

## Measurement of the Gap and Grain Boundary Inventories of Cs, Sr and I in Domestic Used PWR Fuels

### 국내 PWR 사용후핵연료에서 세슘, 스트론튬과 요오드의 갭 및 입계 재고량 측정

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#### Abstract

Inventories of soluble elements in the gap and grain boundaries of domestic used PWR fuel pellets were measured to estimate the quantities of radionuclides that are liable to be rapidly released into the groundwater of a disposal site. The gap inventory of cesium for the pellets in the used fuel with a burn-up range of 45 to 66 GWD/MTU showed 0.85 to 1.7% of its total inventory, which was close to 1/6 to 1/3 of the fission gas release fraction (FGRF). However, the amounts of cesium released from the gaps of the pellets below 40 GWD/MTU of a burn-up and less than 1% FGRF were so erratic that the gap inventory could not be defined by its FGRF. Strontium inventories in the gap and grain boundaries of the pellets in the same rod were not significantly varied, and the iodine inventory in the gap of the used PWR fuels was estimated to be less than or the same as the FGRF.

**Key words** : Soluble Nuclides, Used fuel, Gap, Grain boundary, Inventory

#### 요 약

처분장에서 지하수로 쉽게 유출될 수 있는 방사성 핵종들의 양을 예측하기 위하여 국내 PWR 사용후핵연료 펠렛들의 갭(gap) 및 입계에 있는 용해성 원소들의 재고량을 측정하였다. 연소도가 45~66 GWD/MTU를 갖는 연료봉에서 얻은 펠렛들에서 세슘의 갭 재고량이 0.85~1.7%로 나

타났으며, 이는 핵분열 생성기체 유출률의 1/6~1/3에 해당하였다. 그러나 핵분열 생성기체 유출률이 1%이하인 연료봉에서 취한 40 GWD/MTU이하의 연소도를 갖는 펠렛들의 경우, 세슘의 갭 재고량들을 핵분열 생성기체 유출률과 연관시키기는 곤란하였다. 갭 및 입계내 스트론튬의 재고량은 동일 연료봉내 펠렛에서는 크게 다르지 않았으며, 요오드의 갭 재고량은 핵분열 생성기체 유출률보다 작거나 유사한 값을 갖는 것으로 평가되었다.

**중심단어**: 용해성 핵종, 사용후핵연료, 갭, 입계, 재고량

## I. Introduction

To estimate the amount of radionuclides to be released from a used fuel to an underground repository system, their heterogeneous distribution and chemical characteristics must be considered. Actinides and many fission products, e.g., lanthanides, form a solid solution with  $UO_2$  under reactor operating conditions, and those solid solutions are uniformly distributed throughout the fuel. However, relatively insoluble nuclides in the  $UO_2$  lattice migrate and accumulate on free surfaces such as the voids in the  $UO_2$  matrix, the fuel-sheath gap and the grain boundaries of a fuel[1].

Because of their chemical properties, water-soluble nuclides such as cesium, strontium and iodine are released easily when they are defective and in contact with groundwater, while most of the actinides and lanthanides are released very slowly due to their low solubility[1]. Therefore, according to the extent of their contact with water, the release of soluble nuclides from a used fuel could be divided into three regions: the pellet to clad gap including the dish volume and cracks of the pellets, the grain boundaries of the fuel pellets, and the  $UO_2$  matrix[2].

The cesium in the gap and grain boundaries of a fuel could be released for hundreds of years or more when the fuel pellet is exposed to water[3].

Then the dissolution rate of cesium in the fuel matrix is dependent on that of uranium oxide[2].

For CANDU fuel, the gap inventories of cesium and iodine depend on the irradiation history of the fuel, in particular the linear heat power rate (LHPR). Stroes-Gascoyne et al.[4] insist that the ratios of Cs-137/Xe and I-129/Xe in a gap inventory are about 0.2 for a low LHPR fuel and approach 1.0 for a high LHPR fuel. However, a direct correlation of the FGRF to the cesium inventories is difficult to define for PWR fuels because the gap inventories of cesium show considerably different tendency compared to the other used fuels with a similar FGRF[5].

In this study, the inventories of cesium, strontium and iodine in the gap and grain boundary were measured for four used PWR fuels with different burn-ups and their FGRF rates were compared.

## II. Experiment

Triplicate specimens (Table 1) for measurement of the gap inventory were prepared by cutting used PWR fuel rods to a 2 mm thickness with a diamond blade without cooling water and weighed. Fuel pellet specimen was prepared through a decladding process. The fuel and cladding were put into a bottle filled with 100 ml of distilled water and put under the hot cell

operation conditions. After a soaking of the fuel and cladding, 5 ml of the solutions were sampled with longer than 7 days of time intervals and filtered through 0.2  $\mu\text{m}$  filters to remove the uranium particles.

