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Material Accountancy Measurement Techniques in Dry-Powdered Processing of Nuclear Spent Fuels*

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DISCLAIMER

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ABSTRACT

The paper addresses the development of inductively coupled plasma-mass spectrometry (ICPMS), thermal ionization-mass spectrometry (TIMS), alpha-spectrometry, and gamma spectrometry techniques for in-line analysis of highly irradiated (18 to 64 GWD/T) PWR spent fuels in a dry-powdered processing cycle. The dry-powdered technique for direct elemental and isotopic accountancy assay measurements was implemented without the need for separation of the plutonium, uranium and fission product elements in the bulk powdered process. The analyses allow the determination of fuel burn-up based on the isotopic composition of neodymium and/or cesium. An objective of the program is to develop the ICPMS method for direct fissile nuclear materials accountancy in the dry-powdered processing of spent fuel. The ICPMS measurement system may be applied to the KAERI DUPIC (direct use of spent PWR fuel in CANDU reactors) experiment, and in a near-real-time mode for international safeguards verification and non-proliferation policy concerns.

INTRODUCTION

Proposed alternative fuel cycle concepts involve the recycle of spent fuel without the separation of plutonium, uranium, and fission products. The nonproliferation advantages that are usually associated with the concepts are: (a) the highly radioactive spent fuel presents a barrier to the physical diversion of the nuclear material from the fuel cycle; and (b) there is no need to dissolve and chemically separate the plutonium, uranium, and fission products. Although high radiation levels and non-separation processing may be perceived as barriers to terrorists or other sub-national groups, international proliferation concerns are addressed primarily by the direct material accountancy and verification activities which are the international safeguards measures of fundamental importance. Consequently, the non-separation fuel cycle concepts have to be evaluated on the basis of the impact that the fuel cycle processes may have on direct nuclear materials accountancy. The Argonne experience in measurement analyses of non-separated high burnup spent fuels emphasized the need to develop destructive analyses (DA) methods for direct nuclear material mass accountancy. By direct accountancy is meant direct measurement of the plutonium content in the fuel as compared to the indirect measurement by nondestructive assay

(NDA) of a progeny product (e.g., Cm-244) from which the plutonium content is inferred. The progeny component exacerbates the accuracy and reliability of the plutonium content determination. Safeguards R&D would have to address the implementation of advanced destructive analyses and non-destructive assay measurement methods for flow and inventory operational control in dry bulk powdered processing systems.

The Korea Atomic Energy Research Institute (KAERI) DUPIC fuel cycle concept utilizes dry-bulk processing techniques with no separation of plutonium/uranium/fission products. The dry-powdered process involves the mechanical dismantling, segmenting, and decladding of the PWR fuel elements, and the pulverizing of the U/PuO_2 spent fuel into powder. The spent fuel oxide powder is then subjected to cycles of oxidation/reduction processes, sintered into pellets and configured into CANDU fuel bundles.

Argonne National Laboratory (ANL) investigated the elemental and isotopic measurement methods for highly irradiated spent fuels from the Commonwealth Edison ZION PWR's (18-64 GWD/T) and from the Three Mile Island (TMI) PWR's (45-50 GWD/T). The DA process measurements were performed on aliquot samplings from the bulk dry-powdered spent fuel. The measurement techniques required no separation of the plutonium/uranium/fission products in the dry-powdered fuel element segments.

COMMONWEALTH EDISON ZION-PWR SPENT FUEL ANALYSIS

The determination of the uranium and the plutonium isotopic compositions involved ZION-PWR spent fuel that had spanned five power cycles [Ref. 1]. The analyses were performed on ten samples excised from selected sections of the fuel rods. The uranium oxide fuel rod segments were 7.6 cm in length with an initial composition of 0.03% U-234, 3.31% U-235, and 96.66% U-238. Hot cell operations required the separation of the fuel from the cladding and the comminution of the fuel was accomplished by mechanical impact grinding and blending processes. Each fuel specimen was cut into five pieces approximately 1.5-cm long, and placed into a vial for grinding into powder. The cladding pieces were removed and new pieces added to the same vial, until the entire specimen had been separated from its cladding. The comminution process was continued to ensure complete mixing of the entire specimen (about 51g). Several 200 to 400 mg samplings of the mixed powder were taken for analytical analyses to ensure that the samples taken were representative of the powdered specimen. Sample aliquots were then used for establishing representative homogeneity and measurements of elemental and isotopic nuclear material concentrations. The Cesium-137 isotopic concentration was used to determine fuel burnup levels. Aliquot samples were chemically analyzed in duplicate several times to demonstrate sample homogeneity for uranium and plutonium content with excellent agreement between duplicates.

