

Radiochemical Analysis of Filters Used During the Decommissioning of Research Reactors for Disposal

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The decommissioning of nuclear facilities produces various types of radiologically contaminated waste. In addition, dismantlement activities, including cutting, packing, and clean-up at the facility site, result in secondary radioactive waste such as filters, resin, plastic, and clothing. Determining of the radionuclide content of this waste is an important step for the determination of a suitable management strategy including classification and disposal. In this work, we radiochemically characterized the radionuclide activities of filters used during the decommissioning of Korea Research Reactors (KRRs) 1 and 2. The results indicate that the filter samples contained mainly ³H (500–3,600 Bq·g⁻¹), ¹⁴C (7.5–29 Bq·g⁻¹), ⁵⁵Fe (1.1–7.1 Bq·g⁻¹), ⁵⁹Ni (0.60–1.0 Bq·g⁻¹), ⁶⁰Co (0.74–70 Bq·g⁻¹), ⁶³Ni (0.60–94 Bq·g⁻¹), ⁹⁰Sr (0.25–5.0 Bq·g⁻¹), ¹³⁷Cs (0.64–8.7 Bq·g⁻¹), and ¹⁵²Eu (0.19–2.9) Bq·g⁻¹. In addition, the gross alpha radioactivity of the samples was measured to be between 0.32–1.1 Bq·g⁻¹. The radionuclide concentrations were below the concentration limit stated in the low- and intermediate-level waste acceptance criteria of the Nuclear Safety and Security Commission, and used for the disposal of the KRRs waste drums to a repository site.

Keywords: Characterization of radioactive waste, Inventory of radionuclides, Radiochemistry, Difficult to measure

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Table 1. Radionuclide Concentration Limit for the LILW Disposal and Measurement Methods in This Work

Nuclide	Concentration limit (Bq·g ⁻¹) ¹⁾	Measurement method
³ H	1.11 × 10 ⁶	Liquid Scintillation Counting (LSC)
¹⁴ C	2.25 × 10 ⁵	Liquid Scintillation Counting (LSC)
⁵⁵ Fe	NA ²⁾	Low energy γ-spectrometry (X-ray)
⁵⁸ Co	NA	γ-spectrometry
⁶⁰ Co	3.70 × 10 ⁷	γ-spectrometry
⁵⁹ Ni	7.40 × 10 ⁴	Low energy γ-spectrometry (X-ray)
⁶³ Ni	1.11 × 10 ⁷	Liquid Scintillation Counting (LSC)
⁹⁰ Sr	7.40 × 10 ⁴	Liquid Scintillation Counting (LSC)
⁹⁴ Nb	1.11 × 10 ²	γ-spectrometry
⁹⁹ Tc	1.11 × 10 ³	Gas Proportional Counting (GPC)
¹²⁹ I	3.70 × 10 ¹	Low energy γ-spectrometry (X-ray)
¹³⁷ Cs	1.11 × 10 ⁶	γ-spectrometry
¹⁴⁴ Ce	NA	γ-spectrometry
Gross alpha	3.70 × 10 ³	Gas Proportional Counting (GPC)
Element analysis	-	Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

¹⁾ Ref. [2]

²⁾ Not available

1. Introduction

Korea Research Reactors (KRRs) 1 and 2 (TRIGA Mark-II and TRIGA Mark-III types, respectively) were operated from 1962 and 1972, respectively, playing important roles in establishing basic nuclear science and technologies, and in advancing nuclear industries in the Republic of Korea. As the utility of these multipurpose research reactors declined with the operation of a new research reactor, HANARO, both of them were shut down in 1995 and decommissioning work began in 1997, with the goal of dismantling all facilities and removing all radioactive materials from the site. The dismantlement of the building structures and the reactor equipment resulted in various types of waste, including radiologically contaminated concrete and steel. In addition, activities

such as cutting, packing, clean-up, and related tasks during the dismantlement process produced secondary waste such as filters, resin, plastic, and clothes. These decommissioning waste materials have been temporarily stored at the reactor site, and the corresponding radionuclide inventory must be assessed for their classification and disposal [1].

In Korea, domestic low- and intermediate-level radioactive waste (LILW) from nuclear power plants, industries, and research and medical institutes has been transported to the Wolsong LILW Disposal Center (WLDC). According to the LILW acceptance criteria of the Nuclear Safety and Security Commission of Korea (NSSC), the radioactivity of thirteen specified radionuclides (³H, ¹⁴C, ⁵⁵Fe, ^{58,60}Co, ^{59,63}Ni, ⁹⁰Sr, ⁹⁴Nb, ⁹⁹Tc, ¹²⁹I, ¹³⁷Cs, and ¹⁴⁴Ce) and the corresponding gross alpha must be identified [2]. Among these radionuclides,



Fig. 1. Photographic images of filter waste samples: (a) air filter, and (b) a mixture of air and water filters.

gamma-emitting radionuclides such as $^{58,60}\text{Co}$, ^{137}Cs , and ^{144}Ce can easily be analyzed. However, chemical separation is generally required to determine the radioactivity of alpha- and beta-decaying nuclides, including ^3H , ^{14}C , ^{55}Fe , $^{59,63}\text{Ni}$, ^{90}Sr , ^{94}Nb , ^{99}Tc , and ^{129}I , because the matrix and coexisting radionuclides can interfere with the radiometric detection of their characteristic emissions [3].