Two types of fuel powder, sawdust produced during the cutting of fuel rod SFR1 and crushed powder produced by crushing the specimens after the gap inventory experiment, were used for a measurement of the nuclide's inventories in the grain boundaries. In the case of the sawdust, the inventory of the nuclides in the grain boundaries was calculated from the instant release fraction (IRF) which is the combined inventories of the gap and the grain boundaries. The powder was leached in 50 ml of 0.1M HCl for about 20 minutes and the solution was sampled by filtering it with a 0.2 $\mu\text{m}$  filter. The solution was replaced with a fresh acid and subsequently sampled.

The concentrations of uranium and cesium in the sample solutions were analyzed by using an inductively coupled plasma - mass spectrometer (ICP-MS) and -spectrometer, respectively. The activity of strontium was measured by using a liquid scintillation counter(LSC) after removing the cesium with ammonium molybdophosphate and a separation of the strontium with SR-resin[6]. The concentration of iodine was measured by a neutron activation analysis method after a separation of the iodine by using the Stroes-Gascoyne's method[7].

### III. Results and Discussion

The measured inventories of the cesium, strontium and iodine in the gap and grain boundaries of four used PWR fuels are summarized in Table 2. Total amounts of the respective nuclides in the specimens were

**Table 1. Characteristics of the used PWR fuels for this experiment.**

Fuel	SFR1	SFR2	SFR3-a*	SFR3-b*
Burnup (GWD/MTU)	39.6	35.0	45.8	65.9
Initial Enrichment (wt.%)	3.2	3.2	4.2	4.2
Xenon release of fuel rod (%)	0.50	0.22	5.0	5.0
Cooling time (days)	5353	7462	909	909

\* SFR3-a and SFR3-b specimens were prepared from the periphery and the center of a SFR3 fuel rod, respectively.

**Table 2. Measured inventories of Cs, Sr and I in the gap and grain boundaries.**

Fuel	Gap inventory (% of total inventory)			Grain-boundaries inventories (% of total inventory)		
	Cs	Sr	I	Cs	Sr	I
SFR1	0.25 $\pm$ 0.05	0.03 $\pm$ 0.01	< 0.2	1.3~2.7	0.3 $\pm$ 0.1	< 0.2
SFR2	0.65 $\pm$ 0.1	0.03 $\pm$ 0.01	< 0.2	0.20 $\pm$ 0.05	0.09 $\pm$ 0.02	< 0.2
SFR3-a	0.85 $\pm$ 0.1	0.21 $\pm$ 0.1	2.2 $\pm$ 1.0	0.20 $\pm$ 0.05	0.06 $\pm$ 0.02	< 0.4
SFR3-b	1.7 $\pm$ 0.2	0.21 $\pm$ 0.1	3.6 $\pm$ 1.5	0.20 $\pm$ 0.05	0.06 $\pm$ 0.02	< 0.4

calculated by using the ORIGEN II code. As the trace amount of nuclides in the uranium matrix would have been dissolved in the solution, especially in 0.1M HCl, their inventories in the gap and grain boundaries were calculated by subtracting the dissolved fraction of the uranium.

Figure 1 shows the cumulative fraction of cesium released into the distilled water as a function of the time. From this figure, it reveals that the gap inventory of cesium in the SFR2 fuel was approximately 0.65%, which is similar to the fraction of cesium released from the J44H08 PWR fuel for 500 days in an Ar-atmosphere[8]. However, this value is unexpectedly greater than the FGRF of SFR2 and the gap inventory of cesium in SFR1 whose burn-up is a little higher than that of SFR2. Gray et al,[5] reported that gap inventories of cesium is greater than the

FGRF of xenon for used PWR fuels with less than a 1% FGRF.

The gap inventories of cesium for SFR3-a and SFR3-b from Figure 1 are estimated to be 0.85 and 1.7 %, respectively. These results are especially useful for establishing disposal design criteria of used fuel because their burn-up and initial enrichment are similar to the Korean reference PWR fuels for a disposal, having a burn-up of 45 GWD/MTU with 4.0% of initial enrichment and a burn-up of 55 GWD/MTU with 4.5% of initial enrichment[9], and the gap inventories of fuels with higher than 50 GWD/MTU of burn-up have rarely been reported. The gap inventories of SFR3-a and SFR3-b indicate that the SFR3rod has a gap inventory of cesium in the range of 1/6 to 1/3 of the FGRF and that the cesium is segregated more in the center than the periphery of the rod. Our results are compared with foreign results[5] as shown in Figure 2, which indicates a gap inventory of cesium is in the range of 1/6 to 1/3 of the FGRF at the pellets with more than 5% of FGRF. Johnson and et al.[10] also reported that the gap inventory of cesium is about 1/4 of the FGRF for fuels with more than 7% of FGRF. However, the inventories of cesium in the grain

boundaries of SFR3-a and SFR3-b were similar to each other.