The measurements from the thermal ionization mass spectrometer, and the alpha- and gamma-spectrometry were systematized to determine the elemental and isotopic compositions of the Zion PWR spent fuels. The plutonium/uranium spent fuel isotopic and assay summary listed in Table I form the basis for material accountancy, needs for fuel management, independent safeguards verification, and non-proliferation concerns. The burnup level of each specimen was

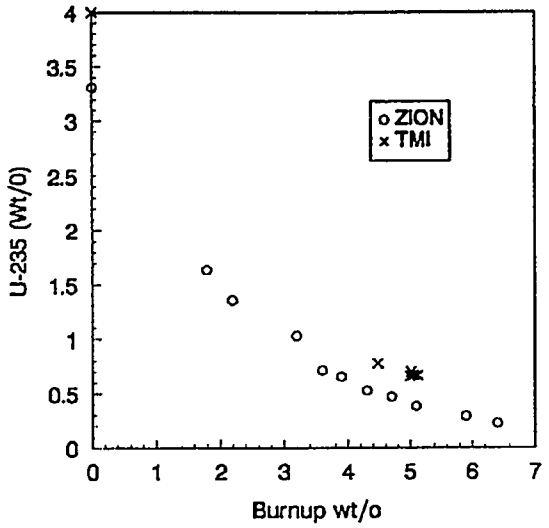
estimated from the concentration measurements of Cs-137 using a fission yield of 6.25%. Good consistency was found between the production and depletion rates of isotopic concentrations and the burnup rates in the 18 to 64 GWD/T range as shown in Figs 1 and 2.

TABLE I. Commonwealth Edison Zion-1 PWR Spent Fuel Isotopic and Assay Summary

Specimen[1]	616-3	616-15	642-3	642-15	699-3	699-13	624-3	624-18	A10-3	A10-8
Burnup Cs (GWD/T)	18	22	32	36	39	43	47	51	59	64
Isotopic (w/o)										
Pu-238	0.561	0.850	1.635	2.042	2.260	2.694	3.120	3.620	4.331	4.823
Pu-239	71.044	66.092	57.124	54.120	52.930	49.911	48.602	46.515	44.773	42.707
Pu-240	19.983	22.384	25.882	26.643	27.078	27.878	27.886	28.110	26.467	26.788
Pu-241	6.472	7.704	9.670	10.163	10.473	10.773	11.269	11.420	12.778	12.721
Pu-242	1.940	2.971	5.689	7.032	7.259	8.784	9.122	10.335	11.650	12.961
Pu (mg/g)	5.424	6.22	7.313	7.957	7.849	8.278	8.609	9.075	9.543	10.036
U-233	<0.0005	<0.0005	0.0020	0.0016	<0.0005	<0.0005	<0.0005	<0.0005	0.0002	<0.0005
U-234	0.0207	0.0188	0.0179	0.0161	0.0159	0.0149	0.0150	0.0137	0.0127	0.0118
U-235	1.6418	1.3630	1.0336	0.7178	0.6597	0.5304	0.4705	0.3826	0.2874	0.2238
U-236	0.3152	0.3636	0.4387	0.4604	0 4674	0.4848	0.4918	0.5009	0.5039	0.5077
U-238	98.022	98.255	98.508	98.804	98.857	98.970	99.023	99.103	99.196	99.257
U (g/g)	0.8554	0.8535	0.8447	0.8362	0.8357	0.8319	0.8302	0.8210	0.8173	0.8134
Pu/U (mg/g)	6.34	7.29	8.66	9.52	9.39	9.95	10.37	11.05	11.68	12.34
Powdered Specimen										
Pu Content (mg)	286.19	328.18	385.18	419.84	414.14	436.77	454.24	478.82	503.52	529.53
U Content (g)	45.13	45.03	44.57	44.12	44.09	43.89	43.80	43.32	43.12	42.92

[1]Commonwealth Edison ZION-1 Initial Enrichment: 3.3 wt% U-235/U

Figure 1. U-235 vs. Burnup in (wt%)



