STUDY ON GASEOUS EFFLUENT TREATMENT
FOR DISSOLUTION STEP OF SPENT NUCLEAR FUEL REPROCESSING

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ABSTRACT

Behavior of radioiodine and carbon-14 during spent fuel dissolution was studied in a bench-scale reprocessing test rig where 29 and 44 GWdt^{-1} spent fuels were respectively dissolved. Decontamination factor of AGS (silica-gel impregnated with silver nitrate) column for iodine-129 removal was measured to be more than 36,000. The measurement of iodine-129 profile in the adsorption column showed that the nuclide was effectively trapped by the adsorbent. Measurement of iodine-129 in the dissolver solution after the iodine-stripping operation using NO_2 gas at 363 K, revealed that less than 0.57% of total iodine-129 generated, which was estimated by ORIGEN II calculation, was remained in the dissolver solution. Also, measurement of iodine-129 by an iodine-stripping operation from the dissolver solution using potassium iodate showed that another 2.72% of total iodine-129 precipitated as iodide. In addition, about 70 % of total iodine generated was measured in the AGS columns. Rest of iodine-129 was supposed to adsorb to a HEPA filter and the inner surface of dissolver off-gas lines. Those results on iodine-129 distribution were found to be almost identical to the results obtained in the study using iodine-131 as tracer and the results reported by other works. It was demonstrated that the two-steps iodine-stripping method using potassium iodate could expel additional iodine from the solution, more effectively than iodine-stripping operation using NO_2 gas. Iodine-131 was also detected on the AGS columns at the spent fuel dissolution. Increasing burnup showed larger amount of iodine-131 since amount of curium-244 contained in the spent fuel increased with the burnup. Release of carbon-14 as carbon dioxide during dissolution was found to occur when the release of krypton-85. From the $^{14}CO_2$ measurement, initial nitrogen-14 concentration in the fuel was estimated to be about several ppm, which was within the range reported.

INTRODUCTION

It is indispensable to control and confine radioactive material safely within an area in the nuclear fuel reprocessing process. Radioactive material contained in spent fuel is mostly separated from nuclear material and finally vitrified as highly radioactive waste. However, some elements like radioiodine are volatile and diffusive. It is, therefore, necessary to study the behavior of such radioactive nuclides in the process and to assure the safety margin of the confinement capability.

In the dissolution process, most of volatile species in the spent fuel are released and transferred into the dissolver off-gas (DOG). Among the volatile species, iodine-129 is a long-lived (half-life: 1.57×10^7 years) and hazardous nuclide. The nuclide should strictly be controlled and confined within the process. Confinement of iodine is done by expelling as much as possible from the dissolver solution to the DOG and then by removing the iodine from the DOG using a caustic scrubber and/or adsorbent, which is called iodine-stripping operation. As a result, small portion of iodine-129 remain in the dissolver solution and the insoluble residue. The iodine distribution behavior over the dissolution process is important for the estimation of iodine release into the environment. Studies using beaker-sized equipment have been carried out, and suggested that the iodine distribution behavior was different from that obtained in a reprocessing plant and that the acquiring data on iodine-129 distribution in a larger experimental rig became necessary (1). Adsorbent, such as AGS (Silica-gel impregnated with silver nitrate), will be used in the large reprocessing plant under construction in Japan. It is important to confirm the confinement capability of the iodine removal system employing the adsorbent using actual spent fuel.

The DOG contains carbon-14, which has a half-life of 5.7×10^3 years, is generated from the neutron absorption by nitrogen and oxygen during the irradiation of nuclear fuel. The nitrogen and oxygen are an impurity and a constituent of fuel, respectively. Most of carbon-14 is released as carbon dioxide during the dissolution (2). In the present, carbon-14 is not included in the nuclides that have to be removed in Japan. The nuclide is, however, the largest contributor to the equivalent dose rate of nearby residents (3), and it is important to study behavior of carbon-14 in the dissolution and off-gas treatment processes.

The aim of the present study is to obtain data on the behavior of the above nuclides during dissolution including off-gas treatment and to confirm the confinement capability. This paper describes the results obtained in the dissolution test using spent fuel up to 44 GWdt^{-1} carried out in a bench-scale reprocessing test rig.