In this work, we analyzed filter waste samples generated during the dismantling of KRRs and determined the inventory of the thirteen aforementioned radionuclides and the gross alpha. Before the analysis of the decommissioning waste, we evaluated destructive analysis methods with simulated filter samples spiked with radionuclides and/or stable isotopes. The radiochemical analysis results were eventually used for the disposal of the filter waste drums to the repository site.

2. Experimental

2.1 Equipment and Chemicals

Table 1 summarizes the measurement methods used in this work. A HPGe detector, a GEM-7084 model (ORTEC), was used to measure gamma emitters such as $^{58,60}\text{Co}$, ^{94}Nb , ^{137}Cs , and ^{144}Ce . A HPGe detector, a GLP 36360-13 model

(ORTEC), was used to measure the Auger electrons and X-rays of ^{55}Fe and ^{59}Ni . A HPGe detector, a GMX60-83 (ORTEC) model, was used to measure the Auger electrons and X-rays of ^{129}I . A Tri-Carb 3110TR (PerkinElmer Inc.) liquid scintillation counter was used to measure the beta emissions of ^3H , ^{14}C , ^{63}Ni and ^{90}Sr . A S5XLB low background alpha/beta counter (Canberra) was used to measure the beta emissions of ^{99}Tc and the gross alpha. A Spectro Arcos (Spectro Analytical Instruments) inductively coupled plasma-optical emission spectrometer (ICP-OES) was used to quantify the stable isotopes. Instrument calibration was performed with standard materials. A gamma-emitting mixed source solution and standard solutions of ^{241}Am , ^{90}Sr , and ^{94}Nb were purchased from Korea Research Institute of Standards and Science (KRISS). Standard solutions of ^3H , ^{14}C , ^{55}Fe , ^{59}Ni , ^{63}Ni , ^{99}Tc , and ^{129}I were purchased from Eckert & Ziegler. Anion exchange resins were purchased from Bio-Rad Laboratory. Sr and Ni resins were purchased from Eichrom Technologies Inc. Other chemicals were purchased from commercial vendors, which were of analytical grade and used as received.

