Radioactivity Monitoring for the Structure of Kori Unit 1

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Abstract. To characterize decommissioning wastes to be raised in unit 1 of Kori NPP, zones of the Kori unit 1 were classified and specified to evaluate the radiological characteristics of the structures. Analytical samples were obtained by rubbing with papers on the wall surface (1 × 1 m) and analysed radiochemically activated radionuclides.

The contaminated smear samples were heated for about 8 hours at 450 ℃ and 25 mL of 10 M nitric acid, 25 mL 4 M hydrochloric acid, and 50 mL of distilled water were added. In order to verify the pretreatment recovery rate, 0.3 mL (3 mg Re) of Re was added into the sample pretreatment solution. The ashed samples were dissolved with the acid solution by using the microwave digestion system. Since the pretreated solution in the chemical analysis contained various elements and compounds such as Na, K, Li, Al, and Ca, separation procedures for ^{55}Fe, $^{59/63}$Ni, and ^{94}Nb were developed and applied. Recovery of Fe, Nb, and Ni extracts was evaluated using a prepared simulated solution whenever the radionuclides (^{59}Fe, $^{59/63}$Ni and ^{94}Nb) from the radioactive samples were individually separated. As a result of evaluating the separation reliability, it was found that all standard deviations were less than 3%. From the analytical results, it was concluded that the radionuclides in the decommissioning wastes had a radiological tendency.

KEYWORDS: Nuclear decommissioning, Scaling factor, activation products, chemical separation

1 INTRODUCTION

The first nuclear power plant that operated in South Korea was Kori Unit 1, which first started commercial operations in 1978 and shut down in June 2015 after 30 years of design life and 10 years of life extension. Since then, NSSC (Nuclear Safety and Security Commission) approved a permanent shutdown of Kori NPP unit 1 as of the 18th June 2017, as requested by KHNP (Korea Hydro & Nuclear Power Co., Ltd.) as of June 2016. Built in Gijang-gun, Busan by *the technology of Westinghouse of the United States* in 1978, Kori NPP unit 1 is a 587 MWe-class PWR reactor and also, was the first nuclear reactor of South Korea, which had contributed a lot to power supply for the economic development. The shutdown was determined after considering various factors of nuclear safety, economical efficiency, regional acceptability, power supply and demand, and mid/long term technology comprehensively. The dismantling method of Kori Unit 1 has been intensively discussed based on overseas cases, mainly by many experts in Korea, but there haven't been any specific plans to date until now. One of the reasons is the lack of radiological measurement data for the main equipment and concrete structures in Kori Unit 1. Even though a lack of policy recognition and technical preparation for nuclear decommissioning is the problem, this is an indispensable item for establishing a nuclear decommissioning plan. For this reason, the whole process of a nuclear fuel transfer and structure dismantling to the site restoration has been delayed by two years. After numerous debates of committee of experts, the NSSC ('15. 10. 5) presented a vision to foster a decommissioning industry with future growth potential and global competitiveness based on securing public safety and economic benefits. Accordingly, the government established a plan to transfer the spent nuclear fuel, stored in the temporary storage of the reactor, out of the park by December 2024. It would be held after the approval of the decommissioning plan in 2022, and completed by December 2032. It has been predicted that approximately 80,000 drums of radioactive waste will be generated from the dismantling process of Kori NPP Unit 1, and a dismantling agency has a plan to reduce radioactive waste to less than 14,500 drums through various physicochemical treatments [1].

