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ARTICLE

Feasibility of Fluorination Treatment Method for Management of Wastes Generated from Fuel Debris Retrieval

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The feasibility and effectiveness of fluorination treatment method for reasonable management of wastes generated from fuel debris retrieval at Fukushima-daiichi nuclear power station was investigated experimentally. The simulated fuel debris assuming the molten core-concrete interaction (MCCI) debris was prepared, and the fluorination behavior of each element in the simulated fuel debris was evaluated. The results indicated that 90 % of the uranium was volatilized by fluorination, and the waste after fluorination treatment can be partitioned into the nuclear fuel material, the radioactive waste, and the silica waste.

KEYWORDS: waste management, fluorination, uranium, debris, MCCI

I. Introduction

The fluoride volatility method has been used conventionally in the nuclear industry field. Since the nuclear fuel material such as uranium and plutonium form hexafluoride by fluorination reaction, fluorination is useful for various chemical processes such as separation and enrichment.

Large amounts of the waste are expected to be generated during fuel debris retrieval at Fukushima-daiichi nuclear power station (1F). The fuel debris contains fuel materials and fission products (FPs), therefore, the radiation shielding and the criticality safety control is necessary for the storage of the waste. Additionally, because the waste is assumed to be a heterogeneous material, it is concerned that conservative safety control would be necessary, and the burdens of the storage would be increased.

The fluorination treatment method was investigated for reasonable management of the waste generated from fuel debris retrieval.[1,2] The process flow of the fluorination treatment method is shown in **Fig. 1**. The waste reacts with F_2 gas, creating volatilized uranium and plutonium. The gaseous phase contains F_2, O_2, and other volatilized fluorides, therefore the volatilized uranium and plutonium are selectively recovered from the other gaseous phase by the condensation method. The recovered uranium and plutonium are converted into chemically stable oxide and stored as the nuclear fuel material. On the other hand, the fluorination residue in the fluorination process is also converted into oxide and stored as the radioactive waste. Because this radioactive waste is separated from uranium and plutonium, the criticality safety control would be simplified.

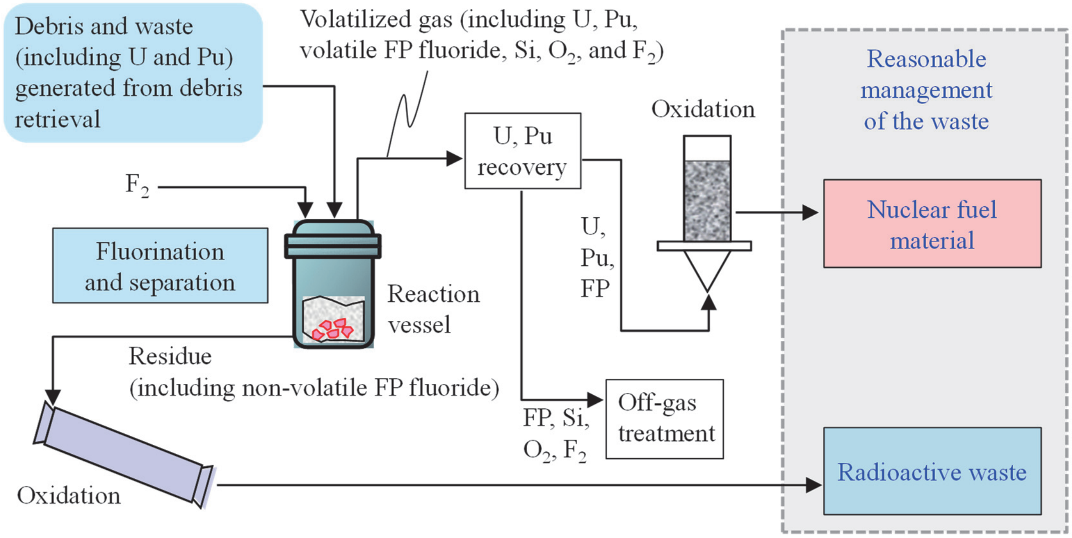

Fig. 1 Process flow of the fluorination treatment method

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In this research, fluorination experiment was carried out on the simulated fuel debris to evaluate its fluorination behavior. In previous research, the simulated material of fuel debris was prepared assuming it remained in reactor pressure vessel (RPV), and its fluorination behavior was evaluated.[1)] In this research, the simulated fuel debris was assumed to be MCCI products, that is, the fuel debris have dropped from RPV and reacted with concrete at the bottom of primary containment vessel (PCV).