EXPERIMENTAL

Dissolution test rig

Figure 1 shows a schematic of experimental reprocessing head-end equipment used in the study. The dissolution process comprised a dissolver, an iodine-stripping tank, a dissolver solution filter, an extraction-feed tank, a condenser, a scrubber, a HEPA filter, iodine adsorbent columns and a blower. The equipment was installed in a heavily shielded concrete cell except for the adsorbent columns and blower, which have been accommodated in a glove box above the cell. The blower is used to maintain the dissolution process under negative pressure for all operating condition.
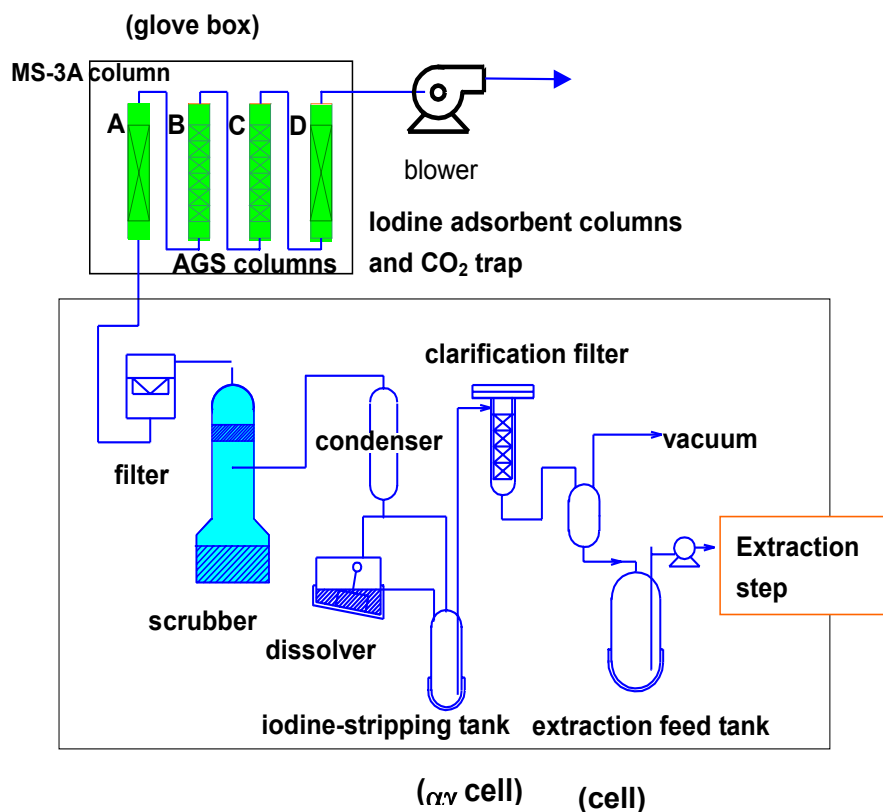

Fig. 1. Schematic diagram of dissolution test rig.

Figure 2 shows a schematic diagram of adsorbent columns used in the present study. The first column (column A) contained MS-3A to remove H_2O in the dissolver off-gas (DOG). Other three columns (Columns B, C and D) were filled with AGS (silica-gel impregnated with silver nitrate). Columns B and C had seven cartridges respectively and each cartridge is filled with 3.4 g of AGS. The AGS was supplied as AC6120 from SÜD CHEMIE AG. More than 98 % of the adsorbent were sized between 1 and 2 mm. The bulk density was 719 kg m^{-3} and its silver content was 12 % in weight. The operating temperature of column A was 333 K and the temperature of other three columns B, C and D were maintained at 423 K.

A Kr monitor and a NO_2 monitor were installed in the same glove box. KOH aqueous solution was used to trap the carbon-14 contained in the off-gas as carbon dioxide. Two KOH traps were connected and used for the measurement of iodine-129 as well as carbon-14 so that the decontamination factor of columns B and C with respect to iodine removal could also be measured.
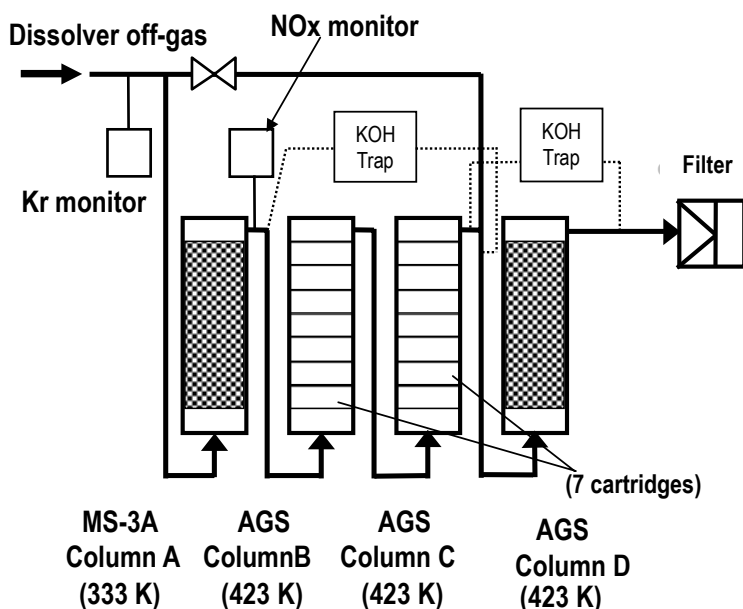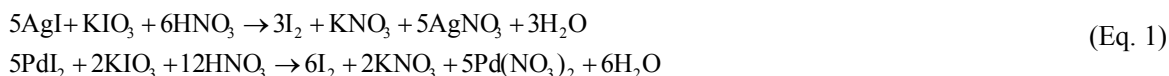