Table 1. Chronicle of the first NPP of South Korea, Kori Unit 1 [1]

Date	Content
’72. 5.	Construction operation permit
’77. 6.	First critical point
’78. 4.	Commercial Operation
’07. 6.	Expiration of design life
’07. 12.	License renewal (until ‘17. 6. 18 for 10 years)
’08. 1. 9	Re-Operation
’15. 6.	Determination of permanent shutdown
’17. 6	Approval of permanent shutdown

In this study, we tried to secure the radionuclide characteristics evaluation data for the structures of Kori NPP Unit 1 so that the government could establish a plan for successful nuclear dismantling. For this, the decommissioning areas of the Kori unit 1 were classified, and analytical samples were obtained by rubbing with paper on the wall surface (1×1 m) and analyzed radio-chemically for activated radionucli des. For the radiochemical separation of ^{55}Fe, $^{59/63}$Ni, and ^{94}Nb, the separation procedures for the radion uclides were developed and applied to extract them from the pretreated solution of the samples. A reco very evaluation of Fe, Nb, and Ni for all of the samples was carried out using a prepared simulated sol ution whenever the radionuclides (^{59}Fe, $^{59/63}$Ni and ^{94}Nb) from the radioactive samples were individuall y separated. Finally, the analyzed results were compared with a waste stream of DAW (Dry Active Wastes), generated during the operation of the NPP.

2 EXPERIMANETAL

2.1 Sampling of the contaminated concrete

For a clear evaluation of the radiological contamination distribution, the sample collection points of contaminated concrete were classified into the reactor building, the inside of the AUX building, the CTMT and the outer area through the drawing of the power plant. The high-dose spot was investigated in advance. In addition, in consideration of radiation safety, such as reduction of radiation exposure, a scenario was planned to minimize the movement distance of the planned collection point according to the ALARA principle. A total of 29 samples were collected, and the collection points are shown in Table 1. All samples were promoted during the O/H period of Kori 1 in March 2014. For sample collection, an area of 1m x 1m was secured as shown in *Fig 1* at the designated collection location. Furthermore, during chemical analysis, the contaminated surface was wiped several times with smear paper for smooth detection of radionuclides, and each process was repeated three times.

Fig1. Contaminated concrete sampling

Table 1. Sampling point for the contaminated concrete in Kori NPP Unit 1.

No.	Sampling point	Expected degree of contamination
1	Floor Drain Tank(FDT) Room	High, medium
2	Waste Holdup Tank Room	High, medium
3	CS Pump Room B	Low
4	RHR Pump Room B	Low
5	Pipe Duct Chase	Low
6	Recirculation Sump Area	High
7	primary make up water storage tank pump	Very low
8	Refueling water storage tank pump	
9	chemical drain tank & pump area	Very low
10	Electrical chase B	Low
11	boric acid tank room B	Low
12	RWST area	Low
13		
14	waste drum storage area	Medium, low
15	BACST transfer pump room	Medium, low
16	holdup tank recirculation pump room	Medium
17	charge pump room C	Medium, low
18	charge pump room B	Medium, low
19	monitor tank area	Low
20	seal water heat exchanger room	Low
21		
22	main feed water piping area	Very low
23	diesel fuel tank B	Very low
24	condensate storage tank	Very low
25	new fuel storage room	Low
26	waste evaporator(15gpm) room	High
27	waste condensate tank & pipe area	Low
28	MCR	Very low
29	plant turbine room & heater bay	Very low

2.2 Chemical analysis of radionuclides

2.2.1 Sample pretreatment

The paper samples of the contaminated concretes were heated for about 8 hours at 450 ℃, and add 25 mL of 10 M nitric acid, 25 mL 4 M hydrochloric acid and 50 mL of distilled water. In order to verify the pre-treatment recovery rate, 0.3 mL (3 mg Re) of Re was added into the sample pre-treatment solution. The ashed sample was dissolved with the acid solution by using the microwave digestion system. Eventually, insoluble residue in the solution was completely dissolved through low temperature heating on a hot plate for 40 minutes, and the total volume was made up to 20 mL through a concentration process [2].

