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The Study about Characterization of Corrosion Products on Surface Materials of Secondary System in Operation Environments at NPPs

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1. Introduction

Kori unit 2 of nuclear power plant began commercial operation on July 25. 1983, and was shut down on April 8, 2023, when it reached its design life. Although it has reached its design life, it is preparing for regulatory approval for continued operation through major system inspection and facility improvement. Regulatory agency approval and facility improvement are expected to take longer than the general planned preventive maintenance (so as called OverHaul) period and are expected to take at least 2 to 3 years.

Generally, OH period takes about 50 days on average and during that period, nuclear power plants use wet or dry lay-up methods to minimize corrosion of system component materials. Wet lay-up is a method of preventing materials from being exposed to atmospheric oxygen by using water whose pH is controlled to above 9.5 by injecting hydrazine below 75 ppm. On the other hand, dry lay-up is a method of controlling the relative humidity to below 40% so that atmospheric oxygen has minimal contact with system materials [1].

In the nuclear power plants experience, these preservation methods had little effect on the integrity of system materials. However, it cannot be guaranteed that this preservation methods will not have an impact on materials integrity in the long term. This is no case of applying that method for a long term in domestic nuclear power plants. In particular, dry lay-up applied to the secondary system is expected to be difficult to control within limits because it is influenced by the atmospheric environment, which is expected to affect the integrity materials. Therefore, it is necessary to evaluate the impact of materials following long-term dry preservation.

This study is a characterization evaluation of corrosion products as part of this evaluation. The study on the characteristics of corrosion products will be conducted by collecting samples with different collection dates (when shut down and when started) for comparative evaluation. In this abstract, the properties and components of the initially collected corrosion products were analyzed, and the relationship between the water environment and the corrosion products was evaluated.

2. Experimental

2.1. Corrosion Product Sampling Locations

In order to evaluate the material integrity following long-term dry layup, the main components of secondary system were selected and corrosion products were collected. Four locations were selected to collect from the main components: the hotwell of condenser (CD), low pressure heater (LPH), moisture separator reheater (MSR) and high-pressure heater (HPH) (Fig. 1). The sample collection location was selected by considering the location where water in secondary system changes significantly physically and chemically.

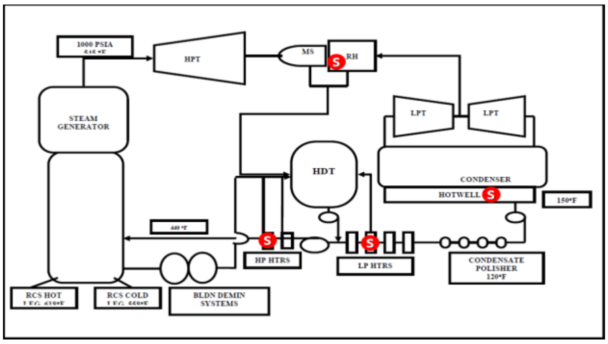


Fig. 1. Schematic showing major components in secondary side and sampling locations

2.2. Corrosion Product Assessment Methods

Corrosion products collected from major components were analyzed for their properties and chemicals composition. SEM (Scanning Electron Microscope) was used for property analysis, and EDS (Energy Dispersive Spectrometer) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) were used for component analysis. XRD (X-Ray Diffraction) was used to analyze the oxide crystal structure. The analyzed results were also evaluated in relation to the water and chemical environment of the normal operating system.

3. Results & Discussion

3.1. Chemical Composition (ICP-MS) of Corrosion Product

Table 1 show the results of chemical composition analysis of oxides collected from selected components. It can be seen that the main element is iron and the rest are small amounts of metal elements. These results appear to be oxides produced by corrosion of materials that make up the components system, and some ingress to be impurity in the makeup water.

Table I: Chemical composition of samples (wt.%)

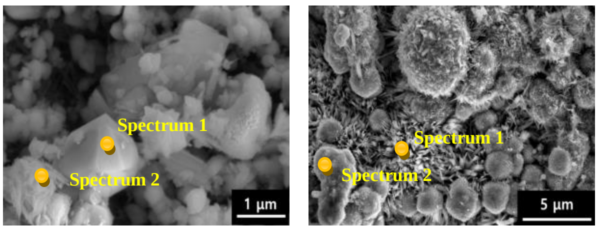
Loc.	Al	Cr	Cu	Mn	Ni	Ti	Mo	Fe
CD	0.07	0.03	0.07	0.07	0.02	0.14	0.00	Bal.
LPH	0.15	0.26	0.14	0.63	0.03	0.02	0.02	Bal.
MSR*								
HPH	0.35	0.10	0.08	2.19	0.03	0.37	0.00	Bal.

