

Characteristics of Reduced Metal from Spent Oxide Fuel by Lithium

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Abstract

The mass balance of the unit processes of the Advanced spent fuel Conditioning Process was calculated to obtain basic information. Based on this mass balance, the changes in decay heat and radioactivity of the spent fuel due to the metallization in the high temperature molten salt system were estimated.

The decay heat and the radioactivity were calculated by using the ORIGEN2 computer code, and the result showed that the decay heat and the radioactivity of the metallized spent fuel ingot were 24.27% and 24.24%, respectively, compared to those of oxide spent fuel.

Key Words : lithium reduction, spent fuel, decay heat, radioactivity, ORIGEN2

1. Introduction

A new approach to spent fuel storage technology based on pyrochemical processing has been proposed and developed at Korea Atomic Energy Research Institute(KAERI) since 1997. The proposed process, the Advanced spent fuel Conditioning Process(ACP), is to reduce oxide spent fuel to a metallic form by lithium in a high temperature LiCl salt bath. Some of the highly radioactive fission products such as Cs and Sr are removed from the spent fuel during the reduction process[1, 2, 3]. The reduced metal is cast into an ingot, put into a storage capsule, and stored using

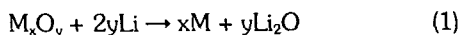
conventional storage methods. This reduction process would reduce the volume of the PWR spent fuel by a factor of 4 and remove Cs and Sr, the highest sources of the decay heat of the spent fuel, and reduce the overall decay heat by a factor of 4. Thus, this process can increase the economic benefit and safety if it is decided to store the spent fuel on a long-term base. If the deployment of the technology is economical and many of the technical issues are resolved, the ACP under development might be the one that meets technical requirements for the intermediate storage of the spent fuel until the final decision for the national plan for the disposition of the spent

fuels.

The inactive experimental tests on some elemental units of the ACP were made to verify the technical feasibility as well as the favorable operational conditions. The laboratory scale experiments showed that more than 97% of the oxide components of uranium and noble metal elements were reduced to metal by lithium, and the alkali or alkali rare earth elements such as Cs and Sr were converted to chloride forms in the proposed reduction process. In this study, the mass balance on the unit processes of the ACP was calculated by using the results of the laboratory scale experiment and literature in order to obtain basic information. The decrease in decay heat and radioactivity of the spent fuel due to the metallization in the high temperature molten salt system was also estimated. The elements in the reduced metal ingots and the molten salt were determined considering the chemical properties of the reaction product in the LiCl-Li-Li₂O system. Decay heat and radioactivity of these elements were calculated by the ORIGEN2 computer code. The result obtained from this analysis can be applied as a baseline for the evaluation of the thermal integrity of a metallized fuel assembly on a long-term dry storage conditions.

2. Reduction of Oxides by Lithium

In the metallization step, the spent oxide fuels are reduced to metal by lithium dissolved in molten LiCl at 650 °C according to the reaction,



where M is the metal to be reduced. The Li₂O formed during the metallization process is soluble in the LiCl salt. It is desirable to maintain a Li₂O concentration below its solubility limit in LiCl (8.7 wt% at 650 °C). Otherwise, the precipitation of

Li₂O will complicate the downstream separation process.

The fission products(FPs) can be divided into four groups depending on their chemical behaviors in the metallization process: (a) uranium and transuranium(TRU), (b) alkali and alkaline earth metals, Eu, Se, and Te, (c) rare earths(RE), and (d) noble metals(NM).

2.1. U and TRUs

Reduction of U and TRUs depends on the concentration of Li₂O dissolved in the molten LiCl. The free energies of formation of the actinide elements are fairly close to that of Li₂O. In particular, the free energies of formation of Pu₂O₃ and Am₂O₃ are quite close to, or even slightly more negative than that of Li₂O. Both experiments and calculations indicated that it is important to keep the activity of Li₂O in the molten LiCl low to ensure that the reductions of these actinide elements are driven to completion. Depending on lithium availability and Li₂O concentration, the actinide oxides are reduced in the following order[4]: CmO₂, AmO₂, NpO₂, Np₂O₃, PuO₂, UO₂, Cm₂O₃, Pu₂O₃, and Am₂O₃. For a complete reduction of actinide oxides, the maximum allowable mole fraction of Li₂O in the molten LiCl should be below that corresponding to the Am₂O₃ reduction, 5 wt%. Laboratory experiments have shown that PuO₂ are completely reduced to metal by lithium up to the solubility limit of Li₂O in LiCl[5].