2.2 Filter Waste Samples and Acid Leaching

Dismantlement activities such as the cutting of

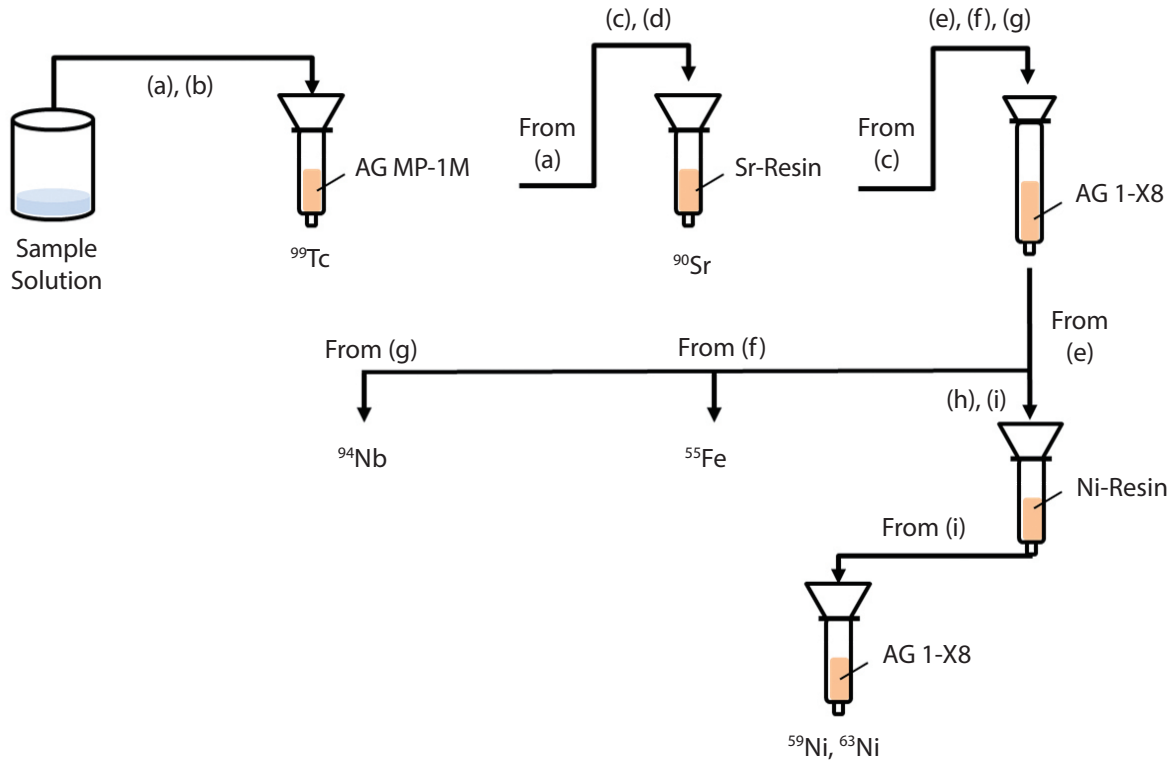


Fig. 2. A scheme of the sequential separation of ^{99}Tc , ^{90}Sr , ^{55}Fe , ^{94}Nb , and $^{59,63}\text{Ni}$. (a) 0.5 M HNO_3 (saved for c), (b) 14% NH_4OH -4% HF and 0.1 M HNO_3 (discarded), and 10 M HNO_3 (^{99}Tc), (c) calcium oxalate co-precipitation (supernatant: saved for e), (d) the precipitate was further purified with Sr-resin (^{90}Sr), (e) 0.1 M ammonium oxalate (pH 4.5–5) (saved for h), (f) distilled water (discard) and 4 M HF (^{55}Fe), (g) 3 M HCl -20% HF (discarded) and 5 M HNO_3 -0.2 M HF (^{94}Nb), (h) 0.1 M ammonium oxalate (pH 9–10) and 0.1 M HCl (discarded), and (i) 9 M HCl (Ni-resin column to AG 1-X8 column, $^{59,63}\text{Ni}$).

contaminated concrete were done in plastic greenhouses temporarily built in the reactor facilities. The working spaces were equipped with air ventilation systems, and water purifying systems were used to clean the cooling water generated at the cutting works. As the filters used there also became radioactive waste, they were sliced after dismantlement and packed in 200 L drums for disposal.

For the radiochemical analysis, amounts exceeding 500 g of the filter waste were randomly taken from each drum and packed into individual plastic bags. In this work, eight samples were analyzed. Five of them were from air filters (F1-F5) and the others (F6-F8) were a mixture of air filter and water purifying filter waste. Fig. 1 shows typical photographs of the two types of filter waste samples in an unpacked state. The filter samples were cut further into small-

er fragments for acid leaching. About 5 g of these samples were placed in a 600 mL PFA beaker, to which 1.5 mL of a Re carrier solution (10 mg $\text{Re} \cdot \text{mL}^{-1}$) and 500 mL of a mixture of 1 M HNO_3 -2.5 M HCl -0.3 M HF were added. The beaker was covered with a Teflon watch glass and the mixture was heated at 200°C for 4 h to leach the nuclides. After cooled down to room temperature, the sample solution was filtered. The volume of the filtrate was adjusted to 500 mL by adding deionized water or through evaporation and was directly used for the determination of gamma-emitting radionuclides.

2.3 Gamma Spectrometry

The radioactivity of gamma-emitting nuclides such

as ^{110m}Ag , ^{144}Ce , $^{57,58,60}\text{Co}$, $^{134,137}\text{Cs}$, ^{152}Eu , ^{59}Fe , ^{54}Mn , ^{94}Nb , ^{95}Nb , ^{125}Sb , ^{65}Zn , and ^{95}Zr in 500 mL of leachate was determined by a HPGe detector that was calibrated using a gamma-emitting mixed source. Gamma-ray spectra were obtained with a 10,000 s measurement.

2.4 Gross Alpha Measurement

After the radioactivity determination of gamma-emitting nuclides, 250 mL of the leachate was taken into a 500 mL PFA beaker and heated to reduce its volume to 20 mL. This solution was used for the gross alpha measurements and the sequential separation of beta-emitting radionuclides such as ^{55}Fe , $^{59,63}\text{Ni}$, ^{90}Sr , ^{94}Nb , and ^{99}Tc . In this case, 1 mL of the concentrated sample solution was spread on a two-inch stainless steel planchet and dried under an IR ramp. After cooling down, the residue was weighed and counting was conducted with a S5XLB low background alpha/beta counter for 50 min.

