OPTIMIZATION OF POWDER/PELLET FABRICATION FOR DUPIC FUEL

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ABSTRACT

The DUPIC(Direct use of spent PWR fuel in CANDU reactors) fuel cycle is an alternative fuel cycle technology for reusing spent PWR fuel in CANDU reactors via direct re-fabrication. For the establishment of optimum process conditions for DUPIC fuel fabrication processes, a series of experiments have been conducted using natural uranium and SIMFUEL(simulated fuel) out cell and actual spent PWR fuel in cell, to evaluate the powder/pellet characteristics of DUPIC fuel. From the experimental results, it is concluded that the properties of powder were more dependent on the number of OREOX cycles rather than treatment temperature. In fabrication of fuel pellets using the DUPIC process, a milling process improved the powder properties and enhanced the densification of fuel pellets. The optimum conditions for fabrication of simulated DUPIC fuel pellet were established and the optimum conditions for fabricating DUPIC fuel pellet were developed by in-cell experiments.

1. INTRODUCTION

DUPIC fuel cycle development has been conducted in a joint program between KAERI, AECL, US DOS and IAEA since 1991. As the name implies, its concept is to fabricate the CANDU fuel directly from spent PWR fuel material using only dry process[1,2]. The DUPIC project is performed in phased approach. Phase I was a feasibility study to select the most promising option among seven different methods of reconfiguring spent PWR fuel to CANDU fuel. Even though all options are technically feasible, but the recommendation was the OREOX option which is a dry thermal process to convert irradiated fuel pellets into resintrable powder. Phase II is being implemented to demonstrate experimentally the feasibility of the OREOX process for fabricating DUPIC fuel and to evaluate its performance in a research reactor.

The heart of the DUPIC fuel fabrication is to produce a resinterable powder from the spent fuel pellet as a starting material. Thus, the OREOX process was chosen to convert the spent fuel pellet into a resinterable powder. During this process, spent PWR fuel is oxidized to U_3O_8 powder and reduced back to UO_2 powder. Once a resinterable powder is produced, the rests of fuel fabrication processes are almost the same as those of normal CANDU fuel. The properties of a powder are dependent on the details of the process used. Thus, it is essential to understand the effects of the powder preparation process, such as OREOX and milling on DUPIC fuel

fabrication.

The direct measurement of DUPIC fuel properties in hot cell is very difficult due to its high level of radiation. Hence, it is necessary, as a first step, to fabricate fuel pellets using natural uranium(NU) and SIMFUEL to investigate its properties without the complications of handling radioactive materials. Then, the process conditions developed in this out-cell experiment are optimized through in-cell experiment using a small quantity of actual spent PWR fuel.

This paper describes the results of out-cell experiments, using NU fuel and SIMFUEL and the results of in-cell experiments conducted with actual spent PWR fuel.

2. OUT-CELL EXPERIMENTS

The detail procedures for the out-cell experiment are as follows:

- Sintered pellet is prepared based on the conventional CANDU fuel fabrication process.
- The pellet is subjected to the OREOX process to convert it to a powder under various experimental process conditions.
- The powder produced from OREOX process is characterized.
- Powder milling is conducted to study its effect on powder sinterability.
- The milled powder is characterized.
- Powders are then pressed into green pellets, and sintered.
- Sintered pellet of simulated DUPIC fuel pellet is characterized.

For out-cell experiments, NU and SIMFUEL were used. In the case of NU experiment, two kinds of UO_2 powder produced from AUC(ammonium uranyl carbonate) and ADU(ammonium diurnate) process were used. The powder properties such as specific surface area, particle size, morphology and sinterabilty were investigated. SIMFUEL is unirradiated UO_2 blended with surrogate additives to simulate fission products. The SIMFUEL used in this experiment simulated the fuel with discharge burnup of 35,000 MWD/MTU. The fourteen elements listed in Table 1 were added as major fission products. Simulated DUPIC fuel was fabricated by sintering the powder which was prepared through the OREOX process of SIMFUEL.

