in adding significant amount of oxalic acid to the heat transport system. The presence of ferrous oxalate on system surfaces may also limit oxide and activity removal during the subsequent CAN-DECON step. CAN-DECON also was incorporated with ion-exchange resin and regenerated the CAN-DECON reagent using cation ion-exchange resin [4].

3. Technical requirements of future system decontamination for PHWR

In this study we investigated the current chemical decontamination for the PHWRs as well as for the PWRs. These technologies, however, have been found some disadvantages from a lots of commercial applications. From the standpoints of reduction of wastes and disposal compatibility and radiation safety we suggest that the following four technical requirements should be incorporated in developing chemical decontamination for PHWRs system.

- High dissolution capability enough to remove radioactive corrosion products from reactor coolant system
- Minimize release of secondary wastes by adopting eco-friendly chemical reagents
- Simple processes for easy operation and increase economic benefits for decontamination
- Enhance disposal compatibility by reducing organic chemicals in the final disposal wastes

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