Additionally, assuming the application of the fluorination treatment method for the waste containing fuel debris recovered from 1F, the separation behavior and the effectiveness was evaluated.

II. Experimental

1. Fluorination Experiment

The configuration of the experimental apparatus is shown in **Fig. 2**. The sample for fluorination, the simulated fuel debris prepared in this research, was placed on the sample boat, and enclosed in the reactor vessel (inner volume of about 2 L). The sample boat and the reactor vessel were made of nickel. F_2 gas for fluorination was fed into the reactor vessel, and Ar gas was fed to the observation window (made by CaF_2) to prevent contact with F_2 gas. A thermocouple (TC) was used to monitor temperature variations at the bottom of the boat holder due to the exothermic reaction during the fluorination. The gaseous stream was fed to the cold trap (CT) at -80ºC (dry ice - ethanol bath), and volatilized uranium was recovered by condensation. Off gas was disposed after being treated.

The fluorination conditions are shown in **Table 1**. F_2 and Ar were supplied at a constant flow rate. The reaction vessel was heated in an electric furnace until the temperature of the lower part of the boat holder reached 600℃. The inner pressure was kept at 100 kPa at the exit of reactor vessel. Fluorination period, which corresponds to F_2 flowing time, varied between 65 and 150 minutes depending on the experiment run. The F_2 flow was stopped when the temperature of the bottom of boat holder became constant.

After the experiment, the fluorination residues on the sample boat and the condensed material in the cold trap were recovered for analysis. The fluorination residue was analyzed by X-ray diffraction method (XRD) and scanning electron microscope - energy dispersive X-ray spectroscopy (SEM-EDS) and their chemical form and composition were evaluated.

To evaluate the volatility ratio of each element, the fluorination residue and the condensed material were dissolved into a liquid solution, and its chemical composition evaluated using inductively coupled plasma - atomic emission spectroscopy (ICP-AES) and inductively coupled plasma - mass spectroscopy (ICP-MS). In the case that the residue was not completed dissolved, the remaining residue was collected by filtration, dried, and analyzed by SEM-EDS. In particular, the presence or not of remaining U in the residue was confirmed by the analysis.

The volatilization ratio of each element was evaluated by the following Eq. (1).

$$(1 - [\text{Amount in the fluorination residue}] / [\text{Amount in the initial sample}]) \times 100 \qquad (1)$$

This is based on the idea that everything that did not remain in the fluorination residue was volatilized. On the other hand, for the case of sample-B, which is explained below, that the remaining metal residue and its chemical composition could not evaluated, the volatility ratio was evaluated by the following Eq. (2).

$$[\text{Amount in the recovered material in CT}] / [\text{Amount in the initial sample}] \times 100 \qquad (2)$$

This is based on the idea that the recovered material in CT was the volatilized material by fluorination.

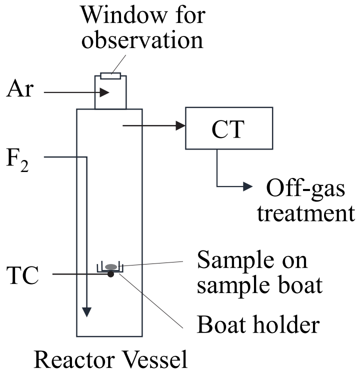


Fig. 2 Configuration of the fluorination treatment apparatus

Table 1 Fluorination experimental conditions

Parameter	Value
F_2 flow rate	300 ml/minutes
Ar flow rate	30 ml/minutes
Initial temperature (lower part of sample boat)	600ºC
Pressure	100 kPa
Fluorination period	65 to 150 minutes

2. Simulated Fuel Debris Preparation

Four types of simulated fuel debris samples (sample-A, B, C, and D) were prepared by the arc-melting method and the light-condensing heating method.

The chemical form of the debris varies depending on the composition and the atmosphere. Therefore, to achieve the desired chemical form of the simulated fuel debris, the oxidation and reduction condition during their preparation was controlled by the mixing ratio of ingredients in **Table 2**.