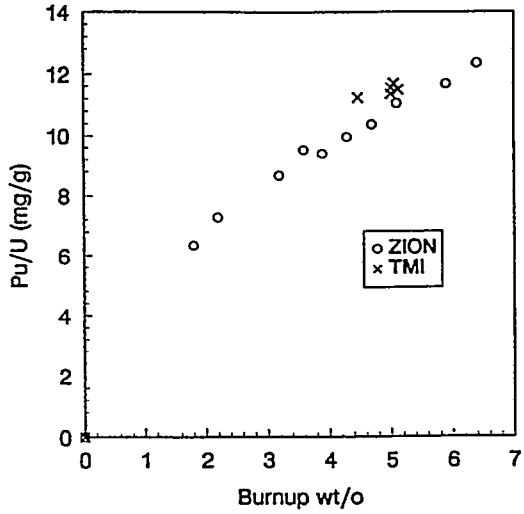


Figure 2. Pu/U (mg/g) vs burnup (wt%)

PROCESS LOSSES (PLUTONIUM/URANIUM RECOVERABILITY)

Although process losses for the dry-powdered operation were not a focus of the analyses, preliminary process losses were estimated by comparing the plutonium content directly measured in the specimen with the plutonium content that should be consistent with burnup. The expected plutonium content was determined from the relationship between the measured Pu/U ratio, the Cs-137 measured atomic fractional burnup, and the fabricator's specification of the pre-irradiated uranium in the specimen (46.51g of uranium). The estimates seem to indicate that the plutonium/uranium recoverability losses from the LWR spent fuel specimens could range from less than 1% to 2% for the dry-powdered technique used in this experiment. The process losses could be in the clad waste (clad-fuel interface interactions), powdered process holdup, and end-effects from the shearing or saw-cutting operations.

THREE MILE ISLAND-PWR SPENT FUEL ANALYSES

The compositions of five segments from the Three Mile Island PWR spent nuclear fuels elements were determined using the dry-powdered technique with no separation of plutonium/uranium/fission products [Ref. 2]. The TMI fuel elements were uranium oxide with an initial composition of 4.0% U-235. The spent fuel analyzed were cross-sections of the clad fuel cut into segments weighing approximately 10 g. The five TMI segments were prepared by separating the fuel completely from the cladding. The separation process was performed using a diamond mortar and a tool steel pestle. The fuel fragments were recovered and further powderized in hardened tool steel vials and ball pestle. New vial and ball pestle were used for each segment to minimize the cross contamination. The powdered fuel was then stored in glass vials and reserved for analysis.

Approximately 0.1 g samples of the powdered segments were diluted to about 50 to 100 ml aliquots and taken through the complete analysis procedure for determining the nuclide concentrations including Nd/Cs for estimating the burnup level. Analyses were performed with ICPMS, gamma-spectrometry (γ-s), and alpha-spectrometry (α-s). Chemical separations were required for those several nuclides that could not be determined directly with the ICPMS due to isobaric interference. Chemical separation of Nd, Pm, Sm, Eu, and Gd were performed using high-performance liquid chromatography (HPLC) with ICPMS functioning as the detector. Actinides were chemically separated using classical radiochemical separation techniques. Table II lists nuclides that were determined and the analytical methodology used.

Results of chemical analyses of the five TMI segments are listed in Table III with concentrations given in units of g/gUO_2. The estimated precision was calculated as the mean of the percent relative standard deviations (%rsd) from replicate analyses of the five dissolved samples. Each replicate analysis was performed on aliquots from the same initial stock dissolution solution in non-consecutive analysis procedures and in most cases on different days. This was done so that the estimated precision took into account the procedure-to-procedure and day-to-day variability of analysis. The level of variability for the measurement of most nuclides is less that the variability between fuel samples. The precision achieved should, therefore, be sufficient to determine if these five samples differ compositionally.

The plutonium/uranium isotopic and assay measurement data are listed in Table IV. The data consistency as a function of burnup determined by the Nd concentration method is included in Figures 1 and 2. The complete analyses of the spent fuel were performed within hours after taking aliquot samplings from the bulk dry-powdered spent fuel segments, giving a near-real-time aspect to the measurement system.

The limited size (1 cm in length) of the TMI segments does not allow estimating the process losses for this experiment. The end-effects introduce uncertainty for material accountancy purposes.