2.2.2 Chemical separation

The pre-treatment solution was evaporated to incipient dryness and dissolved in 2 ml of 1 M HNO_3. Th is solution was added to the 100 ml beaker set aside for the separation of Ni, Fe and Nb. After adjustin g its pH to 4.5–5 with 10 % NH_4OH and diluting it to approximately 70 ml with deionized water, this l oading solution and 100 ml of 0.1 M NH_4-oxalate solution (pH 4.5–5) were sequentially passed throug h the anion exchange resin column. The whole effluent was collected in a 200 ml beaker and reserved t o separate Ni from the matrix elements. After washing the column with 100 ml of deionized water and 25 ml of 4 M HF, Fe was recovered with an additional 60 ml of 4 M HF. For continued elution, 100 ml of 3 M HCl-20 % HF passed through the column, and the final recovery of Nb was completed with 40 ml of 5 M HNO_3/0.2 M HF. The pH of the effluent, set aside during the above separation stage, was ad justed to 9–10 with 10 % NH_4OH. According to the procedure described in a previous paper [3,4], this loading solution, 130 ml of 0.1 M NH_4-oxalate (pH 9–10), and 10 ml of deionized water sequentially p assed through the Ni-Resin column with a peristaltic pump (flow rate: 0.9–1 ml/min). The Ni-retaining column was coupled with an anion exchange resin column preconditioned with 15 ml of 9 M HCl (low er column), as the 10 ml of 9 M HCl passed through these two columns. As a result, Cu and Co were re mained on the lower column, while Ni was selectively recovered during loading and washing. A schematic diagram of the separation process of Fe, Ni, and Nb is shown in Figure 1. In order to verify the recovery rate of each radionuclide from the pre-treatment solution, inorganic acid solutions of Fe, Nb and Ni as a carrier were added to the pre-treated solution.

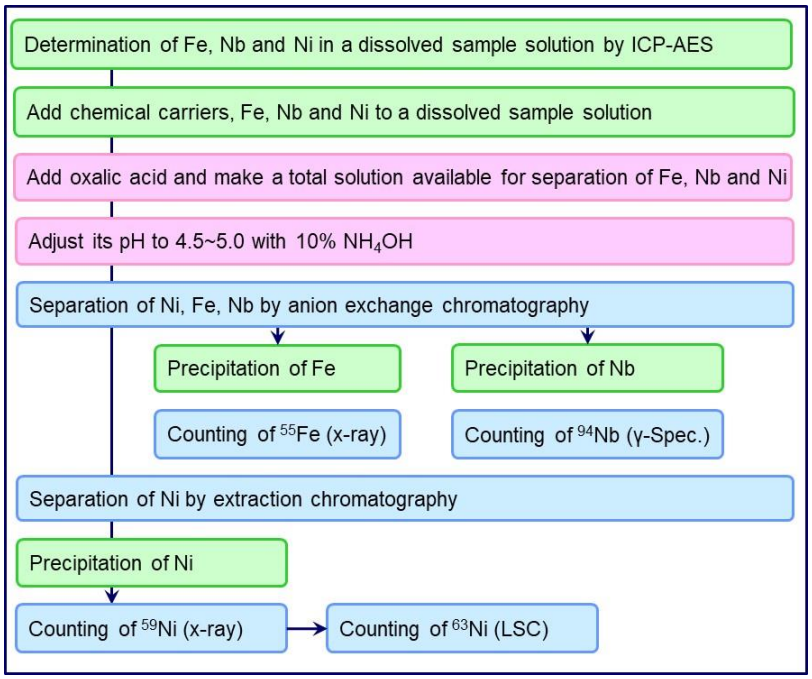

Figure 2. A schematic diagram of the separation process of ^{55}Fe, ^{94}Nb and $^{53,69}Ni$

3 RESULTS AND DISSCUSSIONS

3.1 Individual separation of the radionuclides

3.1.1 Recovery test on individual separation of the radionuclides

To examine the appropriateness of the developed analysis methods, the recovery rate tests were performed by adding standard elements of Fe, Ni, and Nb. Each standard elements were 1,000 to 10,000

mg/L of solution dissolved in a nitric acid. For the recovery test, 20 mg of Fe and Nb elements were added to each test vessel, and 2 mg of Ni elements were also added. In order to examine the interference effect in the process of chemical separation, Al, Ca, Cr, Cu, K, Li, Mg, Na, Zn, Mn, Cd, Ti and Co were additionally added. From the prepared solution, Fe, Ni, and Nb elements were sequentially, purely separated by the individual separation method, presented in 2.2.2, and the contents of the elements were finally measured by ICP-AES. The process of the individual separation and measurement for elements was repeated 4 times, and the results are shown in Table 3.