2.2. Alkali and Alkaline Earth Metals, Eu, Se, and Te

Alkali and alkaline earth elements form stable chlorides in the reduction reaction and become soluble in the LiCl. The oxides of tetravalent elements produce chlorides and Li₂O in the LiCl-Li

Table 1. Free Energy of Formation of Metal Oxides at 650 °C

Oxide	ΔG (kJ/g-O)	Oxide	ΔG (kJ/g-O)
CeO ₂	-448.2	NiO	-155.9
Gd ₂ O ₃	-519.7	CdO	-164.3
La ₂ O ₃	-509.7	MoO ₂	-209.9
Nd ₂ O ₃	-515.3	PdO	-19.7
Pr ₂ O ₃	-514.0	Rh ₂ O ₃	-39.1
Sm ₂ O ₃	-518.3	RuO ₂	-74.9
Y ₂ O ₃	-545.3	Sb ₂ O ₃	-154.5
Eu ₂ O ₃	-456.7	SnO ₂	-194.4
Li ₂ O	-477.1	TcO ₂	-133.4

system. On the other hand, oxides of divalent elements react with LiCl to form chlorides. Especially, Eu₂O₃ reacts with LiCl in the presence of Li₂O to form complex oxides[6]. These complex oxides are expected to recover along with reduced metal powders from the bottom of the reduction reactor because they have the higher density and are insoluble in the molten LiCl. The oxides of Se and Te react with lithium metal to form the lithium compounds such as Li₂Se and Li₂Te which are soluble in the molten LiCl.

2.3. Rare Earths

As shown in the free energy data[4] in Table 1, the oxides of rare earth elements are not reduced to metal by lithium. The oxides of rare earth elements mostly exist in the form of sesqui oxides which are known to be very reactive with Li₂O in the LiCl. La₂O₃ reacts with LiCl to form the complex oxide and the oxychloride. CeO₂ is reduced to trivalent oxide but not reduced to metal in the LiCl-Li₂O-Li system. The oxides of Nd, Sm, Gd, Y, Lu, and Pr form the complex oxides in the LiCl-Li₂O system. These complex oxides have limited solubilities in the molten LiCl[6]. Thus, elements in the rare earth group are expected to recover along with the metal powders reduced.

2.4. Noble Metals

The oxides of the noble metals are reduced to metal by lithium. Especially, the noble metals, if present as oxides, are reduced regardless of Li₂O concentration in LiCl.

3. Mass Balance of the Advanced Spent Fuel Conditioning Process

The generalized flowsheet for the Advanced spent fuel Conditioning Process is shown in Fig. 1. The pressurized water reactor(PWR) spent fuel assemblies are disassembled, and the spent fuel rods are chopped. The chopped spent fuel which mainly consists of UO₂ pellets is put into the voloxidation unit. The spent fuel pellets are pulverized by oxidation under the high temperature air environment, and the spent fuel is separated from the zircaloy cladding. Most of the volatile fission products are assumed to be removed during the voloxidation operation. The oxidized spent fuel powders are loaded into the metallization unit and react with lithium in molten LiCl at 650 °C. Lithium and LiCl react with the spent fuel components to produce metal powders, chlorides, complex oxides etc., depending on the relative stabilities of the compounds. The Li₂O is also formed and dissolves in the LiCl. The