Table II. Nuclides and Analytic Techniques on Sample Aliquots

Nuclide	Technique(s)	Calibration Method(s)	Comments
^{95}Mo	ICP-MS	LR	No isobaric interferences
^{99}Tc	ICP-MS	ES	Negligible isobaric interferences
^{101}Ru	ICP-MS	LR	Negligible isobaric interferences
^{103}Rh	ICP-MS	LR	Negligible isobaric interferences
^{109}Ag	ICP-MS	LR	Negligible isobaric interferences
^{137}Cs	γ-s	ES	
^{143}Nd	ICP-MS	LR, ID	Negligible isobaric interferences
^{145}Nd	ICP-MS	LR, ID	Negligible isobaric interferences
^{148}Nd	HPLC-ICPMS	ID	Isobaric interference with ^{148}Sm
^{147}Sm	HPLC-ICPMS	RD	Isobaric interference with ^{147}Pm
^{149}Sm	ICP-MS	LR, ID	Negligible isobaric interferences
^{150}Sm	ICP-MS	RD	Isobaric interference with ^{150}Nd
^{151}Sm	HPLC-ICPMS	RD	Isobaric interference with ^{151}Eu
^{152}Sm	ICP-MS	LR	Negligible isobaric interferences
^{151}Eu	ICP-MS	LR	Negligible isobaric interferences
^{153}Eu	ICP-MS	LR	Negligible isobaric interferences
^{155}Eu	γ-s	ES	
^{155}Gd	ICP-MS	RD	Isobaric interference with ^{155}Eu
^{234}U	ICP-MS	ID	No isobaric interferences
^{235}U	ICP-MS	ID	No isobaric interferences
^{236}U	ICP-MS	ID	No isobaric interferences
^{238}U	ICP-MS	ID	Negligible isobaric interferences
^{237}Np	ICP-MS	ID	Chemical separation of U from Np
^{238}Pu	α-s	RD, ES	Chemical separation of U from Pu
^{239}Pu	ICP-MS	ID	Chemical separation of U from Pu
^{240}Pu	ICP-MS	ID	No isobaric interferences
^{241}Pu	ICP-MS	ID	Chemical separation of Am from Pu
^{242}Pu	ICP-MS	ID	Chemical separation of Am from Pu
^{241}Am	γ-s	ES	
^{242m}Am	ICP-MS	RD	Chemical separation of Am from Pu
^{243}Am	ICP-MS	ID	Negligible isobaric interferences (^{243}Cm)

LR: linear regression calibration
ID: isotope dilution analysis
ES: external calibration of instrument response
RD: determine isotopic abundance on chemically separated sample and determine concentration compared to nuclide that does not have isobaric interference

Table III. Three Mile Island Spent Fuel Isotopic and Assay Summary
Uranium/Plutonium/Fission Products Measurements (g/g fuel)

