Study on the Removal of Corrosion Oxide Layers in the Heat Transport System of PHWR

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1. Introduction

In June 2018, it was decided to close the Wolsong Unit 1, of which the reactor type is a pressurized heavy water reactor (PHWR) [1]. After this, the importance of the decommissioning of the PHWR has become an issue.

It is necessary to apply the decontamination process to the carbon steel heat transport system of the PHWR before the decommissioning for reducing the radiation expose to the workers [2]. During the decontamination process, the corrosion oxide (mainly Fe_3O_4) layers including radioactive metals can be removed from the carbon steel heat transport system [3].

The Hydrazine Base Reductive metal Ion Decontamination (HyBRID) process was developed by KAERI for the decontamination of the Fe_3O_4 on a primary coolant circuit in a pressurized water reactor (PWR) [4]. This process can also be applied to the Fe_3O_4 decontamination in the PHWR. However, the thickness of the oxide layer in the PHWR (~75 μm) is much greater than that in the PWR (~3 μm) as shown in Table I [5]. The decontamination performance of the HyBRID process solution can be decreased during decontamination of thick oxide layer in the PHWR because the high concentration of Fe ions dissolved in the process solution can prevent the progress of more dissolution reactions. Therefore, it is required to discharge the spent process solution, called the process solution remained after finishing the decontamination cycle, and charge the fresh process solution. The fresh decontamination solution is the solution of which condition is the initial composition of HyBRID process solution. This repetitive replacement of process solution is necessary to keep up the decontamination performance. However, the large amount of secondary wastes can be generated when the process solutions are discharged and charged over agiain.

In this study, the effective decontamination process of the corrosion oxide layers from the heat transport system in the PHWR without any discharge of the spent process solution was suggested. The key method of this process was recycling the spent process solution by reducing the solution to the fresh process solution. This recycling method was derived by the experimental test using spent process solution surrogate. Moreover, the Fe_3O_4 dissolution test using the recycled process solution was also performed.

Table I: Characteristics of corrosion oxide layers in the reactor [2].

Reactor Type		**Deposit Thickness (μm)**	**Deposit Density (g/cm^3)**	**Specific Weight (mg/cm^2)**
PWR	Pipe	3	4	1.2
	SG	2	4	0.8
BWR	Pipe	10	3.5	3.5
	HX	50	3.5	17.5
CANDU	Pipe	75	4	30
	SG	25	4	10

2. Methods

2.1 Preparation of sample solution

The fresh process solution was prepared with 1,600 ppm of $N_2H_4{\bullet}H_2O$ (Junsei, 98.0 %), 2,600 ppm of H_2SO_4 (Showa, 97.0 %), and 31 ppm of $CuSO_4$ (Junsei, 97.5 %). The spent process solution surrogate was composed of 1,000 ppm of $N_2H_4{\bullet}H_2O$, 2,600 ppm of H_2SO_4, 31 ppm of $CuSO_4$, and 350 ppm of Fe^{2+} ions. This Fe^{2+} ions concentration was obtained by complete dissolving 0.52 g of Fe_3O_4 (Junsei, 94 %) in the 1 L of fresh HyBRID process solution for 5 h at 95 ^oC.

2.2 Recycling test of spent process solution

The recycling test was divided to 3 steps; a precipitation step, a filtration step, and a make-up step. In the precipitation step, different amounts of $Ba(OH)_2$ were injected to the each spent process solution surrogate with stirring. The molar ratio (R) of $Ba(OH)_2$ to SO_4^{2-} in the surrogate was from 0.40 to 0.70. The solutions were kept for 10 minutes during stirring after finishing the injection of $Ba(OH)_2$. In the filtration step, the surrogates were filtrated by using a 0.45 μm syringe filter. In the make-up step, insufficient amounts of N_2H_4, H_2SO_4, and $CuSO_4$ were added to the purified solution obtained after filtration step for reducing the solution to the fresh process solution.