Fig. 2. Iodine adsorption columns.

Analysis

Kr concentration in the DOG was measured using the Kr monitor with a NaI scintillation counter. The NO_2 monitor measured the concentration of NO_2 in the DOG. The amount of iodine-129 on each cartridge and the amount of the nuclide in the KOH trap were measured with a Ge detector for low-energy gamma ray (4). The distribution of the nuclide over the dissolution process and DOG treatment system was measured as follows. Iodine-129 in dissolver solution was determined using a method shown by Castleman et al. (5). Iodine remained as precipitates (AgI and PdI_2) in the residues was recovered by the two-steps iodine-stripping method developed by Sakurai et al. (6) which employs KIO_3. The precipitates can be decomposed by the below reactions and the iodine is released into DOG and trapped by the adsorbent.

$$5AgI + KIO_3 + 6HNO_3 \rightarrow 3I_2 + KNO_3 + 5AgNO_3 + 3H_2O$$
$$5PdI_2 + 2KIO_3 + 12HNO_3 \rightarrow 6I_2 + 2KNO_3 + 5Pd(NO_3)_2 + 6H_2O$$

(Eq. 1)

The amount of carbon-14 trapped from the DOG by the KOH aqueous solution was determined by a liquid scintillation counter. Other iodine species such as iodine-131 generated from curium-244 and other nuclides, if exists, were captured by the AGS columns and were detected by the gamma spectrometry.

Experimental condition

The present study used about 1.0 kg of PWR spent fuel (29 GWdt[-1], cooling time: about 17 years) and about 1.2 kg of PWR spent fuel (44 GWdt[-1], cooling time: about 12.3 years), which had respectively been cut into short pieces with a length of 40 mm before transferred into the cell. Table I lists up the dissolution conditions employed in the present study. Dissolution was carried out three times and about 300 to 400 g of the spent fuel was used in one batch of dissolution. 4 to 5 mol l^{-1} of nitric acid was used in the dissolution. The procedure of the dissolution was: 1) prepare HNO_3 with designated acidity and volume in the dissolver, 2) put the spent fuel into the dissolver, 3) start dissolution (time = 0) by elevating the temperature of the dissolver from ambient temperature to 373 – 374 K and 4) hold the temperature for designated dissolution period.

After the dissolution, all the resultant dissolver solution was transferred to the iodine-stripping tank where remaining iodine in the solution was stripped. Table II summarizes the operations of iodine stripping used in the present study. In the 29 GWdt[-1] spent fuel dissolution, two-steps operation was employed. In the first-step operation, KIO_3 is added to the dissolver solution being heated up at 373 K to decompose the iodine precipitates according to the reaction 1, and then the solution is maintained at the same temperature for two hours. In the second-step operation, 50 % NO_2 gas is introduced and maintained at 373 K for two hours. In the 44 GWdt[-1] spent fuel dissolution, as shown in the table, iodine-stripping using NO_2 gas was firstly used, which was normal procedure employed in a reprocessing plant. In addition, the two-steps method was used as well, in order to enhance the effect of the method and to measure the amount of iodine remained as precipitates. In all experiments the flow rate of DOG was maintained at approximately 0.4 Nm^3h^{-1}.