In Table 3, the recovery rates of Fe and Nb were over 95%, and that of Ni was over 85%, and the relative standard deviation for the recovery rate of each element was less than 3% through 4 repeated tests. In addition, it was confirmed that any element among them, added to examine the interference effect, were not even detected in the individually separated Fe, Ni, and Nb extracts. Through the results of such high recovery and reproducibility, the analysis method presented in this paper was considered to chemically extract Fe, Ni, and Nb nuclides appropriately.

Table 3. Results of recovery test on individual separation procedure for the radionuclides

No.	Recovery, %		
	Fe	Nb	Ni
1	95.9	99.2	90.5
2	97.2	95.1	89.2
3	98.1	96.2	85.7
4	94.8	99.3	89.2
Mean	96.5	97.5	88.7
RSD	1.5	2.2	2.3

3.1.2 Recovery test on individual separation of the radionuclides

The samples obtained from the contaminated concretes of Kori NPP Unit 1 were chemically analyzed by applying the method of 2.2.2. In order to check certain errors that may occur during the chemical separation and extraction process, the recovery rate of radionuclides was measured in the same method applied in 3.1.1 to all samples. Here is the reason why the recovery rate of ^{94}Nb is slightly lower than that of Table 3. First of all, the pretreatment solution treated from the real samples has a more chemically complex matrix than pure solutions containing only the standards. Furthermore, it was considered that the procedure of chemical separation and extraction of ^{94}Nb nuclide was not easy.

In Figure 3, the relative standard deviations of ^{55}Fe, ^{94}Nb, and $^{59/63}$Ni nuclides for the analysis results were calculated as 5.0, 2.8, and 2.8%, respectively. These relative standard deviation results could be evaluated with high precision of the analytical results after the repeated tests. Ultimately, it was reviewed that the reproducibility of the analysis was excellent in terms of reliability of the analysis result.

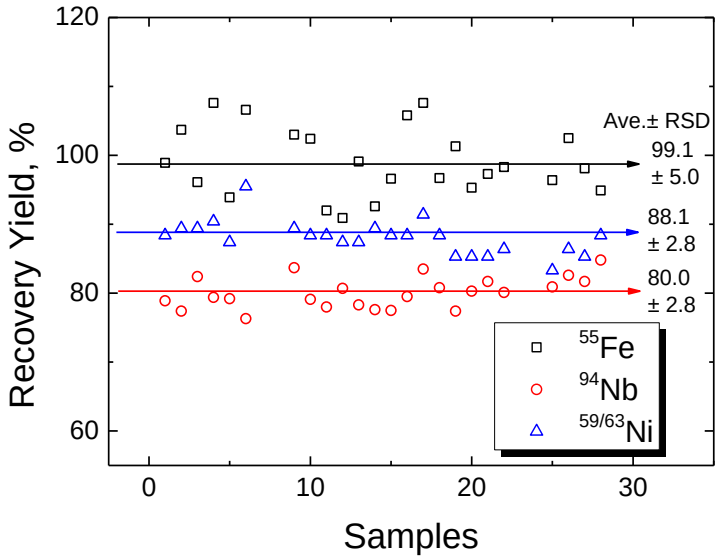

Figure 3. Recovery results on individually chemical separation for the radionuclides

3.2 Radioactivity distributions of the radionuclides

3.2.1 Analytical Results on radioactivity distributions

The radionuclides were individually separated and measured for the samples obtained from the contaminated concretes through the established analysis process, and the results are shown in Table 4 and Figure 4. Although all the analysis procedures were precisely measured with a high recovery rate, there was a limitation in detecting radionuclides from a very small amount of analytical samples. Hence, most of the samples were measured below a detection limit. Eventually, the available data was approximately 10 as shown in Table 4. Since the concentration distributions of all the radionuclidse did not show standard normal distribution, the results were expressed through the log function transformation as shown in Figure 4 as a box plot.

