A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 60 2015 Issue 2
DOI: 10.1515/amm-2015-0097

K.H. KANG[*,♯], C.H. LEE[*], M.K. JEON[*], S.Y. HAN[*], G.I. PARK[*], S.-M. HWANG[**]

CHARACTERIZATION OF CLADDING HULL WASTES FROM USED NUCLEAR FUELS

CHARAKTERYSTYKA ODPADÓW Z OKŁADZIN REAKTORA WODNEGO CIŚNIENIOWEGO

Used cladding hulls from pressurized water reactor (PWR) are characterized to provide useful information for the treatment and disposal of cladding hull wastes. The radioactivity and the mass of gamma emitting nuclides increases with an increase in the fuel burn-up and their removal ratios are found to be more than 99 wt.% except Co-60 and Cs-137. In the result of measuring the concentrations of U and Pu included in the cladding hull wastes, most of the residues are remained on the surface and the removal ratio of U and Pu are revealed to be over 99.98 wt.% for the fuel burn-up of 35,000 MWd/tU. An electron probe micro-analyzer (EPMA) line scanning shows that radioactive fission products are penetrated into the Zr oxide layer, which is proportional to the fuel burn-up. The oxidative decladding process exhibits more efficient removal ratio of radionuclides.

Keywords: Used nuclear fuels, Metal wastes, Cladding hulls, Zircaloy, Radioactivity

1. Introduction

Pyroprocess developed at Korea Atomic Energy Research Institute (KAERI) aims to recover uranium (U) and transuranic elements from used nuclear fuels (UNFs), thereby reducing the amount of high-level wastes and recycling for sodium-cooled fast reactors (SFRs) [1-3]. In the pretreatment step of the pyroprocess, cladding hull wastes are expected to be generated as much as about 250 kg for the treatment of 1 ton of UNFs [4]. In addition, the cladding hull wastes are supposedly categorized as an intermediate-level or a greater-than-class C (GTCC) level waste owing to residual actinides and fission products incorporated in the surface by pellet-cladding interaction (PCI) during the reactor operation [5-7]. Rudisill investigated the feasibility of decontaminating spent fuel cladding hulls and found that the TRU concentration in the hulls exceeded the Class C LLW limit [7].

The alloy elements and impurities including in the cladding matrix are also activated by neutron irradiation in the reactor [8]. For better understanding of the waste properties, the characterization of the cladding hull waste such as radioactivity and oxide layer thickness is required because it greatly influences the activity level, treatment method, immobilization, and recycling of the waste. In addition, a removal ratio of radionuclides or a decladding ratio at the pretreatment step of pyroprocess is assumed to be 99.98 wt.% at KAERI, however, it is required to be experimentally evaluated.

In this study, the cladding hull wastes generated from pressurized water reactor (PWR) were characterized by spectroscopic and chemical analyses. The result will provide valuable information for a further recovery process and/or disposition policy of the hull wastes.

2. Experimental

Quantitative analysis of cladding hull wastes

To quantify the concentrations of radioactive nuclides that are incorporated and/or adhered to the surface of Zircaloy-4 cladding hull wastes, γ-spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS) were used. The cladding hull waste samples were prepared by mechanically decladding the nuclear fuels taken from the Kori 2 reactors [9, 10]. The burn-up of the used nuclear fuel ranged from 27,000 MWd/tU to 58,000 MWd/tU. The concentrations of representative fission products included in the hull wastes were calculated from their radioactivities measured by γ-spectroscopy.

For uranium (U) and plutonium (Pu), the cladding hull tubes were washed in a nitric acid first, followed by a complete dissolution of the tubes in a mixture of hydrofluoric acid and aqua regia. The concentrations of uranium (U) and plutonium (Pu) that exist on the surface and penetrated into the cladding were separately determined by analyzing the wash solution and the dissolved solution using γ-spectroscopy and ICP-MS.