(1) Ingredients

Ingredients and their mixing ratio for preparation of the simulated fuel debris are shown in **Table 2**. The powders of $(U,Zr)O_2$ synthesized by sintering method, $GdO_{1.5}$, Zr metal, ZrH_2, SUS316L and concrete were used as ingredients. A higher amount of Zr metal implies a more reducing environment. For safe handling in the atmospheric environment, ZrH_2 was used in the case of sample-D preparation. The concrete was a mixture of ordinary Portland cement, river sand, and river gravel in a weight ratio of 1:2:3.

(2) Preparation Method

The sample-A and B were prepared by arc-melting method in Ar atmosphere. Since it is not possible to liquefy the entire substance at once, the process of arc melting and sample inversion were repeated four times to ensure that the entire substance undergoes melting and solidification. The prepared solid material and the recovered soot, which was attached to the inner surface of the apparatus, were used as the fluorination sample.

The sample-C was prepared by the light-condensing heating method in Ar atmosphere using Xe lamp. Tungsten crucible was used to keep the oxide melted. After melting, the tungsten crucible was removed from the oxide. The recovered oxide was used as the fluorination sample.

The sample-D was prepared to simulate the melting of debris on concrete. The pelletized mixture (about 1.4 g), indicated in Table 2, was put on a concrete piece (about 11g) within the cylindrical frame of SUS304 with ZrO_2 as spreading powder (about 0.1 g). The material was heated from the top by the light-condensing heating method in Ar atmosphere using Xe lamp, melting only the upper part of the material. When the heating stopped, the melted part on the upper part of the sample was solidified. On the other hand, on the lower part of the sample, a layer of concrete that has become brittle due to heat degradation, even though it did not reach a molten state. After the cylindrical frame was removed from the sample, the residual concrete layer of the lower part of the sample was removed as much as possible, and mainly the melted portion was supplied as the sample for the fluorination experiment.

Table 2 Mixing ratio of ingredients for preparation of simulated fuel debris samples

Ingredients	Weight ratio in sample (wt.%)			
	Sample -A	Sample -B	Sample -C	Sample -D*
$U_{0.5}Zr_{0.5}O_2$	39	39	58	62
$GdO_{1.5}$	1	1	2	2
Zr	30	6	-	-
ZrH_2	-	-	-	9
SUS316L	10	34	-	27
Concrete	20	20	40	-
Total	100	100	100	100

*Only pelletized mixture containing uranium.

3. Evaluation of Separation Behavior

The separation behavior of elements in the case of the fuel debris treatment was calculated to examine the applicability of the fluorination method. The uranium volatilization ratio was set to 90% based on the values evaluated in the experiments conducted in this study. The same value of 90% was adopted for the plutonium. Other researches evaluated the plutonium volatilization ratio as 99 % for MCCI debris,[2,3] and the temperature dependence of plutonium volatilization ratio assuming the fluorination of spent nuclear fuel, was evaluated as about 60-70 % at about 750 °C[3]. Since plutonium had trend to be volatilized by fluorination, we assumed that plutonium was volatilized with uranium by fluorination in this study. Silicon reacts with fluorine to form silicon tetrafluoride (SiF_4), which volatilizes. Therefore, the separation behavior was evaluated based on vapor pressure. For the other elements contained in FP, structural material of stainless steel, cladding, and concrete, the separation behavior was also evaluated based on vapor pressure of its fluoride.

The total amount and composition of the waste was estimated based on values reported in literature.[4-6] The composition ratio of FP was based on Nishihara's report,[4] and the total debris amount based on Washiya's[5] and Tanaka's reports.[6] Washiya et. al. estimated the amount of UO_2, zircalloy, stainless steel, B_4C, and inconel in the fuel debris, and Tanaka estimated the amount of MCCI debris.

III. Results and Discussion

1. Fluorination Experimental Results

(1) Weight Change Before and After Fluorination

Because of the volatilization of uranium and silicon by fluorination, as well as the fluorination of oxides and metal in the simulated fuel debris, the material weight before and after the fluorination was different. Weights of major materials are summarized in **Table 3**. Samples before fluorination is the simulated fuel debris prepared in this research; sample-A, B, and C had almost the same weight, while sample-D was relatively heavy sample. Fluorination residue is the recovered material from reactor vessel after fluorination. Recovered material in CT is the condensed UF_6; SiF_4 does not condense at the temperature of the cold trap, so Si component was almost not present.