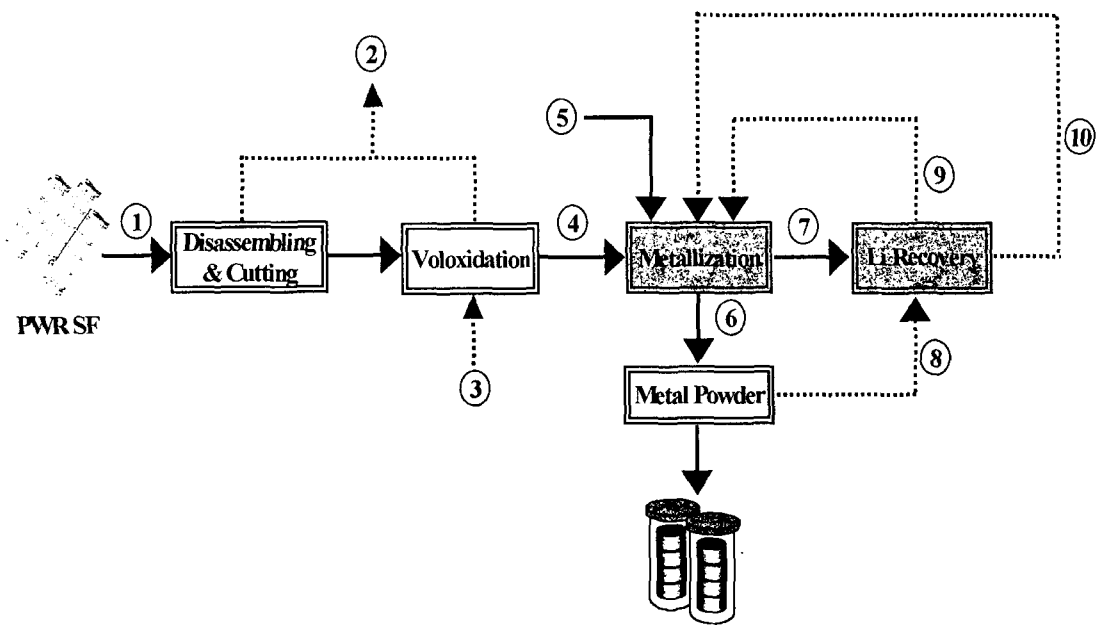


Fig. 1. Flow Sheet of the Advanced Spent Fuel Conditioning Process

metallized spent fuel and complex oxide compounds are separated from the salt phase by filtration and transferred to the casting unit to manufacture the rods to be packed in a storage canister. The remaining salt is transferred to the

lithium recovery unit and regenerated by electrolysis to convert the Li_2O to lithium. Both the lithium and the LiCl are recycled to the metallization unit.

The composition of the PWR spent fuel with

Table 2. Composition of Reference PWR Fuel by Weight

Group	Element (%)					
U	U	95.5				
TRU	Am	8.68×10^{-2}	Cm	4.96×10^{-3}	Np	5.36×10^{-2}
	Pu	0.847				
AM, AEM Eu, Se, Te	Ba	0.193	Cs	0.23	Eu	1.60×10^{-2}
	Rb	3.60×10^{-2}	Se	5.60×10^{-3}	Sr	7.90×10^{-2}
	Te	4.70×10^{-2}				
VFP	Br	2.20×10^{-3}	I	2.40×10^{-2}	Kr	3.50×10^{-2}
	Xe	0.544				
RE	Ce	0.245	Dy	1.00×10^{-4}	Gd	1.40×10^{-2}
	La	0.125	Nd	0.412	Pm	7.00×10^{-4}
	Pr	0.115	Sm	8.60×10^{-2}	Tb	2.00×10^{-4}
	Y	4.70×10^{-2}				
NM	Ag	5.40×10^{-3}	Cd	9.10×10^{-3}	Mo	0.345
	Nb	6.90×10^{-7}	Pd	0.147	Rh	4.20×10^{-2}
	Ru	0.219	Sb	9.00×10^{-4}	Sn	4.90×10^{-3}
	Tc	8.40×10^{-2}	Zr	0.372		

Table 3. Mass Balance of the Advanced Spent Fuel Conditioning Process (20 kg HM/batch basis)
(unit : g-mole)