[*] NUCLEAR FUEL CYCLE PROCESS PROCESS DEVELOPMENT DIVISION, KOREA ATOMIC ENERGY RESEARCH INSTITUTE, 989-11 DAEDEOK-DAERO, YUSEONG-GU, DAEJEON 305-353, REPUBLIC OF KOREA
[**] HYDROGEN AND FUEL CELL DEPARTMENT, KOREA INSTITUTE OF ENERGY RESEARCH, 152, GAJEONG-RO, YUSEONG-GU, DAEJEON 305-343, REPUBLIC OF KOREA
[♯] Corresponding author: nghkang@kaeri.re.kr

Cross-sectional analysis of cladding hull wastes

The distribution of fission products perpendicular to the inner surface of Zircaloy-4 cladding hull wastes with various burn-ups was examined using electron probe micro-analyzer (EPMA). The used cladding hull specimens were selected from the used fuels with a burn-up of 27,000 MWd/tU, 37,000 MWd/tU, and 58,000 MWd/tU. The thicknesses of fission product layers, which are penetrated and adhered to the surface, were determined on the basis of zirconium oxide layer.

3. Results and discussion

Quantitative analysis of cladding hull wastes

Figure 1 shows the radioactivities of representative gamma-emitting radionuclides remained on the cladding hull wastes after a mechanical decladding process for used nuclear fuels with various burn-ups. As listed in table I, the concentrations of the radionuclides were calculated by the following equation

$$\mathrm{Bq(dps)} = \lambda N = 0.693 \times N/T_{1/2} \times (365 \times 24 \times 3,600) \quad (1)$$

$$m = (N/6.023 \times 10^{23}) \times \mathrm{Bq} \quad (2)$$

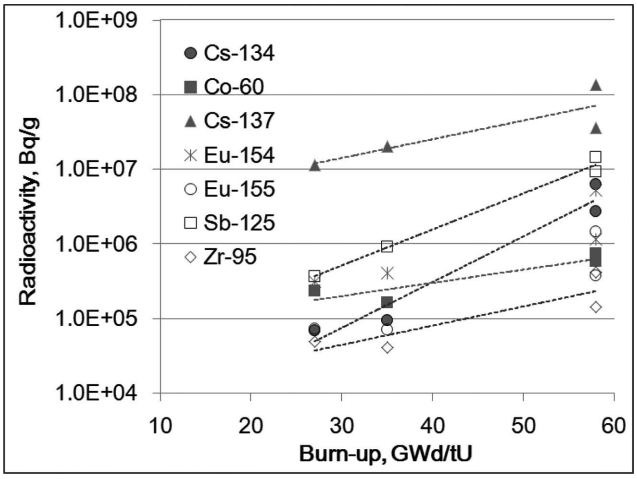


Fig. 1. Radioactivities of representative nuclides from cladding hull wastes in accordance with a burn-up

TABLE 1

Radioactivities and concentrations of major nuclides adhered to the surface of cladding hull wastes in accordance with burn-up