2.5 Determination of the Radioactivity of ^{55}Fe , $^{59,63}\text{Ni}$, ^{90}Sr , ^{94}Nb , and ^{99}Tc

The sequential separation of ^{55}Fe , $^{59,63}\text{Ni}$, ^{90}Sr , ^{94}Nb , and ^{99}Tc was conducted according to the method developed at Korea Atomic Energy Research Institute (KAERI) [4]. The procedure is briefly depicted in Fig. 2. The amounts of carriers to add were determined from the ICP-OES measurements; 8 mL of the concentrated sample solution was used for separation, where the gross amounts of the carriers were adjusted to 3 mg of Re, 3 mg of Sr, 20 mg of Fe (or less than 50 mg), 20 mg of Nb, 2 mg of Ni, and 50 mg of Ca. First, ^{99}Tc was separated from the other radionuclides with an anion exchange resin (Bio Rad AG MP-1, 100-200 mesh). The ^{99}Tc effluent was evaporated to dryness and dissolved in 3 mL of 0.1 M HNO_3 . The addition of 0.5 mL of ethanol and 0.02 M of tetraphenylarsonium chloride (TPAC) in H_2O precipitated $[\text{ReO}_4(^{99}\text{TcO}_4)](\text{TPA})$, which was dried to weigh for chemical recovery and counted with a S5XLB

low background alpha/beta counter for 50 min. The coprecipitation of calcium oxalate at pH 4.5–5 and extraction chromatography with Sr resin (Eichrom Technologies, Inc., 100-150 mesh) isolated ^{90}Sr . The ICP-OES and LSC measurements correspondingly determined the chemical recovery and radioactivity of ^{90}Sr . ^{55}Fe and ^{94}Nb were separated with an anion exchange resin (Bio Rad AG 1-X8, 100-200 mesh). The ^{55}Fe effluent was collected into a saturated boric acid solution and 25% NH_4OH was added up to pH 9–10. The precipitate was collected and heated at 800°C for 30 min. The resultant Fe_2O_3 was weighed for chemical recovery and the X-ray emission of ^{55}Fe at 5.9 keV was counted for 50 min. The ^{94}Nb effluent was counted with a HPGe detector for 5,000 s and chemical recovery was determined via the ICP-OES measurement. Lastly, the $^{59,63}\text{Ni}$ was purified with Ni resin (Eichrom Technologies, Inc.) and an anion exchange resin (Bio Rad AG 1-X8, 100-200 mesh). To the Ni effluent was added ~5 mL of 25% NH_4OH , 2 mL of 30% ammonium tartrate, and 9 mL of H_2O . The pH of the solution was adjusted to 9–10 with the slow addition of 10% NH_4OH . The addition of 5 mL of 1% dimethylglyoxime (DMG) in 95% ethanol resulted in red $\text{Ni}(\text{DMG})_2$ (s). Chemical recovery was determined from the weight of the precipitate, and the X-ray emission of ^{59}Ni at 6.9 keV was counted for 50 min. Then, $\text{Ni}(\text{DMG})_2$ was dissolved in 2–3 mL of HNO_3 and evaporated to near dryness. The residue was dissolved in 3 mL of HClO_4 and evaporated to incipient dryness, with this step repeated once more. The residue was dissolved in 2 mL of 0.7 M HCl and mixed with 18 mL of the UltimaGold LLT scintillation cocktail. The radioactivity of ^{63}Ni was measured with a liquid scintillation counter for 30 min.

2.6 Determination of the Radioactivity of ^3H and ^{14}C

A wet oxidation method developed at KAERI [5, 6] was slightly modified and used for the separation of ^3H and ^{14}C . To a 250 mL round flask, ~5 g of the filter slices, 5 g of

Table 2. Leaching Results of Simulated Filter Waste Samples

Element ¹⁾	Added (μg)	Found in the leachate (%) ²⁾			
		Test 1	Test 2	Test 3	Avg \pm SD
Ce	1,000	94.7	98.0	97.7	96.8 \pm 1.8
Co	250	99.7	99.3	98.3	99.1 \pm 0.7
Cs	200	98.1	98.6	93.1	96.6 \pm 3.0
Fe	10,000	95.6	100.1	89.7	95.1 \pm 5.2
Nb	250	102.2	106.7	103.8	104.2 \pm 2.3
Ni	250	97.8	98.8	101.2	99.3 \pm 1.8
Re	250	91.5	99.4	96.7	95.9 \pm 4.0
Sr	2,500	104.5	97.5	87.7	96.6 \pm 8.4
U	250	96.6	103.8	99.8	100.1 \pm 3.6

¹⁾ Triplicate analyses of fresh filter samples determined the contents of Ce, Cs, Fe, Ni, and Sr to be 263 ± 13 , 4.3 ± 0.2 , $2,860 \pm 250$, 5.4 ± 0.3 , and $468 \pm 27 \mu\text{g}\cdot\text{g}^{-1}$, respectively.