2.1 Characteristics of oxidized powder

The particle size and specific surface area of the oxidized powder which were treated at 350 to 500 °C are summarized in Table 2. Particle size increases with oxidation temperature while specific surface area decreases, which is in good agreement with other study[3]. As the shape of the powder is irregular and flaky as shown in Figure 1, it is difficult to measure the exact particle size. The variation of the specific surface area and the powdered fraction as the oxidation time increases is shown in Table 3. The specific surface area initially increases with time and then decreases. Maximum specific area was reached at 30 min. Powdered fraction increases linearly with time. Within 10 min. oxidation, the powdered fraction is very low. This seemed to be due to incubation time[4], which is the time required for initially cracking the grain boundary by the formation of intermediate phases.

2.2 Characteristics of OREOX-treated powder

The particle size and specific surface area of the OREOX-treated powder which was oxidized at 400 °C and reduced at 600 °C are summarized in Table 4. Particle size decreases with the number of oxidation and reduction cycle while specific surface area increases. The sintered density increases with the number of oxidation and reduction cycle, but reaching to only a final density of 9.58 g/cm^3 (87% of theoretical density). This may be due to the poor sinterability of the powders produced only by the OREOX process. For further improvement in powder sinterability, a dry-milling was adopted in addition to the OREOX process.

The mill used in this experiment was a horizontal rotary ball mill, which was specially modified to allow remote handling and operation in hot cell. The optimum milling parameters for the production of high density pellets were established. Figure 2 shows the particle size distributions of UO_2 powders for three different sample preparations; the fresh powder, the powder produced by 3 cycles of OREOX treatment, and the powder milled after 3 cycles of OREOX. A cyclic operation for 10 minutes at 450 rpm followed by 10 minutes at 600 rpm was applied to the milling of OREOX-treated UO_2 powders. As shown in this figure, the mean particles size of the milled UO_2 powder was reduced from 16.7 ㎛ to 1.6 ㎛ by 20 minutes milling, which is smaller than that of fresh UO_2 powder. This trend is consistent with the results of the milling of ceramic powder[5]. The particle size distribution for the OREOX-treated powder shows the Gaussian form with a narrow range of particle size. In contrast, the fresh and milled powders follow the typical bell curve with a wide range of particle size. In other words, the distribution curve of the milled powder is almost the same as that of the fresh powder, but the particle size is further reduced to 1.6 ㎛. This implies a higher packing density in powder compaction.

Figure 3 shows SEM micrographs of OREOX-treated and milled powder. As shown in this figure, the OREOX-treated powders are generally coarse and angular with a lot of micro-cracks, and are easily breakable. After milling, the coarse particles are broken up into micro-particles. Figure 4 shows pour and tap densities of fresh, OREOX-treated, and milled powder. This exhibits that these powder densities are very dependent on their preparation methods and that the milled powder has the highest pour and tap densities among powder samples prepared. This trend is well consistent with the results shown in Figure 3. Therefore, it is anticipated that the milled powder will have a higher packing density and sintered density than the OREOX-treated powder during compaction and sintering.

Generally the sintering can be enhanced by using fine powders due to increasing the surface activity[6]. The surface activity is directly related to the particle size and morphology. It is generally known that finer powders have an excess surface energy which serves as a driving force for the sintering process, and hence attain higher density than coarser powders[7].

Figure 5 shows the variations of green and sintered densities as a function of compaction pressure, with and without milling process. The green and sintered densities using milled powders are much higher than those of only OREOX-treated powder. The value of sintered density using the milled powders satisfies the density requirements of CANDU fuel pellets(95% of theoretical density), but the powders without milling process failed in meeting the required sintered pellet density. Therefore, it is concluded that a milling process in manufacturing DUPIC

fuel pellets is essential and leads to enhancement of densification of fuel pellet.