Burn-up (MWd/tU)	Nuclides	Radioactivity Bq (dps) /1 g hull	No. of atom /1 g hull	Mass (g) /1 g hull	Mass (g)/ 10 ton used fuel	Decladding ratio (%)
27,000	Cs-134	6.94E+04	6.54E+12	1.46E-09	2.38E+01	99.98
	Co-60	2.37E+05	5.69E+13	5.67E-09	2.02E-01	93.00
	Cs-137	1.13E+07	1.55E+16	3.52E-06	8.02E+03	99.89
	Eu-154	3.14E+05	1.23E+14	3.14E-08	6.05E+01	99.87
	Eu-155	7.29E+04	1.58E+13	4.07E-09	7.40E+00	99.86
	Sb-125	3.64E+05	4.57E+13	9.49E-09	4.88E+00	99.51
	Zr-95	4.93E+04	3.81E+11	6.02E-11	5.55E-15	–
35,000	Cs-134	9.52E+04	8.96E+12	1.995E-09	3.76E+01	99.99
	Co-60	1.64E+05	3.94E+13	3.927E-09	2.59E-01	96.21
	Cs-137	2.03E+07	2.78E+16	6.336E-06	1.03+04	99.85
	Eu-154	4.00E+05	1.57E+14	4.003E-08	9.85E+01	99.90
	Eu-155	7.12E+04	1.54E+13	3.969E-09	1.13E+01	99.91
	Sb-125	9.05E+05	1.14E+14	2.361E-08	6.27E+00	99.06
	Zr-95	4.06E+04	3.14E+11	4.959E-11	5.34E-15	–
58,000	Cs-134	6.18E+06	5.82E+14	1.295E-07	8.667E+01	99.63
	Co-60	5.89E+05	1.41E+14	1.407E-08	4.185E-01	91.60
	Cs-137	1.38E+08	1.89E+17	4.310E-05	1.674E+04	99.34
	Eu-154	5.16E+06	2.02E+15	5.162E-07	2.184E+02	99.41
	Eu-155	1.46E+06	3.16E+14	8.140E-08	2.466E+01	99.17
	Sb-125	9.13E+06	1.15E+15	2.380E-07	9,841E+00	93.95
	Zr-95	4.16E+05	3.22E+12	5.080E-10	4.814E-15	–
58,000	Cs-134	2.75E+06	2.59E+14	5.76E-08	8.667E+01	99.83
	Co-60	7.33E+05	1.76E+14	1.75E-08	4.185E-01	89.54
	Cs-137	3.60E+07	4.95E+16	1.13E-05	1.674E+04	99.83
	Eu-154	1.15E+06	4.48E+14	1.15E-07	2.184E+02	99.87
	Eu-155	3.72E+05	8.05E+13	2.07E-08	2.466E+01	99.79
	Sb-125	1.44E+07	1.81E+15	3.76E-07	9,841E+00	90.46
	Zr-95	1.43E+05	1.10E+12	1.74E-10	4.814E-15	–

TABLE 2

Concentrations of U and Pu in accordance with burn-up

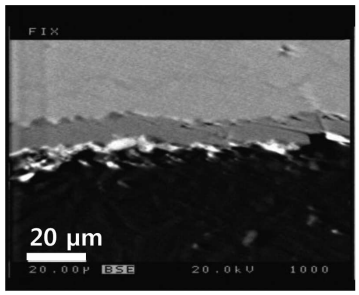
Burn-up (MWd/tU)	Solution	U (μg/g)	Residue (%)/ Removal ratio (%)	Pu (μg/g)	Residue (%)/ Removal ratio (%)
35,000	Wash liquid	481.7 19	0.0148 99.985	7.1±1.0	0.0195 99.981
	Dissolved liquid	91.5±4.0		0.3±0.03	
58,000	Wash liquid	9.155±275	0.2430 99.757	214.7±21	0.4596 99.540

where Bq is the radioactivity, λ is the decay constant, N is the atomic number, $T_{1/2}$ is the half-life, and m is the mass of radionuclide. The radioactivities and mass for the selected nuclides exponentially increase with the burn-up owing to the generation of fission products. In particular, the activity of Cs-137 exceeds the criteria of the present Korean intermediate-/low-level waste disposition regulation, whereas that of Co-60 is found to be lower than the criteria [11]. Based on the mass of radionuclides contained in 10 tons of used fuel, removal ratios by decladding process can be calculated as shown in Table I. Although most of radionuclides appear to be removed more than 99 wt.% regardless of the burn-up after the decladding process, Co-60 and Sb-125 show relatively lower removal ratios. This is caused not only by the radionuclides included in the residual used fuel, but also the ones newly generated from cladding hull components by irradiation. In our other study [8], we calculated radioactivity of each nuclides using the ORIGEN-S code [12] to investigate effect of burn-up on the radioactivation behavior of cladding materials. In the results of irradiation calculation, concentrations of Co-60 and Sb-125 are 9.96×10^{6} and 7.47×10^{3} for Zircaloy-4 cladding hull wastes with a burn-up of 60,000 MWd/tU, respectively.