In Table 4, the log mean averages of ^{55}Fe and ^{63}Ni nuclides were 1.95E+0 and 1.97E+0 Bq/m^2, respectively, and ^{59}Ni nuclides were found to have a radioactivity value of 1.09E-1 Bq/m^2, which is about 1/10 of the concentration of ^{55}Fe and ^{63}Ni nuclides. Although only two of the data for ^{94}Nb nuclides were available, it was found to be distributed at the level of radioactivity of 2.73E-1 Bq/g. In the radioactivity distribution results, the difference between the maximum and minimum values of ^{55}Fe nuclides showed 390 times, while ^{63}Ni nuclides showed a difference of 122 times. The maximum radioactivity values of ^{55}Fe and ^{63}Ni nuclides were 6.33E+1 and 4.94E+1 Bq/m^2, respectively. This shows the reason why contaminated concrete samples had to be obtained from various zones from high-radiation zone to low-radiation zone.

Table 4. Analytical results on the radioactivities for the radionuclides

	Radioactivity, Bq/m^2			
	^{55}Fe	^{59}Ni	^{63}Ni	^{94}Nb
No. of data	9	9	12	2
LMA	1.95E+0	1.09E-1	1.97E+0	2.73E-1
25th percentile	3.40E-1	4.45E-2	6.50E-1	-
75th percentile	6.73E+0	2.92E-1	5.42E+0	-

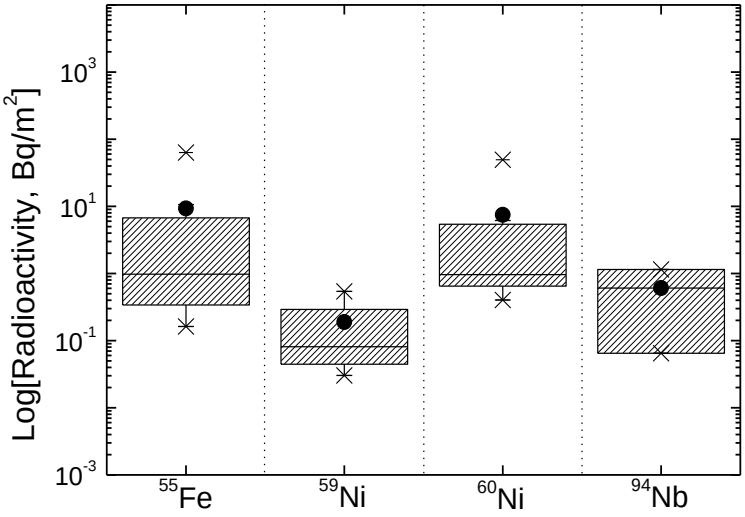

Figure 4. Box plot on radioactivity distributions of the radionuclides

3.2.2 Review on waste streams for decommissioning wastes

Since nuclear power plants have differences in design and construction methods and operation methods such as nuclear fuel, radioactive waste has unique characteristics to each power plant [5]. The characteristics are sometimes expressed as a waste stream. Using these properties, DTM (Difficult-to-measure) nuclides are also evaluated in a statistical way of a scale factor. In South Korea, the scale factor was determined for the DAW of Kori NPP Unit 1 generated in 2003-2008. DAW refers to combustible waste such as cotton, paper, and vinyl which are generated during the operation of NPPs.

Since decommissioning wastes are generated after permanent shutdown of NPPs, it is believed that decommissioning wastes differ in waste streams from radioactive waste applied to the scale factor. Therefore, as shown in Figure 5, the decommissioning wastes analyzed in this study, were compared with radionuclide properties the DAWs generated during the operation of NPP. The comparison method was reviewed through the ratio with the ETM (Easy-to-measure) nuclide used in the scale factor method. For this, it was necessary to convert the value of radionuclide activity per unit area measured from the contaminated concrete to unit mass. In other words, since the density of paint on the surface of contaminated concrete has been known to be 1.67~1.93 g/mL [6,7], on average, about 1.8 g/mL was applied to convert the radioactivity value for each sample from unit area to unit mass, as the comparison results for each radionuclide are presented in Figure 5.