2.3 Characteristics of the powder made from SIMFUEL

The particle size and the specific surface area of the powder were measured as milling times respectively. The specific surface area of the powder increased from 5.33 m^2/g to 6.06 m^2/g, and the particle size reduced from 3.2 μm to 0.5 μm as milling times increased. The microstructures of the powder after being mixed, milled and after the OREOX process were observed. The shapes of the particles before being milled are large lumps, and the small particles are agglomerated. The particles of the powder after milling are crushed into small sizes. The particle sizes and shapes of mixed and milled powders are distributed irregularly. To confirm the homogeneity of the additives as surrogate fission products in the powder, samples were analyzed by chemical analysis at three positions : top, middle and bottom of bottle of the mixed and 1^{st}, 3^{rd} and 5^{th} milled powder. The concentrations of the typical elements of mixed powder vary slightly depending on the sampling point of the bottle, and the variations of their concentrations after milling is reduced. It can be concluded that the additives are distributed homogeneously in the powder after milling. The sintered density of simulated DUPIC fuel pellets ranges from 10.365 g/cm^3 to 10.398 g/cm^3 (96.560 ~ 96.867% of TD) which is within CANDU fuel specifications. There are some micro-cracks on the surface of the fuel pellets due to the poor sinterability of mixed powder and friction between die wall and green pellets. But no crack is found at the pellet made with low compaction pressure below 130 MPa and the powder treated by even only 1 cycle of OREOX.

3. IN-CELL EXPERIMENTS

The optimun conditions to fabricate DUPIC fuel pellets might be established from those established in out-cell experiments. In order to reconfirm the process conditions developed, a series of in-cell experiments using actual spent PWR fuel have been conducted in a hot cell of PIEF(Post Irradiation Examination Facility) prior to the start of main fabrication campaign of DUPIC fuel.

DUPIC fuel fabrication process mainly comprises of decladding, powder preparation, pelletizing, sintering and fuel element manufacturing processes. Based on the optimun conditions developed in the out-cell experiments, OREOX, pre-compaction, final compaction and sintering processes were conducted to produce DUPIC fuel pellets. Since the characterization of DUPIC fuel in hot cell is very restricted due to its high radioactivity and required remote operation, only sintered density and microstructure of the sintered pellets were measured for checking the optimum process conditions for DUPIC fuel fabrication.

The spent PWR fuel used in this experiment has undergone a nominal burnup of 35,500 MWD/MTU and was discharged in 1986 from Gori unit 1 power plant. The spent fuel rod was cut into pieces of 15cm rod cuts. Nine rod cuts were decladed to produce 900 grams of spent fuel fragments that were used as a feedstock for this experiment. The DUPIC fuel fabrication process is schematically shown in Figure 6. The PWR spent fuel rod is decladed by mechanical slitting prior to OREOX process. The spent fuel fragments resulting from decladding process is treated by successive oxidation and reduction processes to produce a sinterable powder as a feedstock for

the fabrication of DUPIC fuel pellets. The pre-compaction and granulation processes are performed to improve the powder flowability. Compaction and granulation processes are performed with hydraulic press and a sieve, respectively. After final compaction, the green pellets are produced and sintered at 1700℃ in an Ar-4%H_2 atmosphere.

The optimum process conditions for DUPIC fuel fabrication were investigated in terms of density and microstructure of the sintered pellets. Table 5 shows the process conditions used in this experiment. Since it was the first try to fabricate DUPIC pellets in Korea, lots of difficulties in remotely fabricating DUPIC pellets in hot cell were encountered, but it was very useful to understand the remote operation of the developed equipment and to confirm the process parameters which had been established in out-cell experiment prior to the main DUPIC fuel fabrication.

4. SUMMARY

In order to develop the optimum process conditions, a series of experiments were conducted in out-cell and in-cell. The direct measurement of DUPIC fuel properties is very difficult in a hot cell due to its high radioactivity. Hence, out-cell experiments to fabricate fuel pellets using natural uranium and SIMFUEL and in-cell experiments to fabricate DUPIC fuel pellets were carried out and the results are as follows:

- The properties of powder were more dependent on the number of OREOX cycles rather than treatment temperature.
- In fabrication of fuel pellets using the DUPIC process, a milling process improved the powder properties and enhanced the densification of fuel pellets.
- The optimum conditions for the fabrication of simulated DUPIC fuel pellet were well established.
- The optimum conditions for fabricating DUPIC fuel pellet were established and confirmed by in-cell experiments.

