

COMPOSITION OF INSOLUBLE RESIDUES GENERATED DURING SPENT FUEL DISSOLUTION

Y. Pokhitonov, V. Aleksandruk, B. Bibichev, G. Novikov, V. Riazantsev, V. Saprykin
Khlopin Radium Institute, 194021, St. Petersburg, 2nd Murinsky Ave, 28, Russia
P. Rance
British Nuclear Fuels, Sellafield, U.K.

ABSTRACT

One type of HLW associated with the procedures of spent fuel reprocessing or conditioning as would be required in order to implement accelerator driven transmutation of waste, is the insoluble residue, which remains after the majority of the fuel, is dissolved. This material is separated as part of the head-end processing and must be suitably encapsulated within a waste-form to permit its disposal. In spite of the fact that the specific contribution of insoluble deposits, arising from SNF dissolution does not exceed 0,5-1 % of the general volume of wastes, the radionuclides, contained in them introduce a rather significant hazard and demand the most careful treatment of the material during its treatment and subsequent disposal. The main contributors to the insoluble residues are the slowly dissolving metallic fission product inclusions found in spent fuel and the certain fission products which although initially soluble precipitate during the dissolution process. The most significant elements, in mass terms are the platinum group metals (PGM) and, also molybdenum and zirconium. In turn, the formed deposits are capable of adsorbing fission products and actinides, for example, antimony, uranium and plutonium. This group of elements presents two issues one relating to the activity and heat of the relatively short-lived isotopes, in particular $^{106}\text{Ru}/^{106}\text{Rh}$ and ^{125}Sb and the other due to the presence of the long-lived and potentially environmentally mobile ^{99}Tc . The main factors determining the amount and composition of insoluble residues are the temperature and degree of burnup and conditions of fuel dissolution. In this paper the results on composition and mass determination of insoluble residues (primary and secondary), derived from samples of fuel with burnup from 15 up to 54 MWd/kgU are given. Dissolution of spent fuel samples was conducted at the boiling temperature and at 80°C. The concentration of nitric acid in the final solutions varied within the limits 1, 7 - 3,5 mole/l and concentration of uranium from 250 to 350 g/l. The mass of insoluble residues obtained during experiments was from 0,03 to 0,5 % (calculated for 1 kg of UO_2 in spent fuel). Secondary residue examination has shown that their amounts were from 0,01 to 0,3 % of fuel mass (from ≈ 5 to 50 % of whole residue mass). The results of chemical analysis of primary and secondary residues and specific β - and α - activities will be presented. The main elements, defining residue composition are as follows: metals of platinum group (palladium, ruthenium, rhodium), molybdenum and zirconium. The specific β - activity of the residues was 20 to ~ 840 Ci/kg and α - activity 0,01 - 8 Ci/kg. Depending on dissolution conditions uranium and plutonium contents in specimens analyzed were as much as 0,2 - 4% and 0,1 - 3% respectively. These results are compared with other literature data for residue arising and the significance of the insoluble residues in the context of long-term waste behavior will be discussed.

INTRODUCTION

In the beginning of the radiochemical industry development the problems with insoluble residues during the operation of spent fuel dissolution practically did not exist, as in the time of reprocessing irradiated uranium with the aim of weapons plutonium production, the content of fission products in uranium with low burnup did not exceed 0,1-0,3 kg/ton. The increase of burnup and specific activity of NPP fuel and, accordingly, change in composition of solutions demanded to essentially changes the reprocessing technology and the radwaste management, including insoluble deposits. It is quite obvious the problem of insoluble residues will be more serious while reprocessing FR spent fuel with the more burnup. The interest shown by the researchers in insoluble residues is determined by two following reasons. In the first place the amount and the constitution of residues determine the choice of the equipment and operational mode at the stage of solution clarification before extraction and for the units intended for technological (HLW) solution evaporation as well. Secondly, taking in account the accumulation of fission products - platinum group metals in the residues, the latter may be considered as a potential source of reactor's palladium (rhodium). (It should be noted that high specific activity and the presence of fission products in these residues arise some difficulty when burying them). The main part of insoluble residues is generated within those units where fission product amount into the solution is maximal, namely: within the unit of fuel dissolution and solution preparation for the extraction; within the unit of evaporation of 1st extraction cycle raffinate. In each case the residues are mainly composed of fission products having a high yield: first of all, platinum group metals, zirconium and molybdenum. These residues may involve an important amount of other fission products, for example, antimony-125, ruthenium-106, uranium and plutonium. In this paper the results on composition and mass determination of insoluble residues (primary and secondary), derived from samples of fuel with burnup from 15 up to 54 MWd/kgU are given.