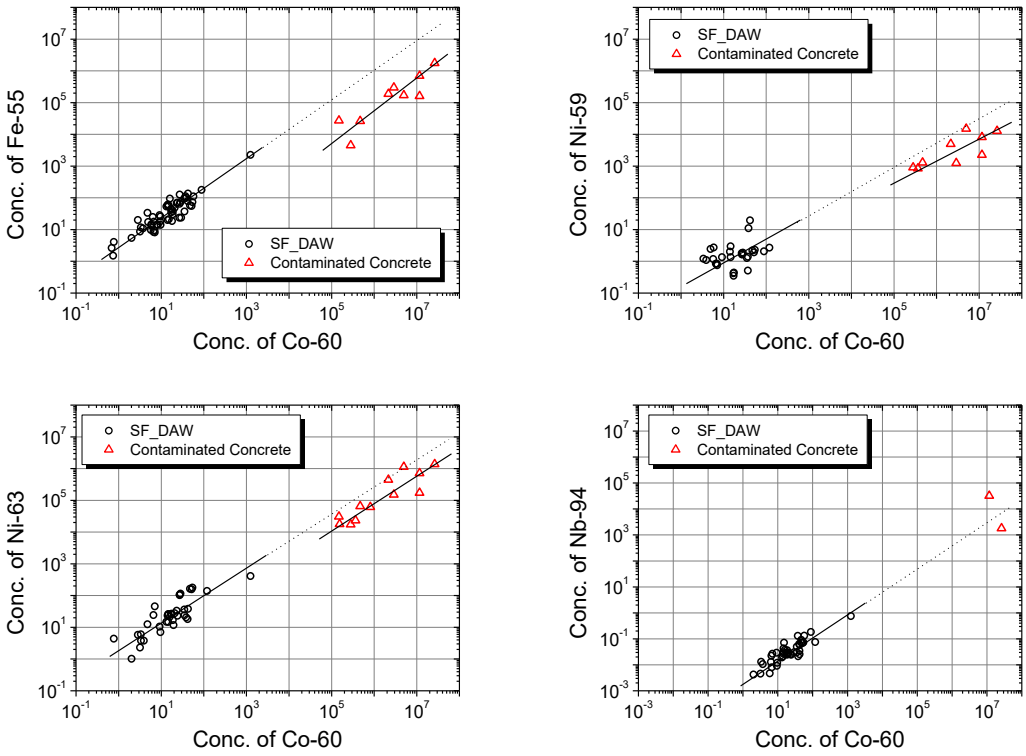

Figure 5. Review on waste streams for the decommissioning wastes arising in Kori unit 1.

It is well known that DTM nuclides in DAW generated during the operation of NPP is related to ETM nuclides [5]. It was confirmed that the concentrations were distributed. Similarly, in Figure 5, it was verified that the concentrations of DTM and ETM nuclides analyzed from the contaminated concrete were distributed in the extension of the fitting curve or in a similar trend with that of the actual data of DAW. This shows that since the waste stream of contaminated concrete shows a similar tendency compared to the DAW generated during the operation of the power plant, it was identified that it is possible to apply a scale factor to the decommissioning wastes.

4 CONCLUSION

The radionuclide characteristics data was secured through smearing on the surface of the contaminated concrete structures of Kori NPP Unit 1 and radiochemical analysis. For this, the chemical analytical methods for activation products such as ^{59}Fe, $^{59/63}$Ni and ^{94}Nb have been developed, and the reliability of the analysis method was evaluated through review of the recovery rate using the standard materials and reproducibility. Finally, it was confirmed that the analytical results of the radionuclides have a waste stream using the results of the scale factor of Kori Unit 1. Using the analytical data of the radionuclides in the contaminated concrete, it is expecting that Korean government will establish a plan for successful nuclear decommissioning of Kori Unit 1.

5 ACKNOWLEDGEMENTS

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