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TABLE 1 : CONTENTS OF THE ELEMENTS ADDED IN UO_2 POWDER

Elements	Composition(wt.%)
Zr (ZrO_2)	0.422
Mo (MoO_3)	0.392
Ru(RuO_2)	0.269
Pd (PdO)	0.187
Ba ($BaCO_3$)	0.218
La (La_2O_3)	0.143
Ce (CeO_2)	0.278
Pr (Nd_2O_3)*	0.131
Nd (Nd_2O_3)	0.476
Sm (Nd_2O_3)*	0.101
Sr (SrO)	0.084
Y (Y_2O_3)	0.052
Rh (Rh_2O_3)	0.049
Te (TeO_2)	0.058

* Pr and Sm were replaced by Nd_2O_3

TABLE 2: CHARACTERISTICS OF POWDER OXIDIZED AT VARIOUS TEMPERATURE

Temp. (°C)	Average particle size (μm)	Specific surface area (m^2/g)	Remarks
350	3.43	0.76	AUC
400	3.69	0.59	AUC
	3.83	0.63	ADU
450	4.23	0.52	AUC
	3.9	0.53	ADU
500	4.61	0.39	AUC
	4.70	0.49	ADU

TABLE 3: EFFECT OF OXIDATION TIME ON SPECIFIC SURFACE AREA AND POWDERED FRACTION OXIDIZED AT 400°C

Time (min)	Specific surface area(m^2/g)	Powdered fraction
10	0.56	0.058
20	0.71	0.172
30	0.80	0.336
40	0.71	0.497
50	0.643	0.619
60	0.641	0.784
70	0.647	0.904

TABLE 4: CHARACTERISTICS OF POWDER PRODUCED BY THE OREOX PROCESS
(Oxidized in air at 400°C and reduced in H_2 at 600°C)

No. of cycles	Particle size (μm)	Specific surface area (m^2/g)	Green density (g/cm^3)	Sintered density (g/cm^3)
Cycle 1	0.3579	5.70	6.588	8.115
Cycle 2	0.7447	4.10	6.279	9.048
Cycle 3	0.9695	3.15	6.034	9.585

TABLE 5 : OPERATING CONDITONS FOR IN-CELL EXPERIMENTS

	Process	Operating Condition			
		1st Experiment	2nd	3rd	4th
1	OREOX Process	3 Cycles of Oxidation and Reduction oxidation : 500°C, 1hr, air 1.0L/min reduction:700°C,2.0hrs, Ar/4%H_2, 1L/min Passivation : 80°C , 2hrs, Ar/2%O_2, 1L/min Heating rate : 4°C/min	Same as the 1st experiment	Oxidation : **450°C**, **4hrs**,air **3.0L/min** reduction:700°C, 2hrs, Ar/4%H_2, **3L/min**	oxidation : 450°C, **5hrs**,air 3.0L/min reduction:700°C, **3hrs**, Ar/4%H_2, 3L/min
2	Milling Process	Milling time: 24hrs	Milling time: 24hrs	Milling time : **2hrs**	Ball Milling : 2hrs
3	Pre-compaction Process	Manual Hydraulic Pump 0.8 ton/cm^2	**0.3 ton/cm^2, 0.5 ton/cm^2, 0.6 ton/cm^2, 0.8 ton/cm^2**	**0.2 ton/cm^2**	0.2 ton/cm^2
4	Final Compaction	Pressure : 0.8 ton/cm^2	0.8 ton/cm^2	**1.0 ton/cm^2** **1.2 ton/cm^2** **1.4 ton/cm^2**	**1.2 ton/cm^2**
5	Sintering Process	Sintering Temp. : 1700°C, 4hrs, Ar/4%H_2, 0.5L/min Heating rate : 4°C/min	Same as the 1st experiment	Sintering Temp.: 1700°C, 4hrs, Ar/4%H_2, **3.0L/min**	Sintering Temp. : 1700°C, 4hrs, Ar/4%H_2, 3.0L/min