2.3 Dissolution test using recycled process solution

The Fe_3O_4 dissolution test was performed using fresh and recycled process solutions. The recycled process solutions were prepared by recycling the spent process solution. The optimized recycling method including the precipitation, the filtration, and the make-up steps were obtained by above recycling test. Every dissolution tests were conducted for 5 h at 95 °C using water bath. The solutions were mixed with 200 rpm during dissolution test.

3. Results and Discussion

3.1 Equilibrium calculation using HSC-Chemistry 9.0

An equilibrium calculation about the precipitation condition was conducted using HSC-Chemistry 9.0 before recycling test. The calculation condition was same with the condition of spent process solution, and the R was changed from 0 to 1. From the equilibrium calculation results, it was confirmed that the Cu^{2+} ions and Fe^{2+} ions were completely converted to $Cu(OH)_2$ and $Fe(OH)_2$ when the R was less than 0.40. From these results, the recycling test condition was decided that the R was necessary to be over 0.40 for removing the all Fe^{2+} from the spent process solution. The decided value of R was also less than 0.70 because it could contribute to reduce the amounts of secondary wastes generation.

3.2 Reducing of spent process solution to the fresh process solution

The recycling test was conducted by using spent process solution surrogate. Firstly, the precipitation and the filtration steps were carried out. When the R was from 0.40 ppm to 0.50 ppm, the concentration of Fe^{2+} ions in the solutions were over 0.70 ppm after the filtration steps. The colors of the solutions were light yellow at the same conditions. It was predicted that the light yellow particles were the tiny $Fe(OH)_2$ particles. However, the colors of solutions obtained after filtration were clear and the Fe^{2+} ions concentration were less than 0.60 ppm when the R was from 0.55 to 0.70. Moreover, the concentrations of Cu^{2+} ions were less than 0.50 ppm in all R conditions. The pHs of the solutions increased from 8.0 to 9.5 with increasing R.

The purified solutions obtained after the filtration step were reduced to the condition of the fresh process solution in the make-up step. In this step, 600 ppm of N_2H_4, 31 ppm of $CuSO_4$ were injected and pH of the solution was adjusted to 2.75 by adding H_2SO_4. The amounts of injected decontamination reagents were calculated by comparing the purified solution to fresh process solution.

Based on these results, the R was decided 0.60 because the Fe^{2+} ions could be effectively removed and the amounts of secondary wastes generation could be decreased at this condition. Finally, the decontamination method suggested in this study can be diagrammed as shown in fig. 1.

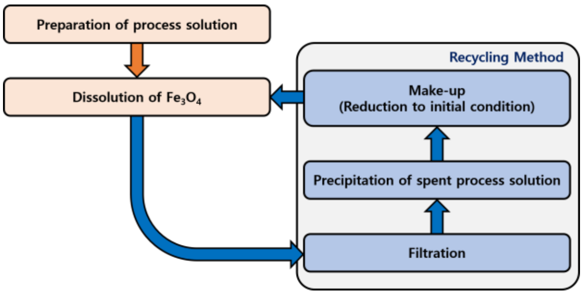

Fig. 1. Process flow diagram of the decontamination of heat transport system in the PHWR using recycled HyBRID spent process solution.

3.3 Dissolution performance of the recycled process solution

When 0.52 g of Fe_3O_4 was added in 1 L of fresh HyBRID process solution, 350 ppm of Fe^{2+} ions were completely dissolved for 5 h. It was investigated that 350 ppm of Fe^{2+} ions were dissolved when the same amount of Fe_3O_4 was added in 1 L of recycled process solution. The recycled process solution was obtained by using the recycling method derived in *3.2*. Through these results, it was confirmed that the dissolution performance of the recycled process solution was similar to that of the fresh process solution.

3. Conclusions

In this study, a recycling method including precipitation, filtration, and make up steps was derived for the decontamination of heat transfer system in the PHWR using the existing HyBRID process. It was verified that a spent process solution could be effectively reduced into fresh process solution by the recycling method. The dissolution performance using recycled process solutions was similar to that using a fresh decontamination solution. Through this decontamination method, the secondary wastes generation can be reduced by 40 % when compared with the existing HyBRID process.

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