Table 3 Weight of debris samples before and after fluorination treatment

Material	Weight of each sample material (g)			
	Sample -A	Sample -B	Sample -C	Sample -D
Sample before fluorination	3.38	3.21	3.27	7.69
Fluorination residue	3.35	2.83	1.54	4.95
Recovered material in CT	1.16	1.25	1.97	1.4

(2) Fluorination Period

As mentioned in the experimental section, the fluorination period, which corresponded F_2 flowing time, was modified for each sample. The fluorination period was about 90, 100, 65, and 150 for sample-A, B, C, and D, respectively.

(3) Fluorination Behavior

The appearance and composition of the simulated fuel debris are shown in the upper part of **Table 4**. Samples-A and B, prepared by arc melting method, consisted of particulate solids and soot that adhered to the equipment. The particulate solids contained oxides and metals. Sample C, which was prepared using the focused light heating method, broke into small pieces when it was taken out from the tungsten crucible. Since no metal was used for raw material, sample-C consisted only of oxides. Sample-D, prepared by focused light heating method, was a single large block. Sample-D contained regions of oxides and metals.

The appearance and components of the fluorination residue, and the uranium volatility ratio were also shown in the lower part of Table 4. The simulated debris reacted well with F_2 gas and the fluoride was formed. The surface color of the samples was changed after fluorination. The fluorination residue was crushed into powder or grain as seen in Table 4, showing that the color in its interior also changed. The shape of sample-A was drastically changed by fluorination, it looked like it was being expanded. On the other hand, the change of shape by fluorination looked relatively small for sample-B, C, and D. These samples contained silicate glass, therefore, chemical composition would affect shape change by fluorination.

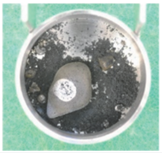
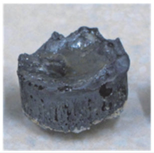
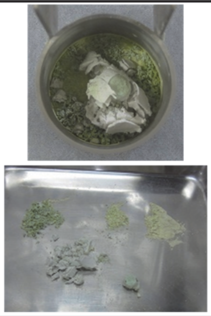
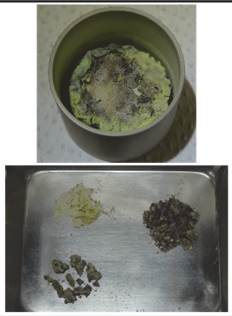
The uranium volatility ratio was over 90%; it means that it is possible to selectively volatilize uranium from the bulk materials by fluorination. Sample-B, C, and D seemed to be fluorinated keeping original form; it means that fluorinated uranium moved from the bulk to gaseous phase. This result suggests that even solid material of a certain size could be fluorinated and the uranium in the solid material could be separated. Additionally, almost all Si was volatilized by fluorination as well as uranium. The residue was fluoride, and the fluoride such as ZrF_4 and the fluoride complex such as $CaZrF_6$ were observed in the residue.

As described above, this study evaluated the fluorination behavior of four types of simulated MCCI debris. Although the samples contained many chemical forms present in MCCI debris (oxide, silicate glass, and concrete), it was found that the uranium could be volatilized by fluorination. In addition, although the sample was a particle of about 0.5 to few cm, it was found that it is possible to fluorinate to the interior of solids. This suggests that debris of this size can be fluorinated without further pulverization. It was also shown that the metallic components could be fluorinated, but that Fe-Cr-Ni was difficult to fluorinate; since Ni is used as a corrosion-resistant material when fluorine is used, it is thought that a high Ni content would make it difficult to fluorinate.

2 Effectiveness of the Fluorination Treatment Method

In order to examine the effectiveness of the application of the fluorination method to debris treatment, the mass balance

Table 4 Summary of experimental results on fluorination treatment of simulated fuel debris

