

Reduction of occupational radiation exposure nuclear power plant using chemical decontamination

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Abstract: Chemical decontamination at the beginning of a periodical inspection is applied to many Japanese nuclear power plants in order to reduce radiation exposure. In the chemical decontamination, oxides formed on the surface of the carbon steel (CS) piping that incorporate Co-60 are dissolved with reductive and oxidative chemical reagents. The CS base metal of the piping is exposed to reactor water after the chemical decontamination and the growth rate of the oxide film that incorporates Co-60 during plant operation just after the decontamination is higher than that just before it. Therefore, there is a possibility that the deposition amount of Co-60 on the piping just after decontamination is higher than that just before the chemical decontamination. Actually, rapid deposition amount increases of Co-60 within a few operating cycles have been observed in some nuclear power plants. Then, we have developed a Ni and Pt coating (NiPt-C) process to lower the recontamination by Co-60 after the chemical decontamination. In the NiPt-C process, a Ni and Pt layer is formed in an aqueous solution on the CS base metal of the piping using Ni formate, sodium hexahydroxyplatinate (IV) and hydrazine. In this study, we confirmed that there was a suppression effect by the NiPt-C toward Co-60 deposition on CS under the Hydrogen Water Chemistry (HWC) condition of BWRs. The amount of Ni formation reached about 420 $\mu\text{g}/\text{cm}^2$ at 363 K. The X-ray diffraction, SEM images and EDX results showed the Ni metal layer uniformly formed on the CS surface. In order to quantify the suppression effect of Co-60 by the NiPt-C, we conducted the Co-60 deposition behavior test under HWC. The amount of Co-60 deposition was about 125 Bq/cm^2 for the non-coated specimen, and the average Co-60 deposition was about 20 Bq/cm^2 when the NiPt-C deposition amount was more than 330 $\mu\text{g}/\text{cm}^2$. The amount of Co-60 deposition by the NiPt-C process was about 16% that of the non-coated specimen.

Keywords: Dose reduction, Chemical decontamination, Carbon steel, BWR, Recontamination

1. INTRODUCTION

Chemical decontamination is an effective method to reduce occupational radiation exposure in Boiling Water Reactors (BWRs) when carrying out such large-scale tasks as overhaul of primary recirculation pumps and shroud replacement. In the chemical decontamination, oxides formed on the surface of the Stainless Steel (SS) and Carbon Steel (CS) piping that incorporate Co-60 are dissolved with reductive and oxidative chemical reagents. The SS and CS base metal of the piping is exposed to reactor water after the chemical decontamination and the growth rate of the oxide film that incorporates Co-60 of the piping during plant operation just after the decontamination is higher than that just before it [1-3]. Therefore, there is a possibility that the deposition amount of Co-60 on the piping just after decontamination is higher than that just before the chemical decontamination. Actually, rapid deposition amount increases of Co-60 within a few operating cycles after chemical decontamination have been observed in some nuclear power plants. Then, we developed the Hi-F coating for SS [4], and the Ni and Pt coating (NiPt-C) for CS under OLNLC condition to lower the recontamination by Co-60 after the chemical decontamination [5]. In the NiPt-C process, a Ni and Pt layer is formed in an aqueous solution on the CS base metal of the piping using Ni formate, sodium hexahydroxyplatinate (IV) and hydrazine. The reason for selecting NiPt-C is that the adsorption energy of Ni on oxide film was clearly lower than that of Co for the OLNLC condition [6]. This means that if the Ni and Pt coated (NiPt-C) for CS, Ni was incorporated into the outer oxide layer instead of Co after plant operation cycles.

In this study, we confirmed that the suppression effect by the NiPt-C toward Co-60 deposition (in a two-layer oxide film) on CS under the hydrogen water chemistry (HWC) condition of BWRs using a Co-60 tracer test. Furthermore, we also investigated the suppression mechanism using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction methods to observe specimens that had occurred reactions between Pt and oxides under BWR conditions.