²⁾ The contents of Ce, Cs, Fe, Ni, and Sr in the simulated spent filters were calibrated based on those of a fresh filter.

potassium persulfate and 0.5 g of AgNO_3 were added, after which the flask was connected to a custom-made distillation apparatus [5]. With purging $\text{N}_2(\text{g})$ through the apparatus, 50 mL of 3 M H_2SO_4 was slowly added. The reaction mixture was stirred and heated at 60°C for 2.5 h, when the evolved $\text{CO}_2(\text{g})$ was trapped in a mixture of 10 mL of Carbo-Sorb E and 10 mL of Permafluor E⁺ placed in a trapping tube at the side end of the apparatus. Then, the reaction mixture was refluxed at 120°C for 30 min and about 10 mL of H_2O was distilled with additional heating. The collected ^{14}C solution was counted with a liquid scintillation counter for 30 min. Five mL of the distillate (i.e. a tenth of the volume of the reaction solution) was transferred to a scintillation vial and 15 mL of UltimaGold LLT was mixed into it, which was counted with a liquid scintillation counter for 30 min.

2.7 Determination of the Radioactivity of ^{129}I

^{129}I was leached by vigorously shaking ~ 20 g of the filter slices in a mixture of 180 mL of H_2O and 20 mL of 7% NaClO with KI (107 mg) as a carrier for 2 h [7]. The leachate was filtered and the residue was rinsed with 15 mL of

H_2O . The filtrate was evaporated up to approximately 100 mL and acidified with 1.25 mL of HNO_3 . After the addition of 20 mL of CHCl_3 , 2 mL of 7.2 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 1 mL of 7% NaClO , the mixture was agitated for 10 min. The organic layer was separated and the aqueous layer was extracted with an additional 10 mL of CHCl_3 and 1 mL of 7% NaClO twice. The combined organic layer was washed with 10 mL of H_2O . Then, the organic solution was extracted twice with 5 mL and 1 mL of 0.2 M NaHSO_3 . The combined aqueous solution was mixed with 0.5 mL of HNO_3 and 3.5 mL of 0.2 M AgNO_3 , resulting in a precipitate of AgI . Chemical recovery was determined with the weight of the precipitate, and the X-ray emission of ^{129}I at 29.8 keV was counted for 10,000 s.

2.8 Calculation of the Minimum Detectable Activity (MDA)

The MDA of the measurement was calculated using the equation below:

$$\text{MDA} (\text{Bq}\cdot\text{g}^{-1}) = \frac{2.71 + 4.65\sqrt{B\cdot T}}{\epsilon\cdot m\cdot Y\cdot T} \quad (1)$$

Table 3. Radioactivity in Bq·g⁻¹ of Selected Gamma-Emitting Radionuclides and Gross Alpha in the Filter Waste Samples

Sample	¹⁴⁴ Ce	⁵⁸ Co	⁶⁰ Co	¹³⁷ Cs	¹⁵² Eu	Gross- α
F1	ND ¹⁾	ND	7.74×10^0	6.40×10^{-1}	6.03×10^{-1}	9.59×10^{-1}
F2	ND	ND	1.41×10^1	8.54×10^0	1.90×10^{-1}	9.17×10^{-1}
F3	ND	ND	1.30×10^0	8.65×10^0	ND	ND
F4	ND	ND	7.47×10^{-1}	1.37×10^0	ND	3.19×10^{-1}
F5	ND	ND	1.24×10^1	3.01×10^0	6.12×10^{-1}	1.03×10^0
F6	ND	ND	6.90×10^0	1.05×10^0	8.11×10^{-1}	1.06×10^0
F7	ND	ND	1.04×10^1	2.29×10^0	4.53×10^{-1}	5.06×10^{-1}
F8	ND	ND	6.97×10^1	2.57×10^0	2.87×10^0	ND

¹⁾ Not detected

Here, B is the background count rate in cps, T is the background and sample counting time in s , ϵ is the counting efficiency, m is the weight of the sample used in the measurement in g, Y is the chemical recovery yield.

3. Results and Discussion

3.1 Acid Leaching of Filter Waste Samples

The leaching of filter waste samples in a mixed-acid solution was selected for the gamma measurement. Prior to the sample analysis, the leaching condition was tested with simulated filter samples spiked with stable isotopes of Ce, Co, Cs, Fe, Nb, Ni, Re, and Sr, and U, where Re was used as a surrogate of ⁹⁹Tc. To ~5 g of a fresh HEPA filter, 200 μ g of Cs for the ICP-MS measurement and 1,000 μ g of Ce, 10,000 μ g of Fe, 2,500 μ g of Sr, and 250 μ g each of the other elements for the ICP-OES measurements were added. Three simulated samples were leached in 500 mL of a mixture of 1 M HNO₃-2.5 M HCl-0.3 M HF at 200°C for 4 h. Table 2 shows the element quantification results of the leached solutions from the simulated filter waste samples. Because the HEPA filter contains small amounts of Ce, Cs,

Fe, Ni, and Sr, the chemical recovery outcome was corrected based of the quantification results from the leaching of the fresh filter. All of the elements were nearly quantitatively recovered on average. Among them, Fe showed the lowest average chemical yield ($95.1 \pm 5.2\%$), which is attributable to the highness and inhomogeneity of the Fe content ($2,860 \pm 250 \mu\text{g}\cdot\text{g}^{-1}$) with respect to the amounts of other elements in the HEPA filter.