Table I. Dissolution conditions

Burn-up [GWd/t]	Run No	U element [g]	HNO_3 Concentration [mol l^{-1}] (volume [l])		Temperature [K]	Dissolution time [min]
29	SFD2-1	372.66	5.21	(1.57)	373	220
29	SFD2-2	283.95	3.98	(1.44)	373	160
29	SFD2-3	274.36	4.06	(1.29)	373	140
44	SFD3-1	325.72	5.26	(1.59)	373	220
44	SFD3-2	325.54	4.68	(1.64)	373	220
44	SFD3-3	342.74	3.93	(1.61)	373	220

Table II. Iodine-stripping operations employed

Burn-up [GWd/t]	Iodine-stripping operations	
29	KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min	-
44	1) Normal iodine-stripping method NO_2 gas, 363 K, 120 min	2) Two-steps iodine-stripping method KIO_3, 373 K, 120 min + NO_2 gas, 373 K, 120 min

RESULTS AND DISCUSSION

Radioiodine captured by AGS columns

Profile of iodine-129 captured in the AGS column was illustrated in Fig. 3, which was obtained in the dissolution of 44 GWdt^{-1} spent fuel. Most of the iodine was captured in the first and second cartridges in the upstream AGS column (Column B). The amount of iodine-129 in each cartridge in Column C was found to decrease down to about 10 Bq, which was near detection limit. The decontamination factor of the AGS columns (B and C) used in the study was measured to be more than 36,000 by the analysis of KOH aqueous solution traps. It was demonstrated that the radioiodine was effectively trapped by the adsorbent under the dissolution of actual spent fuel. Table III shows the amount of iodine-129 adsorbed on the columns (A, B, C and D).
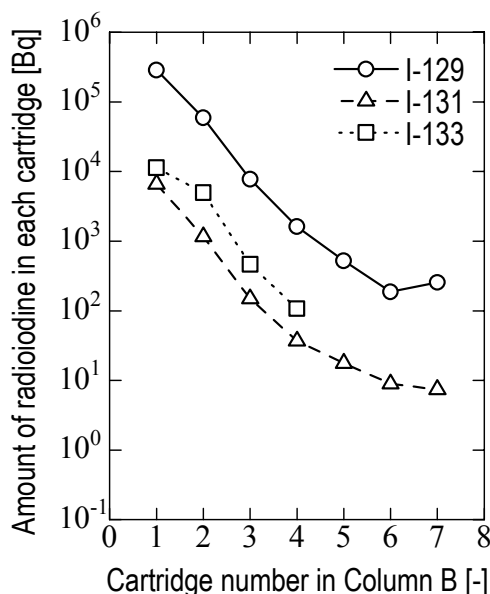

Fig. 3. Radioiodine profiles in AGS column B (SFD3-1).

Iodine-131 and iodine-133 were also detected and plotted in Fig. 3. Those nuclides are short-lived and generated from spontaneous fission of nuclide, mainly curium-244 and also from neutron-absorption fission. The gradient of the profiles should be same as the profile of iodine-129 because the AGS adsorbent captures mainly molecular iodine.

Table III shows the amount of iodine-131 adsorbed on the columns (A, B, C and D) and the ratio of iodine-131 amount captured by the adsorption columns to the amount of iodine-129. The average ratio in the dissolution of 29 GWdt^{-1} spent fuel is about 0.005, which is lower than the ratio obtained in the dissolution of 44 GWdt^{-1}: 0.0285. The ratio (^{131}I/^{129}I) of 44 GWdt^{-1} was, therefore, 5.7 times larger than the ratio of 29 GWdt^{-1}. The ORIGEN calculation showed that the burnup of 29 GWdt^{-1} and 44 GWdt^{-1} generated 6.43 grams and 60.2 grams of curium-244 per 1 tons of uranium, respectively, while 155.9 grams and 246.5 grams of iodine-129 are respectively generated. Assuming that the fraction of curium-244 fissioned was same in both spent fuel dissolution, the ratio of iodine-131 (=curium-244) to iodine-129 was respectively calculated to be 0.0412 for 29 GWdt^{-1} spent fuel and 0.244 for 44 GWdt^{-1} spent fuel. . This ratio (^{131}I/^{129}I) of 44 GWdt^{-1} by ORIGEN is about 5.9 times larger than the ratio (^{131}I/^{129}I) of 29 GWdt^{-1} by ORIGEN, which compare well with the above measured result (= about 5.7). This suggests that the increase in the ratio ^{131}I/^{129}I was due to the increase of burnup of spent fuel used.