Specimen	TMI-H6-1	TMI-H6-2	TMI-H6-3 (top)	TMI-H6-3 (bottom)	TMI-H6-4	% RSD
Burnup (GWD/T)	50.6	50.1	50.2	51.3	44.8	
Mo95	9.88E-04	1.01E-03	9.75E-04	9.14E-04	8.29E-04	1
Tc99	9.59E-04	9.71E-04	9.52E-04	9.37E-04	8.75E-04	2
Ru101	1.03E-03	1.07E-03	1.03E-03	9.31E-04	8.50E-04	2
Rh103	5.49E-04	5.60E-04	5.46E-04	4.98E-04	4.64E-04	2
Ag109	5.3E-05	4.7E-05	4.7E-05	8.4E-05	4.2E-05	5
Cs137	1.56E-03	1.56E-03	1.60E-03	1.55E-03	1.45E-03	4
Nd143	8.46E-04	8.89E-04	8.66E-04	8.68E-04	8.22E-04	3
Nd145	7.79E-04	8.07E-04	7.93E-04	8.15E-04	7.46E-04	3
Nd148	4.88E-04	4.85E-04	4.82E-04	5.08E-04	4.39E-04	6
Sm147	1.74E-04	1.66E-04	1.65E-04	1.66E-04	1.64E-04	5
Sm149	3.38E-06	2.90E-06	2.82E-06	2.64E-06	2.79E-06	5
Sm150	3.32E-04	3.34E-04	3.39E-04	3.29E-04	3.13E-04	5
Sm151	1.11E-05	1.19E-05	1.11E-05	1.14E-05	1.14E-05	7
Sm152	1.17E-04	1.15E-04	1.12E-04	1.14E-04	1.09E-04	1
Eu151	7.8E-07	7.1E-07	6.1E-07	7.7E-07	6.3E-07	15
Eu153	1.51EE-04	1.49EE-04	1.48E-04	1.46E-04	1.41E-04	1
Eu155	1.14E-05	1.17E-05	1.27E-05	1.16E-05	1.11E-05	6
Gd155	4.63E-06	5.83E-06	5.62E-06	6.07E-06	5.04E-06	10
U234	1.70E-04	1.67E-04	1.75E-04	1.68E-04	1.73E-04	1
U235	5.60E-03	5.52E-03	5.82E-03	5.69-E-03	6.64E-03	1
U236	4.88E-03	4.81E-03	4.83E-03	4.85E-03	4.81E-03	1
U238	8.20E-01	8.23E-01	8.17E-01	8.40E-01	8.37E-01	1
Np237	6.14E-04	6.15E-04	6.22E-04	6.21E-04	6.08E-04	1
Pu238	3.14E-04	2.80E-04	2.92E-04	2.29E-04	2.93E-04	7
Pu239	4.74E-03	4.71E-03	4.78E-03	5.01E-03	4.89E-03	3
Pu240	2.47E-03	2.43E-03	2.43E-03	2.59E-03	2.40E-03	3
Pu241	1.20E-03	1.23E-03	1.26E-03	1.28E-03	1.23E-03	3
Pu242	8.19E-04	8.14E-04	7.95E-04	8.40E-04	7.16E-04	3
Am241	2.68E-04	3.03E-04	3.33E-04	2.76E-04	3.11E-04	6
Am242m	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	-
Am243	2.25E-04	2.27E-04	2.17E-04	2.24E-04	1.74E-04	7

Table IV. Three Mile Island Spent Fuel Isotopic and Assay Summary

Specimen[1]	TMI H6-1	TMI H6-2	TMI H6-3 (top)	TMI H6-3 (bottom)	TMI H6-4
Burnup Nd-(GWD/T)	50.6	50.1	50.2	51.3	44.8
Isotopics (w/o)					
Pu-238	3.29	2.96	3.055	2.3	3.07
Pu-239	49.67	49.77	50.016	50.356	51.317
Pu-240	25.88	25.676	25.42	26.032	25.186
Pu-241	12.575	12.99	13.184	12.87	12.908
Pu-242	8.58	8.601	8.319	8.44	7.514
Pu (mg/g)	9.543	9.464	9.557	9.949	9.529
U-234	0.02	0.02	0.021	0.0197	0.02
U-235	0.674	0.6622	0.703	0.669	0.782
U-236	0.587	0.577	0.583	0.570	0.567
U-238	98.724	98.74	98.69	98.74	98.631
U (g/g)	0.8306	0.8335	0.82783	0.85071	0.84862
Pu/U (mg/g)	11.489	11.35	11.545	11.695	11.23
wt. of Powdered Specimen					
(g)	8.16	6.268	6.954	6.481	5.03
Pu Content (mg)	77.4	59.32	66.46	64.48	47.93
U Content (g)	6.736	5.224	5.757	5.513	4.268

[1]TMI initial enrichment: 4 wt% U-235/U.

APPLICABILITY TO THE CANDU/PWR CYCLE (DUPIC)[REF 3]

The direct use of spent PWR fuel in CANDU reactors (DUPIC) fuel cycle research proposed by KAERI, is in the initial phase of experimental verification in cooperation with CANADA, U.S.A., and the IAEA for safeguards. The main objective of the research is to manufacture several DUPIC fuel bundles, including pellets and fuel rods, from spent PWR fuel by only utilizing thermal and mechanical processes, irradiate the DUPIC fuel in HANARO research reactor and perform post irradiation studies to experimentally verify the feasibility of DUPIC. The nuclear materials flow-, inventory, and accountancy measures and suggested measurement locations in the process are included in Figure 3.

The manufacturing program of DUPIC fuels consists of disassembling the spent PWR fuel assemblies at the post irradiation examination facility (PIEF), and the fabrication of several DUPIC fuel bundles, including pellets, mini-elements and fuel rods, at the DUPIC Fuel Development Facility (DFDF). The irradiation of the DUPIC fuel bundles, including pellets and fuel rods would be performed in the HANARO reactor, the examination test in the PIEF/DFDF

after irradiation, and the treatment of the radioactive waste at the RWTF (Radioactive Waste Treatment Facility).