**MSR sample is currently being analyzed*

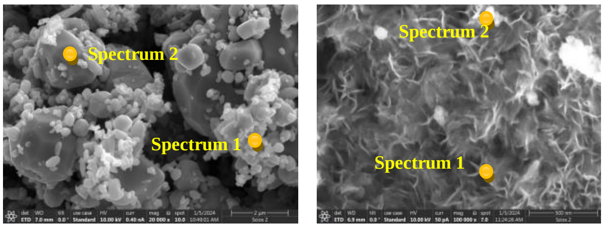
Among the elements, copper was analyzed, and copper is known to cause accelerated SCC of Alloy600MA. In other words, copper accelerates SCC by increasing ECP (Electric Chemical Potential). However, since copper is a very small amount and hydrazine is sufficiently injected in the secondary system, there is unlikely to be an increase in ECP.

3.2 The Morphology and Elements Analysis Results (SEM&EDS) of Corrosion Product

Regardless of the sampling location, corrosion products showed polyhedral, spherical and needle-line shapes (Fig.2). According to the EDS analysis results, the form of corrosion products can be estimated depending on the ratio of iron and oxygen. In general, if it has a polyhedral shape with an iron concentration of 42% (or more) and an oxygen concentration of 56%, It is presumed to be magnetite, and if it is a circular or needle-shaped, it is assumed to have an elemental ratio of 40% (or less) iron and 60% oxygen. It is presumed to be hematite or iron hydroxide. These results are identical to the results of oxides collected from the same location at an overseas nuclear power plant [3].



(a) CD (b) LPH



(c) MSR (d) HPH

Fig. 2. Property analysis results for each oxide (SEM)

Table II: The results of EDS about samples for each oxide

Locations	Point	Elements (at. %)		Remark
CD	Spectrum1	Fe: 44.31	O: 55.69	Fe_3O_4
	Spectrum2	Fe: 40.47	O: 59.53	Fe_2O_3
LPH	Spectrum1	Fe: 40.93	O: 59.07	Fe_2O_3
	Spectrum2	Fe: 40.22	O: 59.78	Fe_2O_3
MSR	Spectrum1	Fe: 47.67	O: 52.33	Fe_3O_4
	Spectrum2	Fe: 42.32	O: 57.68	Fe_3O_4
HPH	Spectrum1	Fe: 26.61	O: 73.39	FeOOH
	Spectrum2	Fe: 30.12	O: 69.88	FeOOH

3.3 Oxide Crystal Structure Analysis Results (XRD)

As a result of the oxide crystal structure analysis, the sample collected from the moisture separation reheater had a crystal structure composed only of magnetite, and the other crystal structures of magnetite, hematite, goethite and lepidocrocite, although the ratios were different (Fig. 3). The crystal structure and ratios produced were different for each component. The reason for having this crystal structure appears to be due to the environment of the power plant's water chemistry during normal operation. It is believed that not only the crystal structure varies depending on the oxygen concentration (oxygen ratio) and temperature in the secondary system [4].

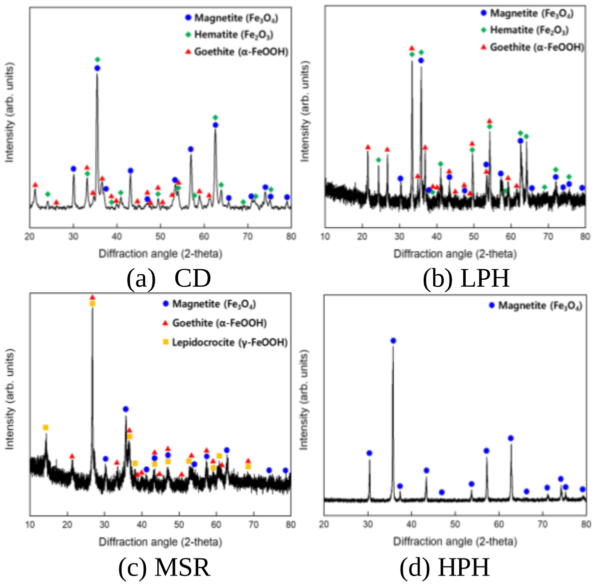


Fig 3. Crystal structure analysis results for each oxide (XRD)

4. Conclusion & Future works

As part of evaluation of material integrity following the long-term layup of secondary system. (excluding steam generators), major components were selected, oxides on the surface were collected, and properties and compositions were analyzed. As results of the property analysis, it was that the polyhedral shape was highly likely to be magnetite, and the circular and needle-like shapes were likely to be hematite or iron hydrate. As a result of analyzing the crystal state of the oxide, it was found that the crystal structure and ratio were different depending on the phylogeny chemistry of water.

In the future, when the long-term layup is over, samples will be collected and analyzed at the same location and compared with these results. Finally, KHNP plan to conduct a comprehensive analysis to evaluate the effect of the integrity of component materials in the secondary system due to long-term layup.

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