The filter waste samples were leached as described in the experimental section. The final volume of the leachate was 500 mL, and this amount was used for the gamma spectrometry. Half of the solution was then concentrated to 20 mL, some portions of which were used for the gross alpha measurements and the separation of beta-emitting nuclides such as ⁵⁵Fe, ^{59,63}Ni, ⁹⁰Sr, ⁹⁴Nb, and ⁹⁹Tc.

3.2 Radioactivity Concentration Determination of Gamma Emitters

Table 3 shows the activity of the gamma-emitting radionuclides of ^{58,60}Co, ¹³⁷Cs, and ¹⁴⁴Ce in the filter waste samples. The activity of ¹⁵²Eu was also reported, as ¹⁵²Eu was mainly detected in activated concrete in KRRs [8, 9] and some of the filter waste was generated during the

dismantling of the reactor shielding concrete. Among the gamma-emitting radionuclides, ^{60}Co and ^{137}Cs were detected in all of the samples at corresponding radioactivity of $0.74\text{--}70\text{ Bq}\cdot\text{g}^{-1}$ and $0.64\text{--}8.7\text{ Bq}\cdot\text{g}^{-1}$. The signals of ^{152}Eu were also found in six samples at radioactivity of $0.19\text{--}2.9\text{ Bq}\cdot\text{g}^{-1}$. These samples had relatively high contents of ^{60}Co ($\geq 6.9\text{ Bq}\cdot\text{g}^{-1}$). Other gamma-emitting radionuclides, such as $^{110\text{m}}\text{Ag}$, ^{144}Ce , $^{57,58}\text{Co}$, ^{51}Cr , ^{134}Cs , ^{54}Mn , ^{95}Nb , ^{125}Sb , ^{65}Zn , and ^{95}Zr , were not detected under the conditions of this work, and their MDA values were in the range of $10^{-2}\text{--}10^{-1}\text{ Bq}\cdot\text{g}^{-1}$. Enough time had passed such that many of the radionuclides stemming from the operation of the reactor likely decayed since the reactor was shut down in 1995. For this reason, the analysis detected relatively long half-life isotopes such as ^{60}Co , ^{137}Cs , and ^{152}Eu .

3.3 Radioactivity Concentration Determination of Gross Alpha

Measuring the gross alpha is a simple approach that can provide a good estimate of the total radioactivity of alpha-emitting nuclides [10]. In this work, a portion of the sample leaching solution was dried in a planchet and the residue was counted using a gas proportional counter (GPC). Because the extent of self-absorption depends on the counting sample thickness, the counting efficiency of the gross alpha measurement was calculated using the ^{241}Am standard with different weights of NaCl as an estimate of the residue thickness in the planchet [10]. Table 3 shows the results of the gross alpha measurements. The gross alpha concentrations of the six samples were measured and found to be $0.32\text{--}1.1\text{ Bq}\cdot\text{g}^{-1}$. The others did not present detectable activities with MDA values of $10^{-2}\text{--}10^{-1}\text{ Bq}\cdot\text{g}^{-1}$. Currently, the WLDC requires activity determinations of alpha emitters such as U, Pu, Am, and Cm isotopes in drums where the gross alpha concentration exceeds $10\text{ Bq}\cdot\text{g}^{-1}$ [11]. In this case, individual quantifications of these alpha-emitting nuclides are needed [12], but this is out of the scope of this work.

3.4 Radioactivity Concentration Determinations of ^{55}Fe , $^{59,63}\text{Ni}$, ^{90}Sr , ^{94}Nb , and ^{99}Tc

The interference of coexisting radionuclides and the sample matrix and the radiation characteristics require chemical separation of beta-decaying nuclides such as ^3H , ^{14}C , ^{55}Fe , $^{59,63}\text{Ni}$, ^{90}Sr , ^{94}Nb , ^{99}Tc , and ^{129}I for proper radiometric measurements. KAERI has developed several methods to separate sequentially ^{55}Fe , $^{59,63}\text{Ni}$, ^{90}Sr , ^{94}Nb , and ^{99}Tc so as to quantify them in LILW [4, 13-16]. One of the purposes behind this was to develop scaling factors for LILW generated from nuclear power plants [15, 17].