RESULTS AND DISCUSSION

Pieces of fuel rods (40 - 50mm) from assemblies for reactor of VVER-1000 type of various burnup and cooling times were used as samples. Dissolution of spent fuel samples was conducted at the boiling temperature and at 80°C. The concentration of nitric acid in the final solutions varied within the limits 1, 7 - 3,5 mole/l and concentration of uranium from 250 to 350 g/l. Experimental conditions and results of deposit mass determination for fuels of various burnup are presented in Table I below.

Table I. Mass of filtered deposit obtained after dissolution of spent fuel samples of different burnup at different temperatures.

Expt #	Characteristics of fuel samples		Dissolution temperature, °C	Filtrate analysis results		Filtered deposit mass, percentage of fuel (UO ₂) mass
	Fuel burn-up, MW*d/kgU	Cooling times, years		U, g/l	HNO ₃ , mole/l	
1	15,0	10,5	Boiling	324	3,1	0,027
2	43,1	6,5	Boiling	278	3,2	0,20
3	15,0	10,5	Boiling	307	1,7	0,25
4	23,8	14,5	Boiling	325	3,3	0,071
5	15,0	10,5	80 °C	342	2,8	0,055
6	43,1	6,5	80 °C	352	3,7	0,44
7	41,1	13,3	80 °C	254	3,3	0,18
8	53,8	5,7	Boiling	344	2,6	0,37
9	41,1	13,3	Boiling	320	3,5	0,27
10	53,8	5,7	80 °C	319	3,2	0,41

As it could be expected, the most important factor, which determined the mass of residues after fuel dissolution, was the degree of burnup. The burnup growth from 15 to 54 MW*day/kg U has led to residue mass increase by a factor 10 (0.027 and 0.37% respectively). The results pointed to increase of residue mass at lower temperature (80°C) of fuel dissolution. In our opinion this result may be explained by incomplete specimen dissolution at lower temperatures.

The deposit "yield" at lower acidity was about 0,25%, i.e. almost 10 times more then that for the same specimen at higher acidity of the filtrate (expt. #.1: ~3.1 mole/l; expt. #.3: ~1.7 mole/l).

The specific activities for all samples were measured and γ -ray spectra were registered. In Table II the averaged values of deposit specific activities and the percentages of the main nuclide contributions to γ -spectra for all experiments are given.

Table II. Residues specific activities and activity of emitters

Expt #	Burnup, MW*.day/kg U	Dissolution temperature, °C	Specific activity, Ci/kg	Activity of emitters, %				
				Cs-137,134	Ru-106	Sb-125	Ce-144	Eu-154
1	15,0	Boiling	64	0,6	90,3	8,4	≤0,5	≤0,2
3		Boiling	27	3,0	67,3	22,7	≤1,1	5,9
5		80 °C	83	4,1	84,9	10,2	≤0,5	≤0,3
4	23,8	Boiling	25	2,1	63,9	25,8	7,4	≤0,8
9	41,1	Boiling	89	38,2	35,4	25,4	≤0,7	≤0,3
7		80 °C	120	34,2	37,8	27,3	≤0,5	≤0,2
2	43,1	Boiling	67	50,4	28,4	19,5	≤0,7	1,0
6		80 °C	140	20,1	73,9	5,1	≤0,4	0,5
8	53,8	Boiling	620	6,4	84,0	7,6	≤0,3	≤1,7
10		80 °C	840	5,6	85,8	8,1	≤0,4	≤0,1

As it is seen from these data, the main contributors to global specific activity are ruthenium-106 and stibium-125. It's quite evident that the ratio of ruthenium, stibium and cesium activities in residues is determined not only by the fuel burnup but by its cooling time after discharge of the fuel from the reactor as well.

