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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.

Table 2. Generated ratio of insoluble sludge

Run No.	Mass of fuel (g)	Mass of insoluble sludge (g)	Insoluble sludge mass ratio (%)
A*1	576.1	3.8	0.66
B	288.47	1.69	0.59
C	148.32	0.78	0.53
D *2	87.84	0.65	0.74
E	268	2.17	0.81
F *2	83	0.77	0.93

*1 Reffered from [3]; *2 Reffered from [4].

3.2. Composition of insoluble sludge

The element compositions of the insoluble sludge are shown in Table 3. Only determined elements are shown here, therefore the total compositions do not reach 100%. Uranium, plutonium and a part of molybdenum present as oxide in the sludge, so the main part of other composition must be oxygen.

The insoluble sludge consisted mainly of uranium, plutonium and FPs. Metallic inclusions, such as molybdenum, ruthenium, rhodium, technetium and palladium phases remain after the dissolution of the irradiated fuel. These platinum-type metallic phases are known to be complex alloys, and their compositions take various forms as pseudoternary Mo-(Tc+Ru)-(Rh+Pd) system[1]. To compare the composition between five elements, relative ratios of the elements (Mo + Tc + Ru + Rh + Pd = 100%) are plotted in Fig. 1. The molybdenum and ruthenium contents are high and of comparable size, while technetium, rhodium and palladium are both present in low levels.

Table 3. Compositions of the insoluble sludge.

Run No.	Compositions (wt%)							
	U	Pu	Mo	Tc	Ru	Rh	Pd	Zr
A*1	<1.5	5.9	23	7.2	22	6.8	6.8	<1.5
B	12	4.4	12	4.1	15	4.6	5.7	<1.4
C	-	1.8	23	-	27	8.0	9.4	<1.6
D *2	-	2.2	19	-	20	6.3	7.6	<5.4
E	4.0	4.3	16	4.6	19	5.5	6.4	<1.8
F *2	2.6	2.8	-	-	-	-	-	-

*1 Reported in [3]; *2 Reported in [4] (U, Pu, Mo, and Ru only).

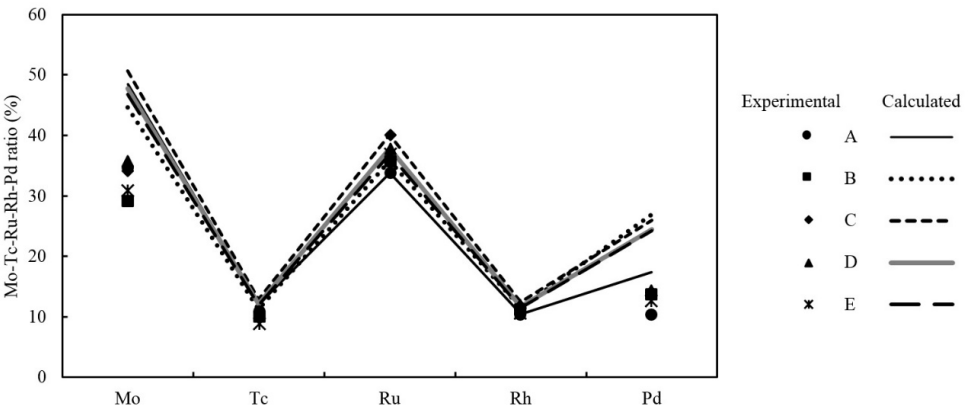

Fig. 1. Ratios of the five elements in insoluble sludge.
The calculated concentration are normalized to the analyzed concentration of Ru.

The platinum-type elements are produced in high fission yields. To compare their levels in the irradiated fuel, the amounts produced were calculated using ORIGEN2.2[6]. The calculated amounts of the five elements are also plotted in Fig. 1 as relative ratios. The generated ratio was normalized to the analyzed ruthenium ratio to compare the trend among the elements. Comparing the analyzed ratio with the calculated ratio, the trends for technetium and rhodium show good agreement with the trend for

ruthenium. However, the molybdenum and palladium contents in the insoluble sludge were lower than expected. It has been reported that molybdenum and palladium show significant differences between their experimental and calculated contents in metallic inclusions at high burnup[7]. Therefore, the trend of the ratio shown in Fig. 1 would originate from when the metals are generated in the spent fuel, not from dissolution process.

The uranium and plutonium compositions exhibit significant variations, although the metallic phases show similar relative compositions. This indicates that the uranium and plutonium contents of the sludge are not related to the FP.

The migration ratio for each element in spent fuel, which is defined as a ratio of the amount contained in the sludge to the generated amount, are shown in Table 4. Uranium and plutonium show low ratios meaning they are well dissolved. Run A shows a higher ratio than that observed for the other conditions, which may be because of the low concentration of nitric acid used. Alloy components were included in the sludge at approximately 30%. Molybdenum and palladium show slightly lower ratios, around 20%, but they are similar to those of ruthenium, rhodium, and technetium.

Table 4. Migration ratio to insoluble sludge.