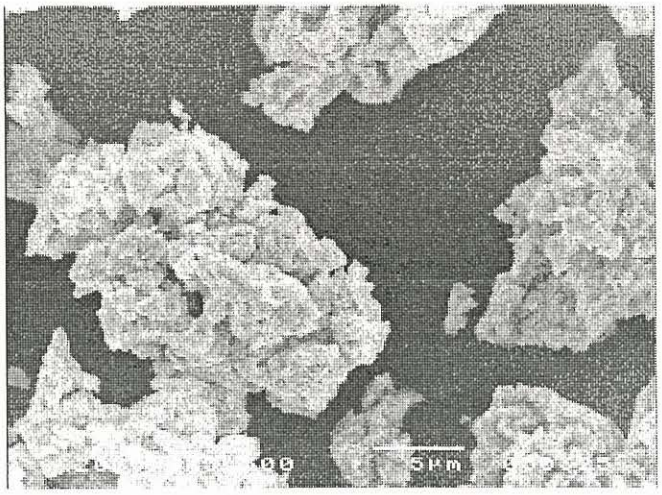


FIGURE 1 : SEM MICROGRAPHS OF THE OXIDIZED POWDER.

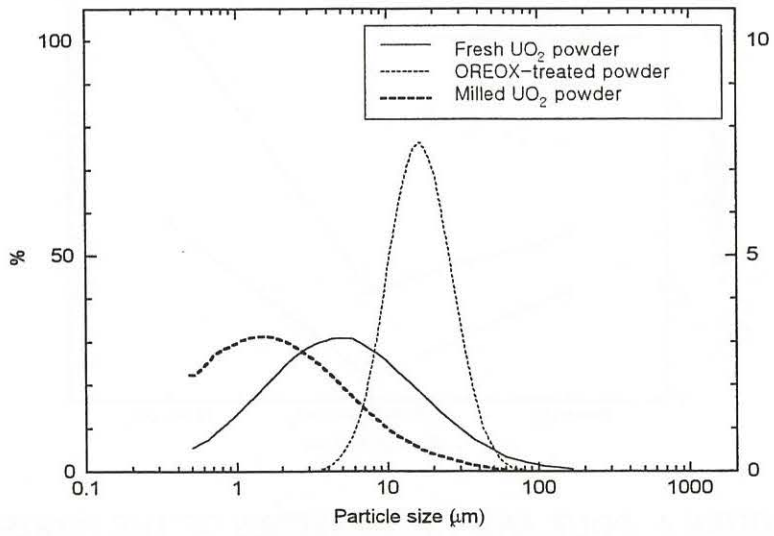
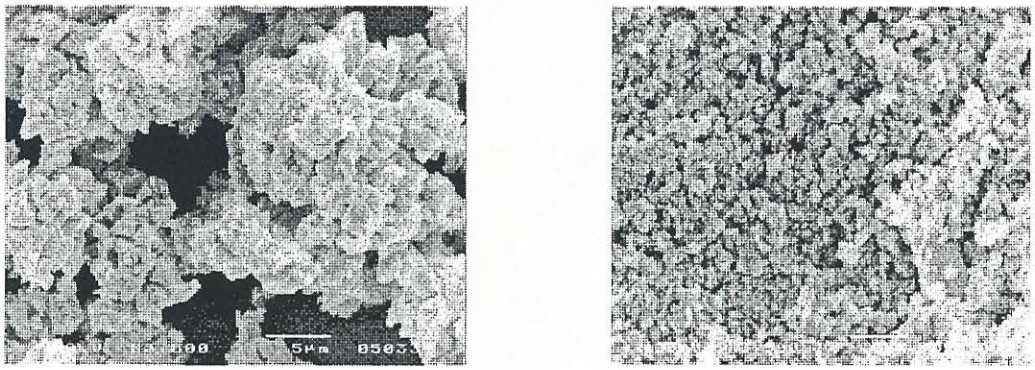


FIGURE 2 : PARTICLE SIZE DISTRIBUTION OF THE POWDERS



(a) OREOX-treated powder (b) Milled powder

FIGURE 3 : SEM MICROGRAPHS OF THE POWDERS.