In our experiments the specific activity of the residues was 20 to ~ 840 Ci/kg.

The other important characteristic of radioactive wastes (here, insoluble residues), which often determines the requirements to waste management, is their alpha-activity. The values of specific alpha-activity of residues were from 0.01 to 8 Ci/kg and depended poorly on fuel dissolution conditions. The principal factor, which determines the concentration of alpha-nuclide, is the fuel burnup degree.

The results of chemical analysis of residues obtained in these experiments are presented in Table III

Table III. Composition of residues, issued from irradiated fuels dissolution.

Expt.# (Burnup, MW*day/ kg U)	Elemental content in air-dried deposit, % by mass										
	Mo	Zr	Pd	Rh	Ru	Σ PM	U	Pu	Σ*	In all	Notes
1 (15,0)	32	1,6	15	8	27	50	≤0,5*	0,1*	0,3	98,9	Si - 1,4 Ti - 6,4 Ca - 2,8 Mg - 3,1
3 (15,0)	13	16	2,3	3,6	8	13,9	0,27	3,5	0,7	54,3	Fe - 0,7 Si - 5,5 Mg - 0,7
5 (15,0)	5,0	3,6	3,6	10	43	56,6	7,2 0,56*	0,1 0,05*	0,6	77,7	Fe - 3,5 Mg - 1,1
4 (23,8)	29	≤0,3	11	14	58	83	2,9	0,1	0,9	115,9	
9 (41,1)	9,4	0,5	12	13,3	19	54	3,4	0,2	2,3	74,5	Tc - 4,7
7 (41,1)	8,0	1,4	7,5	11	32	50,5	1,2	0,1	1,1	64,0	Tc - 0,8 Ag - 0,9
2 (43,1)	16	0,6	8,2	13	48	69,3	4,2	0,05	0,2	93,4	Fe - 0,9 Ca - 2,2
6 (43,1)	4,0	1,0	5,0	3,1	15	23,1	9,3	0,4	1,0	42,2	Tc - 3,4
8 (53,8)	19,0	1,1	8,4	10	25	43,4	8,3	0,6	1,2	74,7	Ag - 1,1
10 (53,8)	12,0	2,3	7,0	4,5	24	35,5	11,6	0,9	1,1	63,4	

Σ* - elements of content <0,5 % (Al, Ni, Cr, Tc, Ag, Sb, Ti, Cu, Pb et al). *After additional washing of residues.

The data of Table III show that the main contributors to precipitation processes were fission products - metals of platinum group (PM) and, to a lesser degree, molybdenum and zirconium. Besides of elements cited, Si, Ca, Fe, Ni, Mg, Ti, Ag and Tc were also detected (0,1 to 4 and more %) in the main part of specimens. In Table 3 averaged values of analysis results for several filters of each experiment are given. It should be noted that chemical composition of grains, which were shaken off the filters, differed from this one for powder particles remained in filter pores.

During fuel dissolution at boiling point uranium and plutonium contents in specimens analysed were as much as 3,0% and 0,1% respectively. At lower temperature of dissolution (80°C) these values increased to 7-10 and 0,9% for uranium and plutonium respectively. Elevated Pu content in residues, resulted from experiment No.3, is, probably, related with low acidity of filtrate and incomplete fuel dissolution. The same interpretation will do for increased zirconium content in residue obtained in Experiment # 3.

The absence of large crystalline inclusions in residues is corroborated by the results of X-ray phase analysis. These analysis reveal the presence of phases MoO₃-H₂O; RuO₂; Ru and Mo in highly roentgenoamorphous material. However, it should be emphasized that this interpretation of diffraction data executed on the base of JCPDS data bank is not exhaustive and the crystalline phases may be not the main ones, as the specimens to be analyzed are high roentgenoamorphous.

While studying secondary precipitation phenomenon, fuel solutions (filtrates) issued from fuel dissolution products filtration were subjected to ageing for 60, 30 and 7 days at given temperature (20, 50 or 80°C), and subsequent clarification.