The method applied in this work used ion exchange and extraction chromatography as well as precipitation to isolate ^{99}Tc , ^{90}Sr , ^{55}Fe , ^{94}Nb , and $^{59,63}\text{Ni}$ in sequence [4]. ^{99}Tc was separated from the leaching solution containing Re as a carrier using an anion exchange resin, where $^{99}\text{TcO}_4^-$ and ReO_4^- are strongly adsorbed but the other metal ions and the matrix elements do not exist in $0.5\text{--}1\text{ M HNO}_3$. A complex of $[\text{ReO}_4(^{99}\text{TcO}_4)](\text{TPA})$ was prepared for counting. The average chemical recovery of Re was 64%. Table 4 shows the concentration of ^{99}Tc in the filter waste samples. One filter sample (F8) showed an activity of $0.078\text{ Bq}\cdot\text{g}^{-1}$. The others did not present detectable activities with MDA values of $0.03\text{--}0.07\text{ Bq}\cdot\text{g}^{-1}$.

Calcium oxalate co-precipitation was used to separate Sr from the solution containing Fe, Nb, and Ni. ^{90}Sr was further purified for the LSC measurement by means of Sr-resin extraction chromatography, which removed Ca and residual interfering radionuclides. The average chemical recovery was 86%. The ^{90}Sr concentrations of F2, F3, and F7 were measured and found to be 5.0 , 2.0 , and $0.25\text{ Bq}\cdot\text{g}^{-1}$, respectively. Those of the other samples were not detected given the MDA values of $0.16\text{--}0.19\text{ Bq}\cdot\text{g}^{-1}$.

Anion exchange chromatography of the oxalate supernatant during Sr separation enabled the individual isolation of ^{55}Fe and ^{94}Nb , the corresponding X-rays and gamma rays of which were measured with HPGe detectors in both cases. The average chemical recovery of Fe was 63%. The

Table 4. Radioactivity in Bq·g⁻¹ of Selected Radionuclides in the Filter Waste Samples

Sample	⁹⁹ Tc	⁹⁰ Sr	⁵⁵ Fe	⁵⁹ Ni	⁶³ Ni	⁹⁴ Nb	³ H	¹⁴ C	¹²⁹ I
F1	ND ¹⁾	ND	ND	6.02 × 10 ⁻¹	5.01 × 10 ¹	ND	1.09 × 10 ³	1.06 × 10 ¹	ND
F2	ND	4.95 × 10 ⁰	1.19 × 10 ⁰	1.04 × 10 ⁰	9.38 × 10 ¹	ND	5.12 × 10 ²	7.52 × 10 ⁰	ND
F3	ND	2.03 × 10 ⁰	ND	ND	1.97 × 10 ⁰	ND	1.72 × 10 ³	2.75 × 10 ¹	ND
F4	ND	ND	ND	ND	6.02 × 10 ⁻¹	ND	3.60 × 10 ³	1.35 × 10 ¹	ND
F5	ND	ND	7.06 × 10 ⁰	ND	2.75 × 10 ⁰	ND	1.38 × 10 ³	1.34 × 10 ¹	ND
F6	ND	ND	ND	ND	1.22 × 10 ¹	ND	2.26 × 10 ³	1.70 × 10 ¹	ND
F7	ND	2.54 × 10 ⁻¹	ND	7.19 × 10 ⁻¹	7.62 × 10 ¹	ND	1.04 × 10 ³	2.07 × 10 ¹	ND
F8	7.76 × 10 ⁻²	ND	3.48 × 10 ⁰	8.34 × 10 ⁻¹	7.86 × 10 ¹	ND	6.01 × 10 ²	2.88 × 10 ¹	ND

¹⁾ Not detected

measured ⁵⁵Fe concentrations of F2, F5, and F8 were 1.2, 7.1, and 3.5 Bq·g⁻¹, respectively. The MDAs of ⁵⁵Fe in this work ranged from 0.9 to 1.2 Bq·g⁻¹.

⁹⁴Nb is not only a beta emitter but also a high-energy gamma emitter. However, directly measuring the gamma rays of ⁹⁴Nb in nuclear waste when large amounts of other gamma-emitting radionuclides are present is sometimes unsuccessful. The separation method in this work featuring the isolation of ⁹⁴Nb resulted in an average chemical recovery of 87%. However, ⁹⁴Nb was not detected in any of the samples. The MDA values determined after separation were 0.55–0.58 Bq·g⁻¹. They were somewhat higher than those from the direct gamma-ray measurements of the leaching solution, which were estimated to be 0.06–0.24 Bq·g⁻¹. The insignificant interference of other gamma-emitting radionuclides and the larger sample amounts as well as the longer counting time in the gamma-ray measurements of the leaching solutions may have lowered the MDA values.