2. Experiments

We prepared the Co-60 deposition behavior test specimens as follows. First, CS specimens (specimens size, 8 mm x 15 mm; thickness, 1.5 mm) were polished with 600-grit emery paper and degreased with acetone. For the deposition of Ni and Pt on their surface, specimens were put in a 1 dm³ glass flask filled with ion exchange water. Three chemical reagents are needed to form the Ni and Pt layer: Ni formate, Na₂[Pt(OH)₆] solution and N₂H₄. The water was heated to 363 K and then Ni formate solution was added to the hot water. After the Ni formate solution had completely dissolved into the water, N₂H₄ was added. Ni coated specimens were obtained after soaking in this solution for 4 h. Next, Na₂[Pt(OH)₆] solution was added to the hot water. After the Na₂[Pt(OH)₆] solution had completely dissolved into the water, N₂H₄ was added. The concentration of Pt ion in the water-filled flask was 1.0 ppm.

We conducted the Co-60 deposition behavior test under HWC to examine the NiPt-C suppression effect. The test specimens with and without NiPt-C were set in an autoclave. A schematic diagram of the Co-60 deposition test apparatus is shown in Figure 1. In order to simulate the HWC that has been applied to BWRs, H₂ and N₂ gases were bubbled into the reservoir tank water at rates to keep their concentrations at the desired levels of under 5 ppb for dissolved oxygen and about 50 ppb for dissolved hydrogen. Co-60 was added (activity, 6.7 Bq/kg) and also cobalt sulfate (cobalt ion concentration, 0.1 ppb). The temperature and pressure were controlled at 553 K and 7 MPa, respectively, to simulate actual plants. H₂O₂ was injected into the autoclave to get a constant amount of about 130 ppb, and 5 ppb zinc ions as zinc nitrate were also injected into the high temperature water.

The amounts of Co-60 on the test specimens were measured using a germanium gamma ray detector with a multichannel pulse height analyzer. The counting rates of gamma rays from Co-60 deposited on test specimens and deposition amounts were corrected for natural decay during the test period. The surface of some test specimens was observed by X-ray diffractometry, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy.

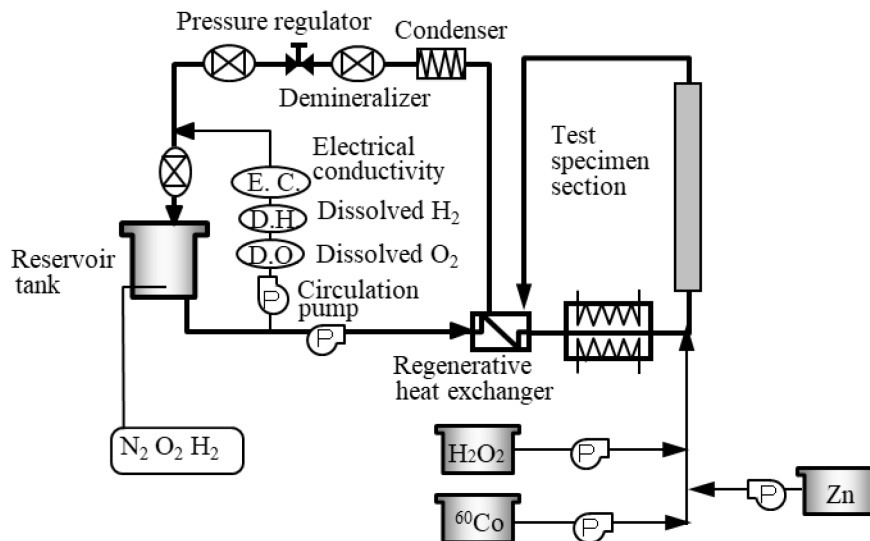


Figure 1. A schematic diagram of the Co-60 deposition test apparatus.

3. Results

To identify the chemical and crystalline form of the NiPt-C film, an X-ray diffraction pattern of the film formed on a CS surface was measured and an example is shown in Figure 2. Here, the amount of film formation on the CS surface was $337 \mu\text{g}/\text{cm}^2$. The main peak pattern of the formed film agreed with the peaks observed in standard Fe_3O_4 , Ni metal and CS.