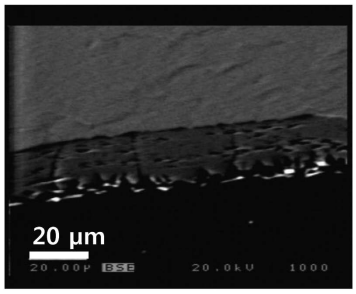
The concentrations of U and Pu included in the cladding hull waste were measured by ICP-MS as shown in Table II. The samples were cleaned with a diluted nitric acid solution in the first step and completely dissolved in a mixture of hydrofluoric acid (HF) and aqua regia (HNO_3+ 3HCl) in the second step to analyze the concentrations of U and Pu separately for the surface and inner hull. Most amounts of residual U and Pu are found to remain on the surface, whereas only traces of U and Pu are penetrated into the cladding hull tube. In the result of calculating the removal rate of radionuclides after decladding process, more than 99.98 wt.% of U and Pu was removed for a burn-up of 38,000 MWd/tU. For a higher burn-up such as 58,000 MWd/tU, however, the removal rate of U and Pu decreases to 99.76 wt.% and 99.54 wt.%, respectively, which is associated with a severe PCI phenomena for high burn-ups. Therefore, the assumption that the decladding ratio in the pretreatment step of KAERI pyroprocess is about 99.98 wt.% is reasonable for low burn-ups, however to meet the criteria of radionuclide removal ratios for high burn-up fuels, an oxidative decladding process is additionally required in conjunction with the mechanical cladding process [9, 10].

Cross-sectional analysis of cladding hull waste tubes

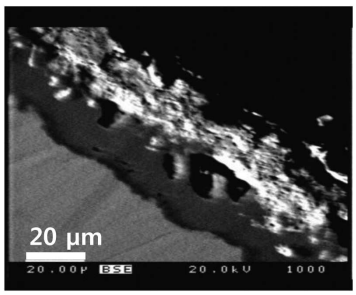
Used cladding hull tube samples at various fuel burn-ups were extracted through a mechanical slitting or an oxidative decladding process as shown in Table III. Figure 2 displays cross-sectional SEM images of the cladding hull tubes after the decladding process. The sections with relatively bright and dark greys correspond to Zircaloy-4 tube bodies and Zr oxide layers, respectively, and whitish parts present nuclides with high atomic numbers such as U and fission products. The roughness of the outer oxide surface cling to the used fuel residue is increased with an increase in the fuel burn-up, which might be caused by recoil process of fission products.



(a) G23-B5 1



(b) TRQ43F16 1



(c) K23-B16 1

Fig. 2. Cross sectional SEM images of used cladding hull tubes with various burn-ups; (a) 27,000 MWd/tU, (b) 37,000 MWd/tU, and 58,000 MWd/tU

TABLE 3

Conditions of hull specimens

Sample name	Burn-up (MWd/tU)	Decladding method	Weight (g)
G23-B5	27,000	Mechanical slitting	0.73
TRQ43F16	37,000	Oxidative decladding	0.92
K23-B16	58,000	Mechanical slitting	0.88

To assess the thicknesses of Zr oxide and fission product layers, EPMA line scanning was performed for various fuel burn-ups. From the tendency of Zr concentration along with the depth of Zircaloy-4 tube in Fig. 3, the Zr oxide layer thickness was measured to be gradually increased from 10 μm for 27,000 MWd/tU to 18 μm for 37,000 MWd/tU, and 22 μm for 58,000 MWd/tU, respectively. Based on the measured Zr oxide layer, the thicknesses of fission product layers that are penetrated and adhered to the hull surface were also estimated as shown in Fig. 4 and Table IV. The penetration depth of fission products is increased from 3 μm for 27,000 MWd/tU to 8 μm for 37,000 MWd/tU, and 15 μm for 58,000 MWd/tU with the fuel burn-up, which is a similar trend of Zr oxide thickness change. However, the adhered fission product layer to the surface for 37,000 MWd/tU was found to be the lowest, which is consistent with the SEM image observed in Fig. 2. This is attributed by a difference of decladding method for the samples; the oxidative decladding process is revealed to be effective for enhancing the removal rate of radionuclides adhered to the surface of cladding hull wastes.