As it follows from experimental data, secondary residue yields are from 0,01 to 0,2 % of fuel mass. At the same time the percentage of secondary residue in total (primary and secondary) deposit mass was from 5 to 50 %. Unfortunately, our experimental results don't allow us to make any definite conclusion about effect of temperature and fuel burnup on secondary residue precipitation processes.

Specific gamma-activity of these secondary residues was from 5 to ~300 Ci/kg and it was generated mainly by the same radionuclides as in case of initial residues. It should be noted that in several experiments the lowering of specific activity with the growth of temperature of solution ageing has been observed. This phenomenon may be explained by modification of residue composition and alteration of these residues sorption characteristics, occurred during a long-term ageing of solutions at higher temperatures.

Specific alpha-activity of secondary residues increased with burnup growth and it was 0,1 to 30 Ci/kg. These values changed slightly with experimental conditions and time of solution ageing prior to control filtration. Plutonium content of residues varied in very large limits from 0,08 to 12%.

The yield of platinum metals was rather poor ($\leq 1-2\%$).

The diffractogram of secondary residue (ageing temperature 80°C) has not revealed any distinction from initial residue structure.

When using the calculated values of fission product concentrations, we tried to evaluate the degree of some nuclides transfer (yield) in insoluble residues. This evaluation results are given in Table IV below.

The accounts evidently show, that depending on conditions of dissolution and ageing of solutions, the output on plutonium and some fission products (Pd, Ru and Rh) in deposits can be rather significant.

Table IV. The evaluated yield of Pu and some fission products in insoluble residues.

Expt.#	Burnup, MW*day/kg U	Possible losses plutonium and platinum metals in initial and secondary deposits, % from the contents in fuel taken on dissolution					
		Pu	Pd	Rh	Ru	Mo	Zr
1	15,0	0,006	7,5	15	15	7,1	0,3
3		1,6	20	47	19	24	22
5		0,01	6,7	37	22	2,0	1,1
4	23,8	0,01	12	33	23	9,9	$\leq 0,08$
9	41,1	0,05	19	76	15	6,8	0,3
7		0,02	7,6	41	17	3,8	0,6
2	43,1	0,01	12	64	33	9,7	0,3
6		0,18	14	29	20	4,6	0,93
8	53,8	0,21	14	69	22	15	0,7
10		0,38	14	47	31	10	1,6

Using the values of specific activities (tab. 2), we tried to evaluate of activity and spectrum of radionuclides variation in a time after spent fuel reprocessing. The obtained results are given in Table. V.

Table. V. Variation of specific activities and activity of emitters, (%) of insoluble residues in a time after spent fuel reprocessing.

Cooling time of insoluble residues after spent fuel dissolution, years	Specific activity, Ci/kg	Activity of emitters, (%)				
		Cs-137	Ru-106	Sb-125	Ce-144	Eu-154
Burnup 15 MW*.day/kg U (Expt. # 1)						
5	3,84	8,84	49,5	39,3	0,097	2,25
10	0,85	35,7	7,37	50,1	$5,1 \cdot 10^{-3}$	6,87
25	0,24	88,7	$9,22 \cdot 10^{-4}$	3,9	$2,82 \cdot 10^{-8}$	7,41
100	0,12	99,9	$6,99 \cdot 10^{-11}$	0,013	-	0,128
Burnup 23,8 MW*.day/kg U (Expt. # 4)						
5	2,96	15,6	17,8	61,3	0,727	4,56
10	1,03	40	1,68	49,5	0,024	8,84
25	0,33	88,1	$1,86 \cdot 10^{-4}$	3,42	$1,19 \cdot 10^{-7}$	8,45
100	0,17	99,9	$1,42 \cdot 10^{-11}$	0,012	-	0,147
Burnup 43,1 MW*.day/kg U (Expt. # 2)						
5	30	79,9	2,09	12,2	0,018	1,51
10	22,9	93	0,09	4,49	$2,8 \cdot 10^{-4}$	1,33
25	15,2	99,2	$4,81 \cdot 10^{-6}$	0,15	-	0,61
100	8,49	100	-	-	-	-
Burnup 53,8 MW*.day/kg U (Expt. # 8)						
5	65,3	39,5	26,2	20,3	0,033	10,9
10	32,4	70,8	1,74	11,5	$7,8 \cdot 10^{-4}$	14,8
25	17,8	91,2	$1,13 \cdot 10^{-4}$	0,46	-	8,27
100	9,31	99,9	-	$1,55 \cdot 10^{-3}$	-	0,14

The obtained results visually demonstrate, that after 20 - 30 years activity of the residues will be generate only by cesium - 137.