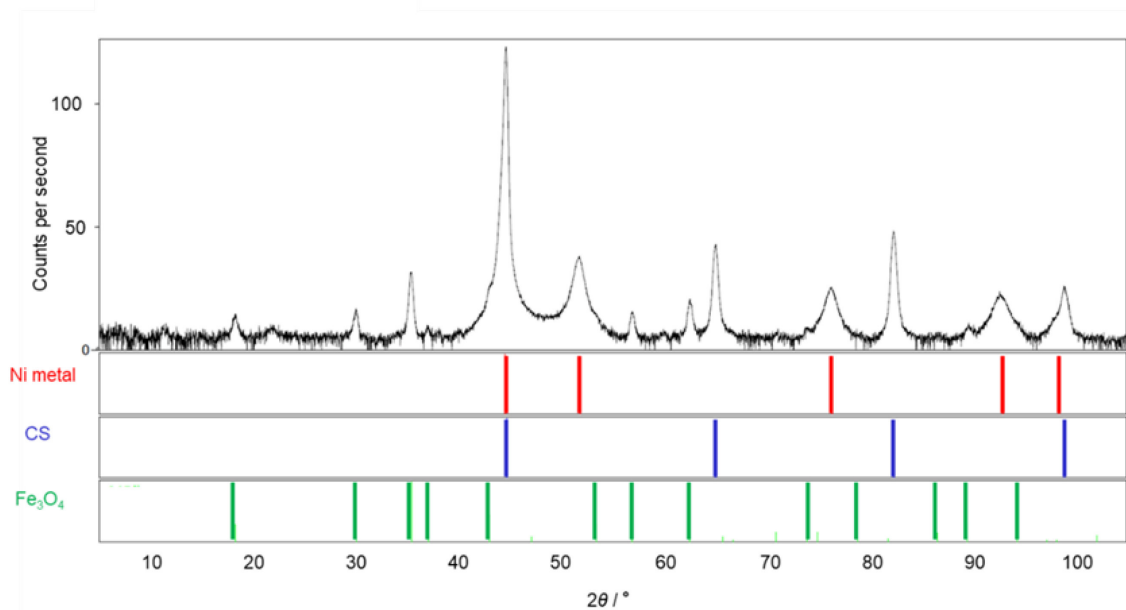


Figure 2. Example X-ray diffraction pattern of the NiPt-C film formed on a CS surface.

The SEM and EDX images of the two layer oxide film formed on a CS surface for the noncoated and NiPt-C specimens are shown in Figure 3. Here, Green color is Ni atom. We observed the Ni particles formed were uniformly distributed on the surface of the CS and the particle sizes were about 100 nm.

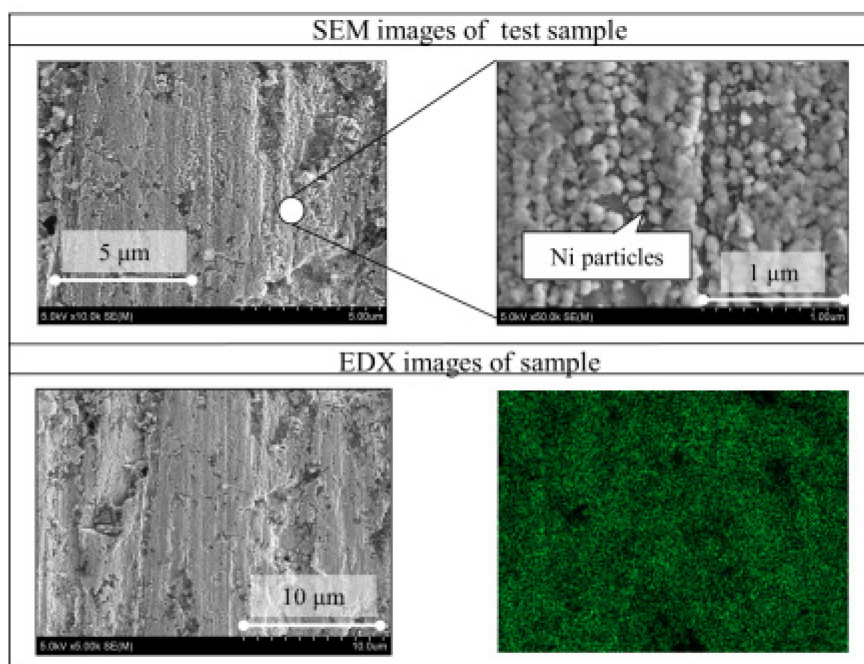


Figure 3. SEM and EDX images of a CS surface.