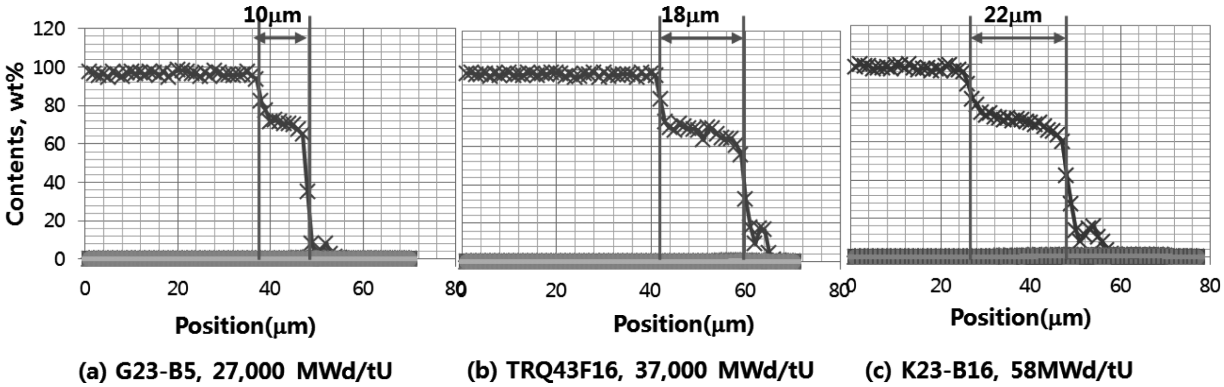


Fig. 3. EMPA depth profiles for Zr in used cladding hull tubes with various burn-ups; (a) 27,000 MWd/tU, (b) 37,000 MWd/tU, and 58,000 MWd/tU

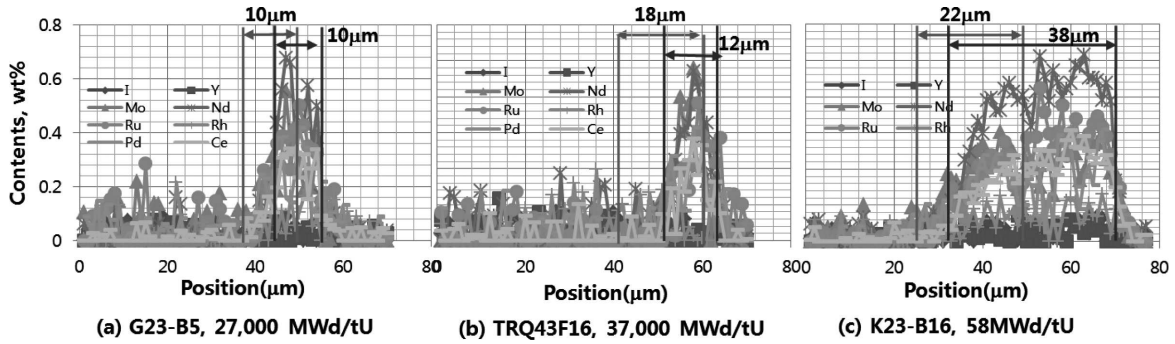


Fig. 4. EMPA line scanning for fission products in used cladding hull tubes with various burn-ups; (a) 27,000 MWd/tU, (b) 37,000 MWd/tU, and 58,000 MWd/tU

TABLE 4

Thicknesses of Zr oxide layer and fission product (F.P.) layer according to a burn-up

Sample name	Burn-up (MWd/tU)	Zr oxide layer (μm)	Penetrated F.P. layer (μm)	Adhered F.P. layer (μm)	Total F.P. layer (μm)
G23-B5	27,000	10	3	7	10
TRQ43F16	37,000	18	8	4	12
K23-B16	58,000	22	15	23	38