It should be noted that in spite of the fact that the specific contribution of insoluble residues, does not exceed 0,5-1 % of the general volume of wastes arising from SNF reprocessing, the radionuclides, contained in them, demand the most careful treatment of the material during subsequent disposal.

One can find in literature very few publications, which discuss the results of studies of insoluble residues resulted from reprocessing. First of all the work should be mentioned which present the yields and compositions of insoluble residues resulted from the dissolution of uranium-oxide and MOX fuels, these fuels burnup range being from 30,65 to 55,9 MW*day/kg U [1]. The residue yield was 0,19-0,64 % depending on burnup value. The PGM content was very high: concentrations of palladium, rhodium and ruthenium were 5-20 %, 4,4-9,0 % and 28-45 %, respectively. Among the other fission products the most important contribution is provided by molybdenum (14-23 %) and zirconium (0,3-4,1 %). The contents of uranium and plutonium in the residues resulted from the dissolution of the fuels of various burnup were determined also (0,1-6,9 % and 0,7-3,5 % of total mass of residue, respectively).

A study of the dependency of insoluble residues composition and amount on PWR fuel on fuel burnup was carried out in [2]. The authors studied the residues resulted from dissolution of fuels with burnup of 7-39 MW*day/kg U. The results obtained has shown that within the burnup range 7-30 MW*day/kg U the amount of insoluble residues is nearly linearly dependent on the burnup. When fuel burnup exceeds 30 MW*day/kg U the amount of insoluble residues grows more rapidly.

It should be noted that experimentally determined ratios of fission products in residues differ essentially from calculated ones for spent fuel. So, for fuel with burnup of 31,4 MW*day/kg U the calculated percentage of each above-mentioned element is: Mo – 42 %, Ru – 25 %, Pd – 16 %, Tc – 10 %, and Rh – 7 % (relatively their sum), whereas experimentally determined ratios of these elements in insoluble residues for a fuel sample with this burnup were: Mo – 23,6 %, Ru – 58,0 %, Pd – 8,9 %, Tc – 1,1 %, and Rh – 8,3 %. This difference is explained by the fact that the fraction of insoluble fission products decreases in the following order:

$$\text{Ru} > \text{Rh} > \text{Mo} > \text{Pd} > \text{Tc}$$

When considering the question of fission product content in insoluble residues it should be noted that the major factors affecting this value are the chemical state of an element in fuel (metal, alloy or oxide) [1] and the solubility of metals, alloys or oxides in UO_2 .

The reason of a low fraction of undissolved molybdenum may be the fact that molybdenum is present in fuel in two forms: metal and oxide, their ratio depending on the potential of oxygen in irradiated fuel. It is known that molybdenum in oxide form precipitates in fuel as

(Ba, Sr)MoO₃ phase having the perovskite structure [1]. But in insoluble residues this phase is not found, since it is readily soluble in nitric acid [3]. It is not clear why the fraction of technetium remaining in insoluble residue is so small, since, judging from its oxygen potential one can expect that this element is present in the fuel in the form of metal.

Platinum group metals (ruthenium, rhodium and palladium) are also present in the fuel in the form of metals (alloys), the fraction of palladium remaining in insoluble residue being the smallest. This is explained by the fact that palladium enters the structure of ruthenium-based alloy, which is poorly soluble in nitric acid but at the same time it enters the composition of intermetallic compound containing silver, tin and tellurium, which is well soluble in nitric acid [4].