In order to quantify the suppression effect of Co-60 by NiPt-C, we conducted the Co-60 deposition behavior test. Figure 4 shows the deposition amounts of Co-60 for NiPt-C and non-coated specimens. Here, the amount of Pt in the NiPt-C was about $0.2 \mu\text{g}/\text{cm}^2$. The amount of Co-60 deposition with the NiPt-C decreased with the increasing amount of Ni metal formation. The amount of Co-60 deposition was about $125 \text{ Bq}/\text{cm}^2$ for the non-coated specimen, and the average Co-60 deposition was about $20 \text{ Bq}/\text{cm}^2$ when the NiPt-C deposition amount was more than $337 \mu\text{g}/\text{cm}^2$. The amount of Co-60 deposition by the NiPt-C process was about 16% that of non-coated specimens. In other words, the NiPt-C process suppressed the Co-60 deposition.

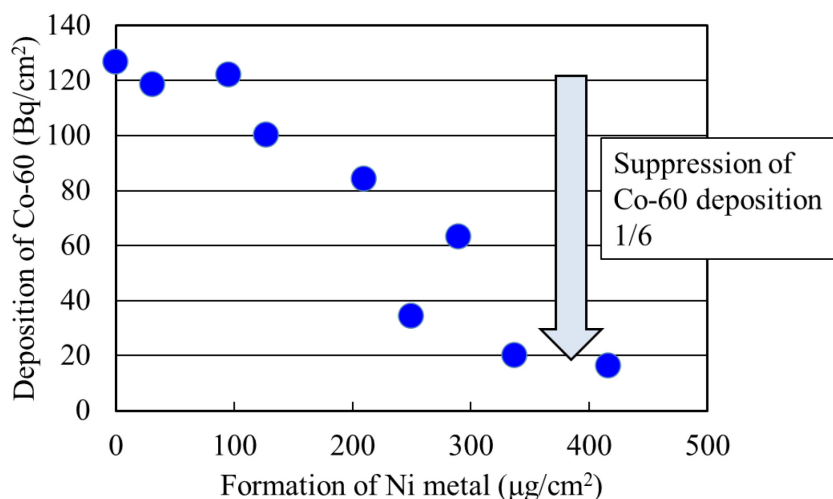


Figure 4. Deposition amounts of Co-60 for NiPt-C and non-coated specimens.

The Raman spectra of the surface of the outer oxide layer for non-coated and NiPt-C specimens after the Co-60 deposition test are shown in Figure 5. Here, the amounts of Ni metal formation were 95, 250 and $337 \mu\text{g}/\text{cm}^2$, respectively. The outer oxide layer of the non-coated specimen and the NiPt-C specimen mainly consisted of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$, and Fe_3O_4 and NiFe_2O_4 , respectively. This result indicated that the surface of the NiPt-C specimens was chemically reduced by the reaction of Pt and H_2 during the Co-60 deposition test.

The peak intensity of NiFe_2O_4 for the NiPt-C specimen increased with increasing Ni metal formation on the CS surface. The Raman spectra shown in Figure 5 and Co-60 results shown in Figure 4 indicated that the amount of Ni metal and NiFe_2O_4 formation increased with suppression of the amount of Co ion incorporation into NiFe_2O_4 oxide. This finding indicated that Ni ions were energetically more stable compared to Co ions in NiFe_2O_4 in this condition.

In order to apply this technology to actual plants, it is necessary to develop multiple technologies, including the following two: Confirmation of the long-term sustainability of the Co suppression effect in a simulated environment of the actual condition. Confirmation of the application method of NiPt-C through a large scale mock up test that can simulate the target system of the actual equipment.