Though the amount of cesium released from the sawdust of SFR1 in 0.1M HCl increased from 3.76 to 5.53% of the total cesium in the sample with the lapse of the dissolving time, it can be seen in Figure 3 that the IRF of cesium did not significantly change in the range of 2.9~3.0% when the fractions of cesium within the uranium matrix were subtracted. It means that the total amount of cesium in the gap and grain boundaries was dissolved in the 0.1M HCl

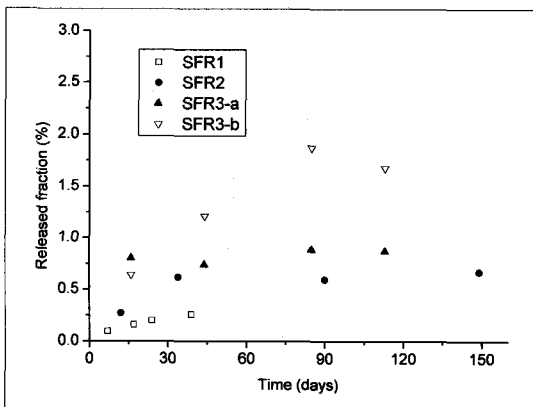


Fig. 1. Cumulated fraction of the cesium released from the used fuels in distilled water.

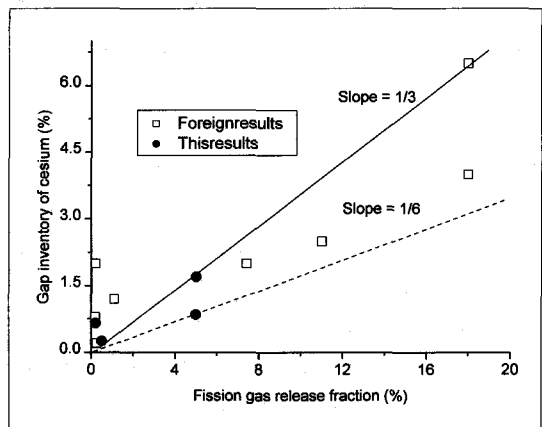


Fig. 2. Gap inventory of the cesium as a function of fission gas release fraction. This results(●) and foreign results(□) were obtained from this study and Gray's study[5], respectively.

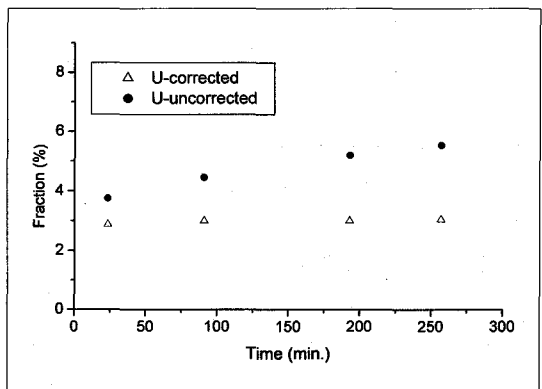


Fig. 3. Fraction of the cesium released into 0.1M HCl from the SFR1 sawdust. U-corrected and U-uncorrected data obtained by subtracting and without subtracting the dissolved fractions of the uranium from those of cesium, respectively.

within 20 minutes and then cesium in the uranium matrix was dissolved congruently with  $\text{UO}_2$ .

Even though the inventories of nuclides in the grain boundaries obtained from the sawdust of SFR1 and the crushed powder of the other fuels can not be compared directly because the fuels used for the experiment were not the same ones, a rough comparison could be drawn that the inventories released from the sawdust are greater than those from the crushed powder. To clarify the difference between the two results, further research is necessary.

The inventories of strontium in the gap and grain boundaries are also given in Table 2. All the data on strontium obtained in this experiment are below 0.4% and similar results can be found in other papers[3,10]. Though strontium has no mobility within a fuel matrix at a reactor operation temperature, a small fraction of Sr-90 at the grain boundaries is produced by the mobile Br, Kr and Rb precursors[3]. However, the fractions of strontium in the gap of SFR3-a and SFR3-b were almost same despite of the difference between the total inventories of strontium for the two pellets. Such results could be explained by the fact that the mobile precursors, even Kr, might remain locally in a matrix and would not diffuse throughout the rod.

For the analysis of iodine, a neutron activation analysis method was used because the activity of I-129 in the sample solutions was too low to be measured directly by a  $\beta$ -count detector. Even though the gap inventories of SFR3-a and SFR3-b showed a considerable discrepancies, the inventory of iodine in the gap of the used PWR fuels was estimated to be less than or similar to the FGRF[10].

#### IV. Conclusions

From the comparison of the gap inventories of the two pellets obtained from the same fuel rod with 5% of FGRF, it can be concluded that the cesium inventory of a high burn-up pellet is greater than that of a low burn-up pellet, and that those results correspond to  $1/6 \sim 1/3$  of the FGRF. The inventories of strontium in the gap and grain boundaries of those two pellets were almost same, which suggests that the mobile precursors of strontium are not diffused throughout the rod. The gap inventory of cesium did not show the strong correlation with the FGRF for the pellets with less than a 1% FRG.

When sawdust and crushed powder were used in measuring the inventory of the grain boundaries, the inventories of the cesium and strontium released from the sawdust were greater than those from the crushed powder in spite of the dissolved uranium fraction compensation.

Iodine inventory in the gap of the used PWR fuels was estimated to be less than or similar to the FGRF.

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