Run No.	Migration ratios (%)						
	U	Pu	Mo	Tc	Ru	Rh	Pd
A	-	0.25	36	46	49	49	27
B	0.05	0.09	13	17	19	19	10
C	-	0.05	19	-	29	27	15
D	-	0.08	22	-	30	30	18
E	0.04	0.17	20	23	31	29	16
F	0.03	0.13	-	-	-	-	-

3.3. Structure of insoluble sludge

The XRD spectra of the samples from runs A and B are shown in Fig. 2. The pattern for the sample from run A shows good agreement with the reported Mo_4Ru_4RhPd pattern, with no peaks being unassigned, indicating that the sludge from run A consists entirely of Mo_4Ru_4RhPd. From the chemical composition analysis, the ratio of these elements is $Mo_4Ru_{3.7}Rh_{1.1}Pd_{1.1}$, which agrees well with the Mo_4Ru_4RhPd structure. Technetium is also contained in the sludge, suggesting that the alloy may consist of five major elements. The sludge from run B provides the same peaks as Mo_4Ru_4RhPd, but also shows peaks derived from other components that could not be identified. Zirconium molybdate hydrate (ZMH; $ZrMo_2O_7(OH)_2(H_2O)_2$) is known to precipitate in reprocessing solutions, but no ZMH is present in the sludge studied here.

The chemical compositions of the sludge from all runs show similar ratios to $Mo_4Ru_4RhPdTc$. Therefore, despite the differences in the dissolution conditions, the sludge was mainly $Mo_4Ru_4RhPdTc$.

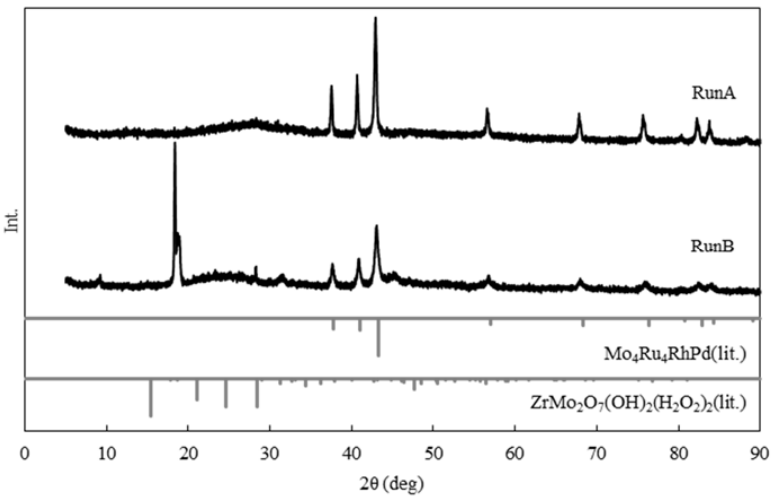

Fig. 2. XRD patterns of insoluble sludge.
Mo_4Ru_4RhPd and $ZrMo_2O_7(OH)_2(H_2O_2)_2$ is referenced from [8] and [9] respectively.

3.4. Molybdenum and zirconium in insoluble sludge

A major component of the sludge recovered from the slab and swarf at the plant has been previously reported to be ZMH[10]. However, the sludge obtained in this study, contained zirconium at low or undetectable levels, as shown in Table 3. Furthermore, ZMH was not detected by XRD, as shown in Fig. 2. The presence of ZMH cannot be completely ruled out, but it may only be present in trace amounts.

ZMH is known to precipitate from solution with high concentrations of zirconium and molybdenum at high temperature[11]. Dissolution experiments were performed by heating at 368 K for several hours, so the production of ZMH would be expected under conditions used in this study. Thus, the fact that ZMH is not precipitated, indicates that the concentrations of zirconium and/or molybdate in the dissolved fuel solution were too low for precipitation to occur.

The molybdenum and zirconium concentrations of the dissolved solutions and the high level liquid waste sampled from the Tokai reprocessing plant are shown in Table 5 for reference. The high level liquid waste was treated during the process, so it cannot be compared with the dissolved solution directly. In this study, the molybdenum concentration should be significantly lower than the zirconium concentration. ZMH is presented as $ZrMo_2O_7(OH)_2(H_2O)_2$, thus, molybdenum is needed at a stoichiometric ratio twice than that of zirconium to precipitate.

The irradiated FBR fuels contain more zirconium and molybdenum as FPs than LWR fuels, therefore, the dissolved amounts may increase with the generated amount. In the case of FBR fuels, the cladding tube will be made of stainless steel, which does not contain zirconium, whereas the cladding for LWR fuels is made of zircaloy. Thus, the contribution from the dissolved cladding may decrease the relative zirconium concentration in the dissolved solution. It is also known that some of the molybdenum may gasify in high burnup fuel[7]. Therefore, the zirconium and molybdenum concentrations in the dissolved core fuel solution may not be high as expected from FBR generated FPs, and the amounts of ZMH precipitating from reprocessed FBR fuel may be lower than predicted.

Table 5. Concentration of zirconium and molybdenum in solutions.

	Run No.	Concentrations (g/L)	
		Zr	Mo
Dissolved solution*1	C	1.7	0.85
	D	1.1	0.61
	E	2.7	0.71
	F	1.1	0.69
High level liquid waste*2		1.5	1.6

*1 Reported in [5];*2 Sampled at the Tokai Reprocessing Plant, average of six samples, reported in [12]

4. Conclusions

The chemical compositions of insoluble sludge obtained by the dissolution of irradiated fuel from the “Joyo” fast reactor were evaluated. The insoluble mass ratios were less than 1%. The major chemical composition of the sludge was $Mo_4Ru_4RhPdTc$. The amounts of molybdenum and palladium in the sludge were lower than the amount expected for spent fuel. The XRD patterns of the sludge were attributable to be Mo_4Ru_4RhPd, regardless of the experimental conditions. Since the concentrations of molybdenum and zirconium in the dissolved solutions of the fast reactor fuels are low, only negligible amount of ZMH is produced in the process.

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