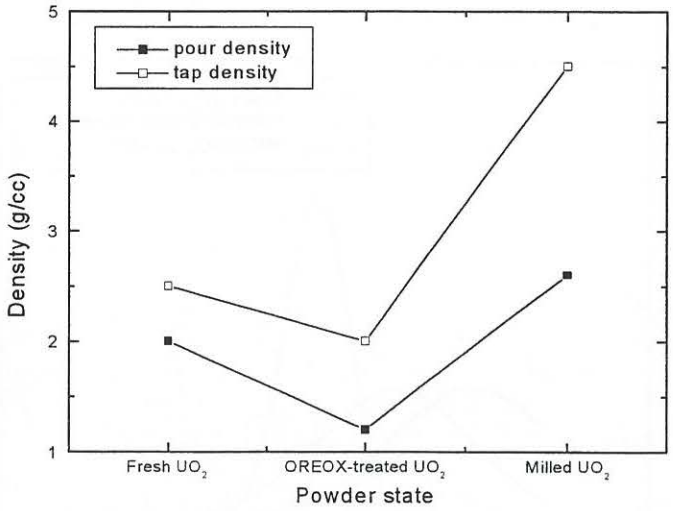


FIGURE 4 : POUR AND TAP DENSITIES OF THE POWDERS

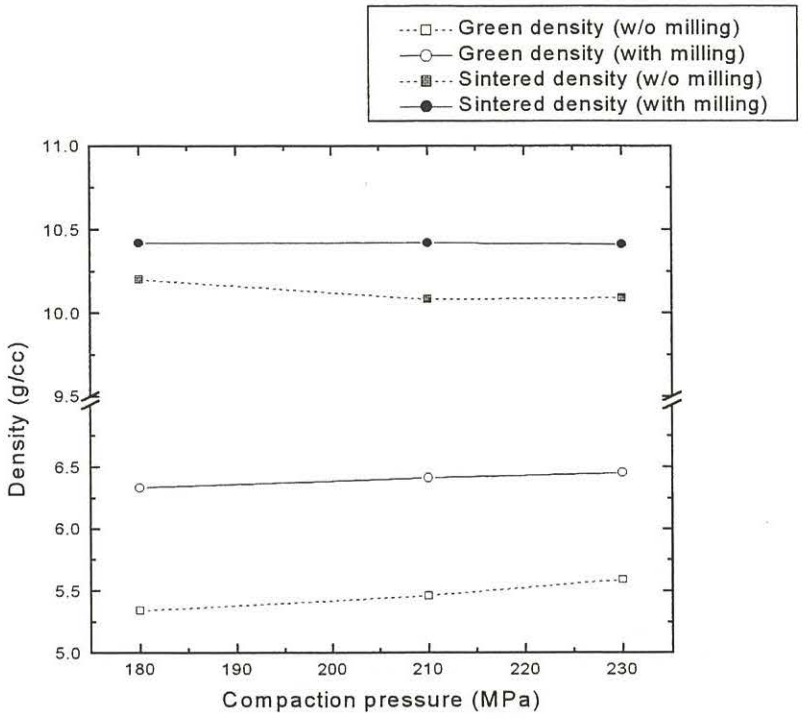


FIGURE 5 : VARIATIONS OF GREEN AND SINTERED DENSITIES AS A FUNCTION OF COMPACTING PRESSURE WITH/WITHOUT MILLING

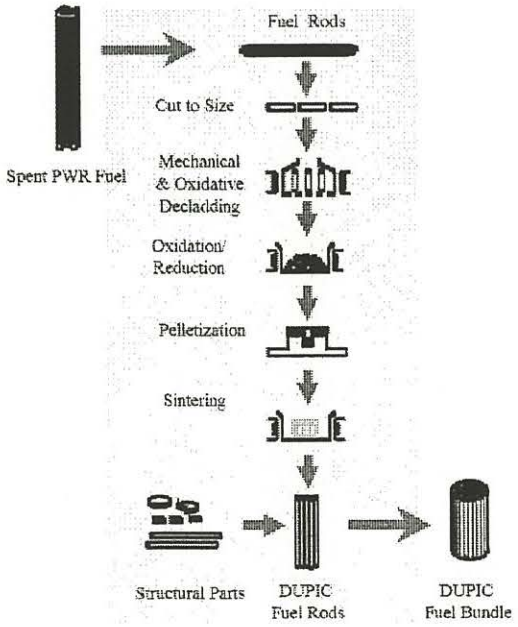


FIGURE 6 : THE SCHEMATIC DUPIC FUEL FABRICATION PROCESS