^{59,63}Ni were isolated with Ni-Resin extraction chromatography followed by anion exchange chromatography. The X-rays of ⁵⁹Ni were measured with the Ni(DMG)₂ complex. The complex was then decomposed by acid digestion, and the beta rays of ⁶³Ni were measured via LSC. The av-

erage chemical recovery of Ni was 85%. The concentrations of ⁵⁹Ni of F1, F2, F7, and F8 were all in the range of 0.6–1.0 Bq·g⁻¹. The other samples did not show detectable activities of ⁵⁹Ni given their MDA values of ~0.09 Bq·g⁻¹. On the other hand, ⁶³Ni was detected in all of the samples at concentrations in the range of 0.60–94 Bq·g⁻¹. Thermal neutron reactions with stable nickel ⁶²Ni (3.65%) and ⁵⁸Ni (68.1%) produced both isotopes, and the initial activity ratio of ⁶³Ni/⁵⁹Ni is expected to be ~100 or higher in nuclear waste [3, 18]. The average activity ratios of ⁶³Ni/⁵⁹Ni of the filter waste samples were ~93, which seems reasonable given that the research reactors were shut down in 1995.

3.5 Radioactivity Concentration Determinations of ³H and ¹⁴C

As ³H exists as HT or HTO and ¹⁴C exists as carbonate or carbon in concrete [19], the secondary filter waste generated during the dismantling of concrete structures may also contain those chemical forms. The wet oxidation method was assessed with simulated filter waste samples. HTO and Na₂¹⁴CO₃ standard solutions were loaded onto ~5 g of a sliced HEPA filter, where the amounts of ³H and ¹⁴C spiked were 153 and 321 Bq, respectively. A strong

acidic condition with oxidants such as potassium persulfate and AgNO_3 facilitated the evolution of $^{14}\text{CO}_2$ [5, 6], which was chemisorbed onto Carbo-Sorb E. Subsequent distillation separated HTO from the reaction mixture. The collected ^3H and ^{14}C were counted as described in the experimental section and five trials led to recovery of 97.1 ± 4.2 and $94.6 \pm 8.3\%$, respectively. The analysis results in Table 4 show that ^3H and ^{14}C were found in all of the filter waste samples. The measured concentrations of ^3H and ^{14}C were 512–3,600 and 7.5–29 $\text{Bq}\cdot\text{g}^{-1}$, respectively. The high content of ^3H in the concrete waste of the KRR-2 [20] most likely led to the high concentration of ^3H in the secondary filter waste generated during the decommissioning process.

3.6 Radioactivity Concentration Determination of ^{129}I

Due to its very long half-life and high mobility in the geosphere, ^{129}I is of long-term concern regarding the safety assessment of the final repository. It is highly probable that most types of LILW contain trace amounts of ^{129}I [21]. When ^{129}I is not detected under analysis conditions applied, MDA values can be used for an inventory evaluation of the repository [22]. Therefore, it is interesting to lower the detection limit with the improvement of the separation methods and instrumentation regarding the safety assessments of disposal facilities [7, 21, 23].

In this work, the activity of ^{129}I was measured by the X-ray counting method, which is less sensitive than mass spectrometry [3, 23]. The sample quantity was adjusted to ~ 20 g to target a MDA value below 10^{-2} $\text{Bq}\cdot\text{g}^{-1}$. The filter waste samples were vigorously shaken in a NaClO solution containing KI as a carrier, similar to the leaching method used for the analysis of dry waste from nuclear power plants [7]. Subsequent redox reactions and liquid-liquid extractions purified the iodine species further. The leached IO_3^- was oxidized to I_2 by hydroxylamine, which was extracted to the organic layer. The stripping of the organic

layer with a NaHSO_3 solution reduced I_2 into I^- . Lastly, the precipitation reaction of Ag^+ and I^- resulted in a counting source for the X-ray measurement. The average chemical recovery was estimated to be 81%. The analysis results in Table 4 show that ^{129}I was not detected in any of the filter waste samples given that the MDA values were as low as ~ 0.007 $\text{Bq}\cdot\text{g}^{-1}$.

4. Conclusion

We determined the radionuclide inventory of filter waste generated during the dismantling of KRRs. For a destructive analysis of the filter waste samples, several pretreatment and separation methods were utilized. The samples were leached in acid solutions for the measurements of gamma emitters such as $^{58,60}\text{Co}$, ^{94}Nb , ^{137}Cs , ^{144}Ce , and ^{152}Eu , and for the determination of the gross alpha concentrations. The leaching solutions were also used to separate ^{99}Tc , ^{90}Sr , ^{55}Fe , ^{94}Nb , and $^{59,63}\text{Ni}$ sequentially using the chromatographic and precipitation methods. On the other hand, ^{14}C and ^3H were separated using the wet oxidation method and ^{129}I was isolated by a procedure that included leaching, purifying based on redox reactions and liquid-liquid extractions, and selective precipitation. Radiometric measurements were used to determine the activities of the separated beta-decaying radionuclides. The concentrations of all radionuclides determined in this work were below the concentration limit of LILW in the acceptance criteria of the NSSC (Table 1). Finally, the radiochemical analysis results were used for the disposal of waste drums from the decommissioning of KRRs to the repository site.

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