	Introduction of Nuclear Materials and Reactants					Metallization Process		Li Recovery Process			
	①*	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	
LiCl					4200		96.6	4103.4	96.6		4200
Li					460		1.560	66.262	1.560	417.657	21.10
Li ₂ O							4.490	190.739	4.490		9.511
O ₂			23.58								
UO ₂	70.741			U ₃ O ₈	23.58	U	70.670				
						UO ₂	0.071				
TRU	AmO ₂	0.066			0.066	Am	0.062				
						Am ₂ O ₃	0.004				
	CmO ₂	0.004			0.004	Cm	0.004				
	NpO ₂	0.037			0.037	Np	0.036				
							Np ₂ O ₃	0.001			
PuO ₂	0.620				0.620	Pu	0.614				
						Pu ₂ O ₃	0.006				
AM	BaO ₂	0.248			0.248	BaCl ₂	0.006	0.242	0.006		0.248
	CsO ₂	0.276			0.276	CsCl	0.006	0.270	0.006		0.276
	Eu ₂ O ₃	0.009			0.009	EuOCl +LiEuO ₂	0.018				
AEM	Rb ₂ O	0.037			0.037	RbCl	0.002	0.072	0.002		0.074
etc.	SeO ₂	0.013			0.013	Li ₂ Se	0.000	0.013	0.000		0.013
	SrO	0.159			0.159	SrCl ₂	0.004	0.155	0.004		0.159
	TeO ₂	0.065			0.065	Li ₂ Te	0.002	0.063	0.002		0.065
RE	CeO ₂	0.285			0.285	CeO + Ce ₂ O ₃	0.285				
	Gd ₂ O ₃	0.008			0.008	LiGdO ₂	0.016				
	La ₂ O ₃	0.079			0.079	LiLaOCl ₂	0.004	0.154	0.004		0.158
	Nd ₂ O ₃	0.252			0.252	LiNdO ₂	0.504				
	Pr ₂ O ₃	0.072			0.072	LiPrO ₂	0.144				
	Sm ₂ O ₃	0.050			0.050	LiSmO ₂	0.100				
	TbO ₂	0.000			0.000	TbO ₂	0.000				
	Y ₂ O ₃	0.047			0.047	LiYO ₂	0.094				
	VPS	Kr	0.074	0.074							
		Br	0.002	0.002							
	I ₂	0.017	0.017								
	Xe	0.731	0.731								
NM	Ag ₂ O	0.004			0.004	Ag	0.008				
	CdO	0.014			0.014	Cd	0.014				
	MoO ₂	0.634			0.634	Mo	0.634				
	PdO	0.244			0.244	Pd	0.244				
	Rh ₂ O ₃	0.036			0.036	Rh	0.072				
	RuO ₂	0.382			0.382	Ru	0.382				
	Sb ₂ O ₃	0.001			0.001	Sb	0.002				
	SnO ₂	0.007			0.007	Sn	0.007				
	TcO ₂	0.150			0.150	Tc	0.150				
ZrO ₂	0.731			0.731	Zr	0.731					

*The encircled numbers in this table correspond to those in Fig. 1.

3.2 wt% enrichment, 10-year cooling time, and 33 GWD/tU burn-up was calculated by using the ORIGEN2 computer code. The result is shown in Table 2.

The mass balance for the main unit processes of the ACP with 20 kgHM/batch scale was made, and the result is shown in Table 3. The encircled numbers in this table represent each steps in the ACP corresponding to those in Fig.1. The composition of the feed material to the ACP was calculated from Table 2, and the mass balance for each steps was calculated from the experimental results and the chemical behaviors of the spent fuel components in the LiCl salt as described in section 2. The criteria for the process to make the mass balance were as follows;

- i) 20 kgHM of the PWR spent fuel is introduced into the process. Voloxidation is carried out under the air atmosphere at 500 °C to produce the oxidized spent fuel powders. All the volatile fission products are assumed to be removed in the disassembling and the voloxidation processes.
- ii) 15% excess lithium is put into the metallization

process, and the final concentration of Li₂O in the LiCl salt is 3.2 wt%. The metal powders filtered from the metallization process contain 2.3% of the LiCl salt, and this salt is recycled to the lithium recovery process.