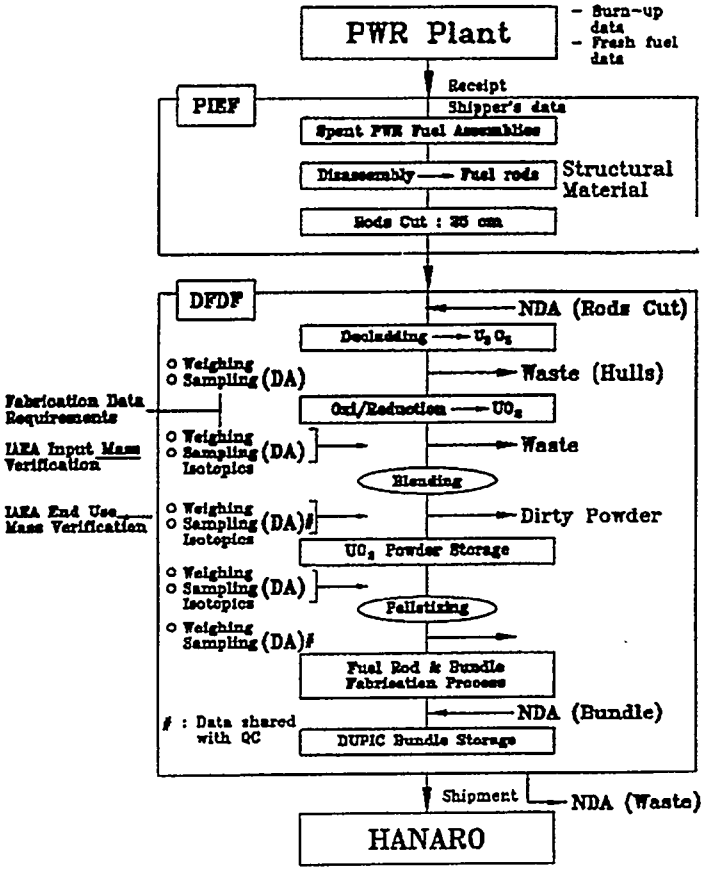


Figure 3. Fabrication and SNM Accountancy Measures in the DUPIC Process

The OREOX (Oxidation and Reduction of Oxide fuel) dry-processing technique was selected for the treatment of spent PWR fuel to produce resinterable powder for fabricating DUPIC pellets. A similar process (AIROX; Atomics International Reduction Oxidation dry processing technology) was developed at Atomics International [Ref. 4]. The pulverization of the UO_2 pellets is effected by slitting the rod-cuts and the oxidation which expands the fuel (U_3O_8 density <UO_2 density) volume. The U_3O_8 is then reduced to UO_2 with hydrogen. Several oxidation/reduction cycles are anticipated. The powder is then blended, pelletized, sintered and finished for fabrication into CANDU fuel bundles.

Although the comminution process differs from the ANL technique, the ANL dry-powdered spent fuel measurement system is directly relevant to the dry-powdered bulk process of the DUPIC fuel cycle. The PWR spent fuel recoverability (process losses and holdup) measurements could be an objective of the DUPIC experiment. The complete isotopic and assay measurements required for fabrication specification needs, independent safeguards verification,

and non-proliferation concerns can be performed within hours after taking aliquot samplings from the bulk-powdered spent fuel, giving a near-real-time aspect to the measurement system.

SUMMARY

The inductively coupled plasma-mass spectrometry (HPLC-ICPMS), thermal ionization-mass spectrometry, alpha-spectrometry, and gamma spectrometry techniques were systematized for in-line analysis of highly irradiated PWR spent fuels in a bulk dry-powdered processing cycle. The technique for direct elemental/isotopic accountancy measurements was implemented without the need for separation of the plutonium, uranium and fission product elements. The program develops the ICPMS method for direct nuclear materials accountancy in dry-powdered processing such as in the KAERI-DUPIC experiment, and in a near-real-time mode for international safeguards verification and non-proliferation policy concerns. The DA direct elemental and isotopic nuclear material accountancy measurements are the fundamental relevant measures that serve to address the stringent fuel fabrication specification requirements in the KAERI-DUPIC experiment.

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