Unfortunately, to present day the processes of spent fuel dissolution and concomitant processes of precipitation aren't quite extensively studied and the authors of many publications don't agree in opinion on the mechanism of insoluble residue generation.

In the middle of the seventies the researchers of the Radium Institute have studied the composition and amount of insoluble residues resulted from the samples of the spent fuel of VVER-440 reactor (burnup 13-48,5 MW*day/kg U). The yield of insoluble residues was 0,08-0,5 %, the fuel being dissolved in concentrated nitric acid. It was shown that at boiling point the major part of PGM is transferred into the uranyl nitrate solution. In contrast to above-mentioned data [1-2] the content of PGMs in obtained residues was < 0,1 %.

In spite of certain discrepancy between the data presented by different authors one can consider as reliably established the fact that the main constituents determining the residue composition are the platinum group metals. Along with PGMs the important quantities of zirconium, and molybdenum, accompanied by some other elements (including uranium and plutonium) enter the structure of these residues.

It should be emphasized again that the influence of dissolution conditions (acid concentration, temperature) on the residue mass and constitution is so important that even the experiments on the samples of the same fuel may result in residues which dramatically differ in their composition.

As it is seen from the foregoing, the residues generated during fuel dissolution and subsequent solution preparation to the extraction are of dual nature.

The primary insoluble residues are formed by the particles of an alloy on ruthenium base, containing also molybdenum, rhodium, palladium and technetium. (Moreover, the primary residues may also include zirconium dust resulted from fuel rod chopping and the impurities accumulated on the surface of fuel rods during their stay in the reactor).

In the course of fuel dissolution the major part of fuel's molybdenum and zirconium comes into solution and provoke the generation of secondary residues, the base of these residues being zirconium molybdate ZrMo₂O₇(OH)₂H₂O. If there is an excess of molybdenum in the solution, the oxide MoO₃ is also presented in the residue. A detailed study of this type residue generation was carried out in [5] on modeling solutions.

The authors noted that the residues of zirconium molybdate have precipitated only when heating the solutions: at ambient temperature the zirconium molybdate didn't precipitate, even if the solution has been subject to a high gamma-irradiation. In zirconium absence hydrated molybdate of uranium (UO₂MoO₇(1-3)H₂O) and/or plutonium (Pu(MoO₄)₂H₂O) precipitation occurs. If zirconium molybdate precipitates from solutions containing plutonium, generated residue carries away an important amount of plutonium.

As it follows from the data discussed in [1, 6] the residue generation in real clarified fuel solutions occurs not only during their heating but also in the course of these solution ageing.

The most important factor which determines the constitution and yield of residues resulted from fuel dissolution are the temperature and acid concentration. Residue composition change may, in its turn, result in modification of their specific activity and content of PGMs, uranium and plutonium.

Apparently, an adequate selection of fuel dissolution process parameters would make it possible to realize the conditions for maximal PGM (palladium, rhodium) separation in the form of insoluble residues with the purpose of their subsequent recovery. Thereto it seems expedient to process the fuels, which have been cooled for a sufficiently long time.

The problem of subsequent PGM recovery from these residues seems rather complicated. Nevertheless, the feasibility of such a process is not to be denied and to our mind it is worthy of special studies.

CONCLUSION

Though the amounts of insoluble residues arising during fuels dissolution are rather low, the radionuclides incorporated in these residues are quite hazardous and require the strictest attention when solving the problem of their disposal.

One of the problems, which are related to present work object, is the choice of efficacious techniques for management of insoluble residues arising in fuel dissolution unit and for isolation of these residues from biosphere.

When summarizing the results of work performed, the following is noteworthy:

The main factors determining the amount and composition of insoluble residues are a degree of burnup and conditions of fuel dissolution. The yield of insoluble residues at stage of 15 to MW*d/kg U irradiated fuel dissolution is ≈ 0,03 to 0,5 % (calculated for 1 kg of UO₂ in spent fuel).

The main elements, defining residue composition are as follows: metals of platinum group (PM) and, to a lesser degree, molybdenum, zirconium.

Secondary residue examination has shown that their amounts were from 0,01 to 0,2 % of fuel mass (from \approx 5 to 50 % of whole residue mass).

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