- iii) In the lithium recovery process, 95% lithium is recovered and recycled to the metallization process together with LiCl.

4. Characteristics of the Reduced Metal

The composition of the reduced metal ingot was estimated from the mass balance in Table 3. The heat source was calculated on the assumption that all the fission product elements except the ones remaining in the LiCl salt phase are included in the reduced metal phase. Radioactivity and decay heat of the elements such as Cs and Sr which are separated from the reduced metal phase are shown in Table 4. Although the yttrium is converted into complex oxide in the LiCl-Li-Li₂O molten system of the metallization process, it is assumed to be removed from the reduced metal phase because the half life of Y-90 is very short.

Table 4. Radioactivity and Decay Heat of Elements Removed in the Advanced Spent Fuel Conditioning Process

Nuclide	Radioactivity		Decay Heat	
	Ci	%	W	%
Te	2.78E+02	9.36E-02	0.23	2.73E-02
Se	0.41	1.38E-04	1.02E-04	1.20E-05
Br	0.00	0.00	0.00	0.00
Kr	4.90E+03	1.7	7.3	0.86
Rb	2.16E-05	7.26E-09	1.80E-08	2.11E-09
Sr	5.78E+04	19.	67.	7.9
Y	5.78E+04	19.	3.21E+02	38.
I	3.16E-02	1.06E-05	1.46E-05	1.71E-06
Xe	2.91E-32	9.79E-36	5.33E-35	6.24E-36
Cs	8.84E+04	30.	1.48E+02	17.
Ba	7.83E+04	26.	3.08E+02	36.
Pm	9.36E+03	3.2	3.4	0.39
Total	2.97E+05	1.00E+02	8.54E+02	1.00E+02

Table 5. Radioactivity and Decay Heat of Elements Included in a Reduced Metal Ingot

Nuclide	Radioactivity		Decay Heat	
	Ci	%	W	%
Si	1.95E-08	2.05E-11	2.42E-11	8.85E-12
P	1.95E-08	2.05E-11	1.97E-10	7.21E-11
Fe	0.69	7.22E-04	2.32E-05	8.47E-06
Co	43.	4.54E-02	0.67	0.24
Ni	1.6	1.63E-03	1.56E-04	5.69E-05
Zn	0.00	0.00	0.00	0.00
Zr	1.8	1.92E-03	2.12E-04	7.74E-05
Mo	0.00	0.00	0.00	0.00
Tc	13.	1.40E-02	6.66E-03	2.43E-03
Ru	5.50E+02	0.58	3.27E-02	1.19E-02
Pd	0.11	1.18E-04	6.67E-06	2.44E-06
Ag	0.16	1.71E-04	2.69E-03	9.83E-04
Cd	34.	3.56E-02	5.70E-02	2.08E-02
Sn	0.95	1.00E-03	1.32E-03	4.82E-04
Sb	1.14E+03	1.2	3.6	1.3
Eu	5.62E+03	5.9	38.	14.
Gd	3.64E-04	3.83E-07	3.29E-07	1.20E-07
U	3.7	3.91E-03	5.30E-02	1.94E-02
Np	20.	2.06E-02	5.71E-02	2.09E-02
Pu	8.27E+04	87.	1.10E+02	40.
Am	1.80E+03	1.9	59.	21.
Cm	1.61E+03	1.7	56.	21.
Rh	5.50E+02	0.58	5.3	1.9
La	1.11E-10	1.17E-13	8.15E-13	2.98E-13
Ce	1.49E+02	0.16	9.88E-02	3.61E-02
Pr	1.51E+02	0.16	1.1	0.40
Nd	1.57E-09	1.66E-12	0.00	0.00
Sm	3.50E+02	0.37	4.10E-02	1.50E-02
Total	9.50E+04	1.00E+02	2.74E+02	1.00E+02