		Sample-A	Sample-B	Sample-C	Sample-D
Before Fluorination					
Content	Oxide	・$(U,Zr)O_2$ ・Concrete origin oxide ・Oxide containing Al etc.	・$(U,Zr)O_2$ ・Silicate glass	・$(U,Zr)O_2$ ・Silicate glass	・$(U,Zr)O_2$ ・Silicate glass ・$FeCr_2O_4$, Concrete
	Metal	・Fe-Si-Zr ・Fe-Cr-Ni-Si-Al-Mo-Zr-U	・Fe-Cr-Ni	none	Ni-Fe
After Fluorination					
Fluorination Behavior		・Reacted into solid inside ・U and Si was volatilized ・Fluoride (ZrF_4,$CaZrF_6$, FeF_3, etc.) was formed.	・Reacted into solid inside ・A part of metal was not reacted. ・U and Si was volatilized ・Fluoride (ZrF_4,$CaZrF_6$, FeF_3, etc.) was formed.	・Reacted into solid inside ・U and Si was volatilized ・Fluoride ($CaZrF_6$, AlF_3, etc.) was formed.	・Reacted into solid inside ・U and Si was volatilized ・Fluoride ($CaZrF_6$, AlF_3, etc.) was formed.
Volatilized U		95 %	95 %	99 %	92 %
Volatilized Si		99 %	96 %	99 %	99 %

during fluorination was evaluated in this study. Since the fluorination experimental results[1,2] showed that some types of simulated fuel debris can be fluoridated, the evaluation was conducted assuming that the entire amount can be fluorinated. Since the properties of 1F debris remain unclear and the effects of parameters, such as debris size and shape, need to be evaluated, we consider that it is important to continue examining the fluorination behavior of 1F debris furthermore.

The material balance of the fluorination of the waste was evaluated and the results are shown in **Fig. 3**. The total amount of the waste of fuel debris retrieval was estimated to be about 900 t. Based on the fluorination, the waste was estimated to be classified into three materials: the nuclear fuel material of about 260 t, the radioactive waste of about 480 t, and the silica waste of about 210 t. The silica waste was the silicon recovered from the off-gas indicated in Fig. 1. The total amount of waste after fluorination was about 950 t, which was an increase from the amount before fluorination. The reason for this is that the metal in fuel debris was finally converted to oxide through the fluorination and oxide conversion processes and the amount was increased by oxygen amount increased.

The nuclear fuel material was mainly derived from the volatilized uranium. It was assumed to contain a small amount of Pu (about 1.6 t). The small amount of FP which formed volatile fluoride and trapped in CT with UF_6 was also assumed to be contained, however, that amount was about 0.3 t which is very small compared to uranium. The elements of these FPs were assumed as Nb, Mo, Tc, Ru, Sb, and Se. In addition, Te would be volatilized by fluorination but not trapped in CT. The chemical compounds of the volatile FP fluorides were assumed as NbF_5, MoF_6, TcF_5, RuF_5, SbF_3 and SbF_5, SeF_4, and TeF_6 in this study. The nuclear fuel material needs criticality safety control, but the radiation shielding should be simplified. The nuclear fuel material is considered to be suitable for recycling because the impurity amount of FP and other elements such as Zr, Fe, Ca and so on was very small.

The radioactive waste contained almost all FPs. Therefore, the radiation shielding should be necessary for storage, but the criticality safety control could be simplified because the amount of uranium was drastically decreased by the fluorination.

The silica waste was derived from Si in the non-radioactive concrete. This waste is recovered separately from the nuclear fuel material and the radioactive waste, and this amount was relatively large as about 210 t. It contained only a small amount of FP, therefore, it had the possibility to be treated as low-level radioactive waste.

These three species of waste can be reasonably managed depending on their required level of the radiation shielding and the criticality safety control. When the nuclear fuel material of about 260 t is recycled, the total amount of waste would decrease from about 900 t of the initial amount to about 690 t which was sum of the radioactive waste and the silica waste.

IV. Conclusion

The fluorination behavior of each element in the simulated fuel debris of MCCI products was evaluated. The simulated fuel debris reacted with F_2 gas and converted to fluoride. The uranium volatilized ratio was over 90%, so the feasibility of the concept separating almost all uranium by fluorination was confirmed.

The feasibility and effectiveness of fluorination treatment method for reasonable management of wastes from nuclear fuel debris retrieval at Fukushima-daiichi nuclear power station was investigated. It was indicated that the waste after fluorination treatment can be partitioned into the nuclear fuel material, the radioactive waste, and the silica waste. These three species of waste can be reasonably managed depending on their required level of radiation shielding and the criticality safety control.