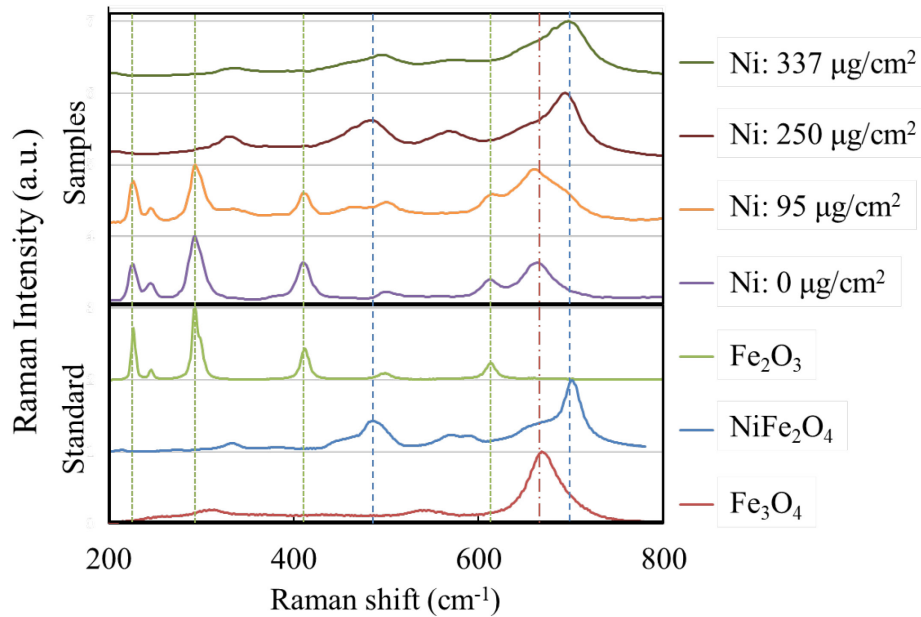


Figure 5. Deposition amounts of Co-60 for NiPt-C and non-coated specimens.

Conclusion

We developed the NiPt-C process as a new suppression method for recontamination after chemical decontamination for CS. In this study, we confirmed the suppression effect of Co-60 deposition by Co-60 tracer test results. Furthermore, the suppression mechanism of Co-60 deposition by NiPt-C was considered. The conclusions are summarized as follows.

1. To identify the chemical and crystalline form of the NiPt-C film, an X-ray diffraction pattern of the film formed on a CS surface was measured. The amount of Ni film formation on the CS surface was $337 \mu\text{g}/\text{cm}^2$. The main peak pattern of the formed film agreed with the peaks in standard Fe_3O_4 , Ni metal and CS. Regarding, the SEM and EDX results of the NiPt-C film formed on a CS surface for a NiPt-C specimen observed formation of the Ni particles were uniformly distributed on the surface of the carbon steel.
2. In order to quantify the suppression effect of Co-60 by NiPt-C, we conducted the Co-60 deposition behaviour test and compared the deposition amounts of Co-60 for NiPt-C and non-coated specimens. The amount of Co-60 deposition with NiPt-C decreased with increasing amount of Ni metal formation. The amount of Co-60 deposition was about $125 \text{ Bq}/\text{cm}^2$ for the non-coated specimen, and the average Co-60 deposition was about $20 \text{ Bq}/\text{cm}^2$ for the NiPt-C specimens when the deposition amount was more than $337 \mu\text{g}/\text{cm}^2$. The amount of Co-60 deposition with the NiPt-C was about 16% that of the non-coated specimen.
3. The Raman spectra of the surface of the outer oxide layer for non-coated and NiPt-C specimens after the Co-60 deposition test were obtained. The outer oxide layer of non-coated specimen and NiPt-C specimen mainly consisted of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$, and Fe_3O_4 and NiFe_2O_4 , respectively. The peak intensity of NiFe_2O_4 for the NiPt-C specimen increased with increasing Ni metal formation on the CS surface. The Raman spectra and Co-60 results indicated that the amount of Ni metal and NiFe_2O_4 formation increased with suppression of the amount of Co incorporation in NiFe_2O_4 oxide. In other words, the Ni ions were energetically more stable than Co ions in the NiFe_2O_4 for this condition.

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