Decay heat and radioactivity of the reduced metal were calculated by using the ORIGEN2 computer code[7]. Decay heat of the reduced metal exhibits a tendency to decrease exponentially as cooling time elapses. In this analysis, the equation of the decay heat is expressed as an exponential function. Radioactivity of the reduced metal was also calculated in the same way, and the resultant equations are;

$$y_1 = 98.18 e^{-0.0072x} + 144.95 e^{-0.0015x} + 23.18 \quad (2)$$

$$y_2 = 905.35 e^{-0.0001x} + 123062 e^{-0.0455x} + 6014.87 e^{-0.0021x} \quad (3)$$

where y_1 , y_2 are decay heat (W), radioactivity (Ci), and x is time (yr). Fig. 2 and 3 show that the decay heat and the radioactivity of the reduced metal depending on the cooling time are well represented by these equations.

Radioactivity and decay heat of the elements included in the reduced metal ingot are summarized in Table 5. Fission products of which

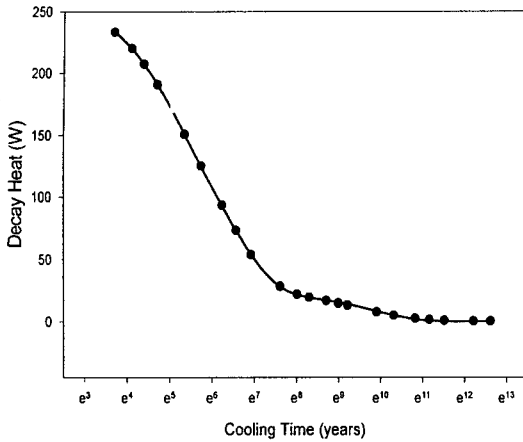


Fig. 2. Decay Heat of a Reduced Metal Ingot as a Function of Cooling Time

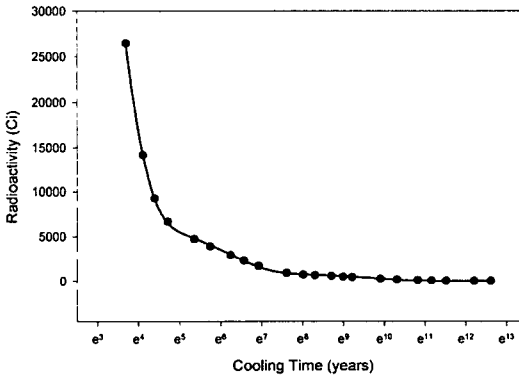


Fig. 3. Radioactivity of a Reduced Metal Ingot as a Function of Cooling Time

mass, radioactivity and decay heat are less than 0.1% of the total amount are excluded in this list. As shown in this table, radioactivity of the reduced metal ingot is ascribed mostly to Pu and decay heat is mostly ascribed to Pu, Am, and Cm. Radioactivity and decay heat of the reduced metal which is converted from the 20 kgHM of oxide spent fuel with 3.2 wt% enrichment, 10-year cooling, and 33 GWD/tU burnup are 1,764 Ci and 4.7 W respectively. These quantities of

radioactivity and decay heat are 24.27% and 24.24% respectively of those of the spent fuel oxide.

5. Conclusions

Mass balance in the Advanced spent fuel Conditioning Process was made from the result of the laboratory scale experiment and literature. Based on this mass balance, quantitative assessment of the reduction in decay heat and radioactivity of the spent fuel due to the metallization was carried out. Decay heat and radioactivity of the reduced metal are calculated by using the ORIGEN2 computer code, and it can be concluded as follows.

- 1) Decay heat and radioactivity of the reduced metal ingot decreased exponentially with time. The equations were obtained to express the decay heat and radioactivity as a function of time, respectively.
- 2) Radioactivity and decay heat of the metal reduced from the 20 kgHM of oxide spent fuel were 1,764 Ci and 4.7 W, respectively, and they were 24.27% and 24.24% respectively of those of the spent fuel oxide. This demonstrates that the Advanced spent fuel Conditioning Process would reduce the overall decay heat of the spent fuel by a factor of 4.

The heat source data of the reduced metal obtained from this study can be used for the evaluation of the thermal integrity of a metallized fuel assembly if it is decided to store spent fuel on a long-term dry storage conditions.

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