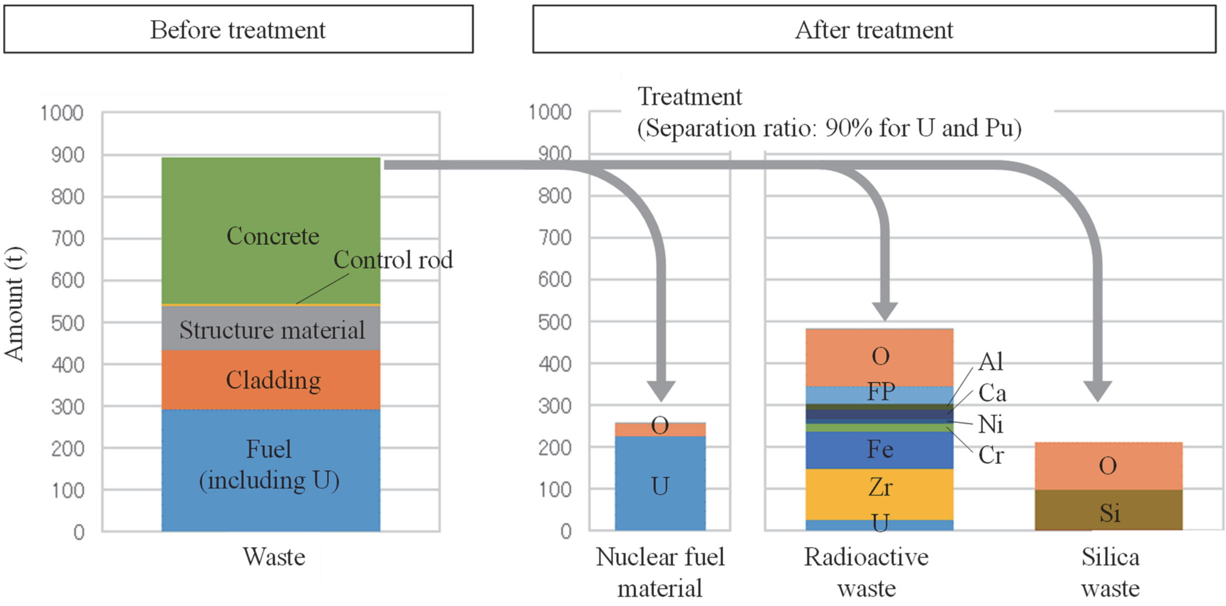


Fig. 3 Material balance of wastes evaluated for fluorination treatment of fuel debris.

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References

1) K. Endo, K. Hoshino, A. Sasahira, T. Fukasawa, T. Chikazawa, A. Kirishima, N. Sato, "Development of Fuel Debris Treatment Technology by the Fluorination Method," *Proc. GLOBAL2019*, Seattle, USA, Sept. 22-27, 2019, 1114-1118 (2019)
2) D. Watanabe, S. Honma, M. Takano, *Fluorination Method for Classification of the Waste Generated by Fuel Debris Removal -FY2021 Nuclear Energy Science & Technology and Human Resource Development Project-,* JAEA-Review 2022-058, Japan Atomic Energy Agency (JAEA) (2023), [in Japanese].
3) T. Fukasawa, K. Hoshino, D. Watanabe, A. Sasahira, "Application of fluoride volatility method to the spent fuel reprocessing," *J. Nucl. Sci. Technol.*, 57[1], 49-56 (2020).
4) K. Nishihara, H. Iwamoto, K. Suyama, *Estimation of fuel compositions in Fukushima-Daiichi Nuclear Power Plant*, JAEA-Data/Code 2012-018, Japan Atomic Energy Agency (JAEA) (2012), [in Japanese].
5) T. Washiya, S. Yamada, K. Yano, N. Kaji, M. Kamiya, "Study of Treatment Scenario for Fuel Debris Removed from Fukushima Daiichi NPS," *Proc. ICONE-23*, Chiba, Japan, May 17-21, 2015, ICONE23-1953 (2015).
6) N. Tanaka, "Technical Feasibility of an Integral Fast Reactor (IFR) as a Future Option for Fast Reactor Cycles ; Integrate a Small Metal-fueled Fast Reactor and Pyroprocessing Facilities," *Nihon- Genshiryoku-Gakkai Shi* (*J. At. Energy Soc. Jpn.*), **59**[6], 10-20 (2017), [in Japanese].