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Table III. Amount of iodine-129 and iodine-131 adsorbed by the columns

Burnup [GWdt^{-1}]	Nuclide and ratio	Dissolution No.1 [x10^5 Bq]	Dissolution No.2 [x10^5 Bq]	Dissolution No.3 [x10^5 Bq]	Iodine stripping No.1 [x10^5 Bq]	Iodine stripping No.2 [x10^5 Bq]	Total amount iodine-129 adsorbed by columns [x10^5 Bq]
29	Iodine-129	2.478	1.935	1.867	0.553	-	6.834
	Iodine-131	0.0147	0.00947	0.00779	0.0284	-	0.0603
	^{131}I/^{129}I	0.0059	0.0049	0.0042	0.0514	-	-
44	Iodine-129	3.706	3.498	3.624	1.580	0.3999	12.81
	Iodine-131	0.083	0.103	0.122	0.141	0.141	0.590
	Ratio (^{131}I/^{129}I)	0.0224	0.0294	0.0337	0.0892	0.3525	-

In the table, it can be seen that the ratio (^{131}I/^{129}I) obtained in iodine-stripping operation is larger than the case of dissolution. Iodine-131 amount in the spent fuel would be at an equilibrium state before dissolution and most of the iodine-131 as well as iodine-129 expelled into the DOG in the dissolution operation. The increase in the ratio (^{131}I/^{129}I) is supposed to be due to additional generation of iodine-131 from curium-244 and other fissile nuclides in dissolver solution during the interval between the dissolution and iodine-stripping operation.

Iodine-129 distribution over the dissolution process and off-gas treatment system

Table IV shows iodine distribution over the dissolution process and off-gas treatment system, together with the result by other previous works. Measurement of iodine-129 in the dissolver solution showed that less than 0.57% of total iodine-129 generated, which was estimated by ORIGEN II calculation, was remained in the solution. Also, measurement of iodine-129 by an iodine-stripping operation from the dissolver solution using KIO$_3$ showed that another 2.72% of total iodine-129 existed as precipitates in the residue phase. Also, about 70 % of total iodine generated was measured in the AGS columns. Rest of iodine-129 was supposed to adsorb to the HEPA filter and the inner surface of dissolver off-gas lines. It was also shown that the two-steps iodine-stripping method using potassium iodate could expel additional iodine from the solution, more effectively than iodine-stripping operation using NO$_2$ gas.

Table IV. Iodine distribution over the dissolution process and DOG treatment system

Authors		Boukis and Henrich (1991)	Herrmann et al. (1993)	This study	
Equipment size		Laboratory scale	Plant	Bench scale	
Burnups of spent fuel used		45 GWdt^{-1}	Spent fuel up to 40 GWdt^{-1}	I-131 tracer with fuel of U and FP simulating 45 GWdt^{-1} spent fuel	44 GWdt^{-1}
Distributions	Off-gas	Balance	Balance	Balance (74 % of total I-129 on columns)	Balance (70 % of total I-129 on columns)
	Dissolver solution	0.52 %	<5 % (2 to 3 % for high burnup spent fuel)	0.37 %	< 0.57 %
	Residue	0.18 %	1 %	1.49 %	≤ 2.72 %

As shown in Table IV the results in the present study were found to be almost identical to the results obtained in the previous study using the same test rig and iodine-131 as tracer (7). The present study obtained comparable results to the study by Boukis and Henrich (8). The fraction of iodine in the residue was, however, somewhat higher. The fraction of 0.18 % was determined from the difference in the concentration measured before and after filtration operation using a 1-μm filter (8). This filtration might not be able to trap fine precipitates including silver iodide and palladium iodide, which are included as iodine in the residue in the present study. This may be the cause of the difference in the fraction for iodine-129 in residue. Also, the dissolution condition affects the amount of precipitates like zirconium molybdate. Their study employed 7.5 mol l^{-1} HNO_3 and the present study used 4 to 5 mol l^{-1} HNO_3 for dissolution. The amount of precipitate was reportedly increased with lower acidity (9). So, the amount of precipitates in Boukis and Henrich study might be smaller than that in the present study, which resulted in smaller amount of iodine trapped in residue as a whole. Herrmann et al. measured higher fraction of iodine in the dissolver solution in a larger dissolver (10). Sakurai et al. suggested that the iodine remained as precipitate would increase in a large dissolver (1). Further studies would be necessary to explain the difference in the distribution behavior of iodine-129, although the difference is not significantly large.

Carbon-14 behavior

Amount of carbon-14 released as carbon dioxide during dissolution was measured. From the measurement results and ORIGEN II calculation for 29 and 44 GWd/t spent fuels, initial concentration of nitrogen-14 in fuels as impurity was estimated to be several ppm, which could compare well with the reported concentration of nitrogen in other PWR fresh fuels ranging between 5 and 20 ppm (11).

