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Characterization of the insoluble sludge from the dissolution of irradiated fast breeder reactor fuel

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Abstract

Insoluble sludge is generated in the reprocessing of spent fuel. The sludge obtained from the dissolution of irradiated fuel from the "Joyo" experimental fast reactor was analyzed to evaluate its chemical form. The sludge was collected by the filtration of the dissolved fuel solution, and then washed in nitric acid. The yields of the sludge weight were less than 1% of the total fuel weight. The chemical composition of the sludge was analyzed after decomposition by alkaline fusion. Molybdenum, technetium, ruthenium, rhodium, and palladium were found to be the main constituent elements of the sludge. X-ray diffraction patterns of the sludge were attributable to Mo_4Ru_4RhPd, regardless of the experimental conditions. The concentrations of molybdenum and zirconium in the dissolved fast reactor fuel solutions were low, indicating that zirconium molybdate hydrate is produced in negligible amounts in the process.

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Keywords: Nuclear Fuel Reprocessing; Insoluble sludge; Platinum group element; Irradiated mixed-oxide fuel; Fast breeder reactor fuel cycle

1. Introduction

Insoluble sludge remains in solution after the dissolution of spent fuel in nitric acid during nuclear fuel reprocessing. There are several types of sludge such as metallic inclusions, precipitations and other undissolved components. Metallic inclusions mainly consist of molybdenum, technetium, ruthenium, rhodium and palladium[1]. Precipitation components are originally dissolved in the nitric acid solution and precipitate over time. When sludge is formed and accumulates in the downstream processing equipment, mechanical failure or blockages can occur. Therefore, enough information on the behavior and characteristics of the sludge is essential in order to develop methods to remove it efficiently and the stable operation of reprocessing facilities.

Fast breeder reactor (FBR) fuels contain nearly 30wt% plutonium and are irradiated at higher burnup than in commercial light water reactors (LWRs). Therefore, the yield of fission products (FPs) is higher in these fuels, it is expected to increase the amount of insoluble sludge. It has been reported that the amount of insoluble residue from dissolving high burnup UO_2 fuel is larger than that expected from the analysis of the data from low-burnup UO_2 fuel, and the amount of residue from mixed oxide (MOX) fuel is slightly more than that from UO_2 fuel at the same burnup[2]. Thus, the characteristics of the sludge from FBR reprocessing are very important for stable process operation.

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The advanced reprocessing process has been developed using irradiated fast reactor MOX fuels, and the characteristics of sludge have been researched during process development at the Chemical Processing Facility (CPF) in Japan Atomic Energy Agency[3]. However, there is little information in previous reports on the characterization of sludge from FBR-MOX fuels. Consequently, in this study, actual sludge obtained from dissolution of fuel irradiated by the experimental fast reactor "Joyo" in Ōarai, Ibaraki, Japan, was analyzed to evaluate its chemical form.

2. Experimental

2.1. Dissolution fuel

Core fuels irradiated at the "Joyo" reactor were used for experiments. The fuel specifications and dissolution conditions are shown in Table 1. Fuel treatment was carried out in a concrete cell at the CPF. The fuel pins were sheared into 1–3cm segments and dissolved with their cladding. However, in the case of run B, the fuel pins were sheared into 1.5 cm segments and then crushed to be decladded.

The dissolution experiments were performed at batch condition. Run A was conducted in a dissolver, and thus required a large volume of nitric acid. All other dissolution experiments were performed in glass flasks. The sheared fuel pieces and nitric acid were placed into a dissolver or flask and refluxed at 368K. The dissolution conditions of run C–F were chosen to obtain a highly concentrated dissolution solution. The dissolution behavior observed in run C–F was evaluated, and has been previously reported[4,5].

After dissolving the fuel, the insoluble sludge was recovered by suction filtration. The filter unit consisted of a stainless steel sieve of 2 mm pore diameter for catching hull, and a glass-fiber filter of 1μm pore diameter for residue. The filtrated sludge was further dissolved in 3 mol/L nitric acid for 2 hours to recover any undissolved uranium and plutonium.

Table 1. Fuel specifications and dissolution conditions.

Run No.	Fuel type	Pu content (%)	Average burn-up (GWd/t)	Sheared length (cm)	Initial/final acidity (mol/L)	Initial HNO_3 volume (ml)	Dissolution time (hour)
A	Joyo Mk-I	18	40.1	3	3.3/1.8	3700	10
B	Joyo Mk-II	29	63.7	powdered	10/2	205	5.83
C	Joyo Mk-III	23.7	53.3	1	8/3.5	325	2.5
D	Joyo Mk-III	23.7	53.3	1	8/4.8	270	2
E*	Joyo Mk-II/ III	29.1/23.7	54.7/53.3	1	11/4	360	4
F*	Joyo Mk-II/ III	29.1//23.7	54.7/53.3	1	11/6.9	240	4

* Fuel used in Runs E and F was a 1:1 mixture of Mk-II and III.

2.2. Analysis of sludge

The obtained sludge was weighed after natural drying. Then a portion of the sludge was dissolved by alkaline fusion prior to elemental concentration analysis. The alkaline fusion was performed by adding sodium peroxide and sodium carbonate as fusing agents followed by heating to 1023K in an electric furnace. Finally, water and nitric acid were added to dissolve the fusion cake.

The plutonium concentration was analyzed by alpha spectroscopy, and those of the other elements were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

X-ray diffraction (XRD) analysis was performed for sample runs A and B. For pretreatment, 0.2 ml of nitric acid (0.1mol/L) was added to the sample sludge and dispersed using an ultrasonic bath for 10 minutes. Then, a drop of the sample was placed on a glass plate and allowed to dry naturally.

3. Results and discussions

3.1. Mass ratio of insoluble sludge

The mass of the fuel and the insoluble sludge, and mass ratio were shown in Table 2. The insoluble mass ratio was less than 1% for all conditions. Furthermore, the insoluble mass ratio was independent of the experimental conditions, i.e., the amount of fuel, burnup, and nitric acid concentration and volume had no significant effect on the insoluble mass ratio in this study.

All of the insoluble sludge was weighed after additional dissolution. However, the insoluble sludge from runs C and D was also weighed after the initial dissolution process. The masses at that point were 3.34 and 2.06 g, respectively. The mass of the insoluble sludge decreased significantly upon further dissolution. Thus, the additional dissolution step is important to reduce the amount of U and Pu in insoluble sludge.