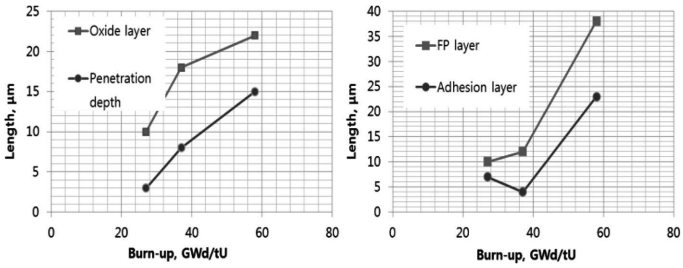


Fig. 5. Thicknesses of Zr oxide layer and fission product (F.P.) layer according to a burn-up

4. Conclusion

For the understanding of cladding hull waste characteristics, γ-spectrometry and chemical analyses using ICP-MS and EPMA line scanning were carried out for the cladding hull tubes selected from used nuclear fuels with various burn-ups.

Based on the calculation converting the radioactivity to the mass, the generation of fission products was increased with an increase in the fuel burn-up. In particular, the radioactivity of Cs-137 did not satisfy the criteria of the present Korean intermediate-/low-level waste disposition regulation. The removal rates of radionuclides by the decladding process using mechanical slitting were found to be mostly over 99.5 wt.%, whereas those of Sb-125 and Co-60 were revealed to be lower because of an irradiation effect of cladding materials.

Chemical analyses also showed that the removal rate of radionuclide decreased with the fuel burn-up due to an effect of PCI. The fission product layer penetrated into the hull surface increased with the fuel burn-ups ranging from 27.000 MWd/tU to 58.000 MWd/tU, which is consistent with the Zr oxide layer thickness. In addition, the fission product adhered to the surface was found to be effectively removed by the oxidative decladding process.

Acknowledgements

This work supported by the Nuclear R&D Program of the Korean Ministry of Science, ICT and Future Planning (NRF-2012M2A8A5025802).

Received: 20 November 2014.

REFERENCES

[1] H. Lee, G.I. Park, K.H. Kang, J.M. Hur, J.G. Kim, D.H. Ahn, Y.Z. Cho, E.H. Kim, Nucl. Eng. Technol. **43**, 317 (2011).
[2] K.C. Song, H. Lee, J.M. Hur, J.G. Kim, D.H. Ahn, Y.Z. Cho, Nucl. Eng. Technol. **42**, 131 (2010).
[3] J.J. Laidler, J.E. Battles, W.E. Miller, J.P. Ackerman, E.L. Carls, Prog. Nucl. Energ. **31**, 131 (1997).
[4] K.H. Kang, C.H. Lee, M.K. Jeon, Y.L. Lee, Y.T. Choi, G.I. Park, Treatment Technology of Hull Wastes, KAERI/TR-5288, 2013.
[5] M. Nutt et al., Information Basis for Developing Comprehensive Waste Management System - US-Japan Joint Nuclear Energy Action Plan Waste Management Working Group Phase I Report, FCR&D-USED-2010-000051, 2010.
[6] R. Restani, E.T. Aerne, G. Bart, H.P. linder, A. Muller, F. Petrik, Characterisation of PWR Cladding Hulls from Commercial Reprocessing, NAGRA technical report 92-13, 1992.
[7] T.S. Rudisill, "Decontamination of Zircaloy cladding hulls from spent fuel", J. Nucl. Mater. **285**, 193 (2009).
[8] M.K. Jeon, C.H. Lee, C.J. Park, K.H. Kang, G.I. Park, Effect of Burn-up on the radioactivation behavior of cladding materials, KAERI/TR-5100, 2013.
[9] G.I. Park, K.K. Kim, D.Y. Lee, J.W. Lee, J.J. Park, K.C. Song, Global 2009, Paris (2009).
[10] G.I. Park, K.H. Cho, J.W. Lee, J.J. Park, K.C. Song, ANS spring meeting, Anaheim, California (2008).
[11] http://www.oecd-nea.org/rwm/profiles/Korea_report_web.pdf.
[12] M.J. Bell, ORIGEN-The ORNL Isotope Generation and Depletion Code, ORNL-TM4397, 1973.
[13] International Atomic Energy Agency, Management of cladding hulls and fuel hardware, Tech. Report Series No. 258, Vienna, 1985.