Fig. 4 shows beta radioactivity of carbon-14 measured in the sample as a function of time, which was obtained in the dissolution of 29 GWd/t spent fuel. This Kr-monitor reading was also plotted in the same figure. It was found that release of carbon-14 as CO_2 into dissolver off-gas occurred when gaseous radionuclides such as Kr-85 were released. It seems that the peak of the $^{14}CO_2$ release delayed by about 10 minutes in the case of SFD2-2 where the concentration of nitric acid was low. Chemical form of the carbon in spent fuel is not well known. It may present as free element or as traces of metal carbide (12). $^{14}CO_2$ in spent fuel is produced by oxidation of carbon-14 during spent fuel dissolution. Further kinetic study on the CO_2 release from dissolver solution is necessary.

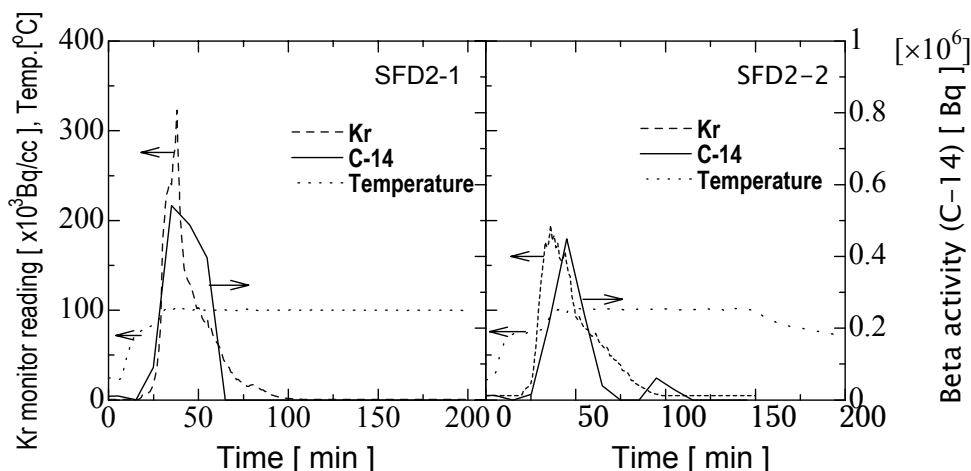**Fig. 4.   Change in Kr-monitor reading and carbon-14 released during dissolution (29 GWdt^{-1} spent fuel dissolution. SFD2-1: 5.21 mol l^{-1} HNO_3, SFD2-2: 3.98 mol l^{-1} HNO_3).**

CONCLUDING REMARKS

Behavior of radioiodine and carbon-14 during spent fuel dissolution was studied in a bench-scale reprocessing test rig where 29 and 44 GWdt^{-1} spent fuels were respectively dissolved.

The decontamination factor of the AGS (silica-gel impregnated with silver nitrate) columns used in the study for the iodine removal was found to be more than 36,000. It was demonstrated that the radioiodine was effectively confined by the adsorbent under the dissolution of actual spent fuel.

The fraction of iodine-129 remained in dissolver solution was measured to be less than 0.57 % of total generated I-129. Another 2.72 % was detected as iodine in precipitates. In addition, about 70 % of total iodine generated was measured in the AGS columns. Rest of iodine-129 was supposed to adsorb to the HEPA filter and the inner surface of dissolver off-gas lines. It was demonstrated that the two-steps iodine-stripping method using potassium iodate could expel additional iodine from the solution, more effectively than iodine-stripping operation using NO_2 gas.

The iodine-129 distribution data compared well with the results previously obtained using simulated spent fuel with iodine-131 tracer. Also, the results were similar to those obtained in other previous works using equipment with different size. Further study was, however, necessary to explain the small difference in the distribution behavior of iodine-129 reported by the other previous works.

Iodine-131 and iodine-133 generated from spontaneous fission and neutron adsorption fission were detected in AGS columns in the dissolution tests. Higher burnup of spent fuel generated larger amounts of iodine-131.

It was found that release of C-14 as $^{14}CO_2$ into dissolver off-gas occurred when gaseous radionuclides such as Kr-85 were released. From the measurement of $^{14}CO_2$, concentration of Nitrogen-14 initially contained in fuels as impurity was estimated to be several ppm for 29 and 44 GWdt^{-1} spent fuels, which could compare well with the reported concentration of nitrogen in other PWR fresh fuels.

ACKNOWLEDGEMENT

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