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Development of AUH Wet Reconversion Process

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1. Introduction

As a part of the uranium refinement and separation technology development project, we, the engineers at KEPCO Nuclear Fuel (KNF) have developed ammonium uranate hydrate (AUH) wet reconversion process. Based on the analysis results, chemical composition, particle shape, and characteristics of UO_2 powder prepared from this process are different compared to those of AUC and ADU process. Therefore, we name this process as AUH wet reconversion process.

As a result of this development, we have developed several process equipment (Crystallization Reactor and Pulsed Fluidized Bed Reactor (PFBR)), designed process, and performed the process by our own EPC (Engineering, Procurement, and Construction) work.

Generally, there are two types of reconversion processes in manufacturing nuclear fuel for PWR. One is wet process, and the other is dry process. The most important unit process in wet and dry processes is the crystallization of uranium compounds from solution and gas phase [1]. Uranium scrap, by-produced during manufacturing nuclear fuel, can be recycled in wet processes solely because both uranium hexafluoride (UF_6) and uranium nitrate hexahydrate (UNH) aqueous solution are used as feed materials. Therefore, dry processes certainly require additional wet processes to recycle uranium scrap. For this reason, wet processes are very important in a manufacturing process of UO_2 powder for nuclear fuel.

According to the intermediate, wet processes are generally divided into AUC and ADU process. The intermediate of AUC process is referred to as AUC (ammonium uranyl carbonate, $(NH_4)_4UO_2(CO3)_3$), and that of ADU process is referred to as ADU (ammonium diuranate, $(NH_4)_2U_2O_7$). According to the chemical composition of ADU, it is accurate to call ADU as ammonium uranate (AU) [2]. Nevertheless, the precipitate is usually referred to as ADU in the technical literature [3].

In order to move particles independently in the minimum fluidization state, the particle size distribution should be narrow, the shape of particles should be spherical, and the surface of particles should be smooth [4].

Since the mean particle size of AUC is 30 ㎛ and the shape of particles is spherical, a fluidized bed reactor (FBR) can be used in fluosolids reduction process. However, since the uranium content of AUC filtrate produced by PWR conversion plant and HWR conversion plant is 800ppm and 1,000ppm, respectively [5], filtrate treatment process must be required. In addition, a number of unit processes must be required such as exhaust gas treatment, waste treatment, methanol recovery, and incineration.

The mean particle size of ADU is less than 1 ㎛, and its particles form irregular agglomerates. For these reasons, a rotary kiln has been mainly used in fluosolids reduction process. ADU filtrate has an approximate concentration of 130ppm [6], so filtrate treatment must be required. Also, a number of unit processes must be required such as exhaust gas treatment, waste treatment, incineration, and powder pretreatment.

And to verify AUH wet reconversion process, ex-AUH UO_2 powder performance test has been performed, and the process procedures and analysis results are presented below.

2. Process procedure

In this section AUH wet reconversion process developed by the Uranium refinement & separation development team of KNF is described. We have experimented with four batches on commercial scale.

2.1 Crystallization process

As an initial solution, demineralized water and filtrate were fed in the crystallization reactor.

The initial solution was circulated and heated by a steam jacket. After this, ammonia gas was fed at the bottom of the reactor, and pure UNH solution was simultaneously fed to the top of the reactor via crystallization controller, which KNF has developed. For all experiments ammonia gas was fed until set pH. When reaching to set pH, the feeding of ammonia gas was stopped.

2.2 L/S Separation process

The final slurry was then filtered under the vacuum. The cake obtained was then washed with demineralized water and dried in a hot air dryer for 12 hours.

2.3 Fluosolids reduction process

The fluosolids reduction process was carried out in the PFBR. AUH powder was held into the reactor.

In the step of calcination, the calcination-reduction pulse supply chamber was filled with nitrogen gas. Then, nitrogen gas was supplied in the form of pulse more than the minimum fluidization velocity of AUH powder by using the solenoid valve.

In the step of reduction, the calcination-reduction pulse supply chamber was filled with the nitrogen-hydrogen mixed gas. Then, it was supplied in the same way as the step of calcination.

Stoichiometric UO_2 is not stable in the air at ambient temperature [7]. It absorbs oxygen in an exothermic process and the rate of absorption depends on the temperature, surface area of the powder, and the oxygen partial pressure [7]. With UO_2 powder of surface area greater than 3 ㎡/g, the rate of oxidation may be sufficiently high to make the powder pyrophoric [7]. It must therefore be stabilized by controlled oxidation before exposure to air, and then further oxidation proceeds slowly [7]. Before beginning of the stabilization step, nitrogen gas was supplied to cool down the internal temperature of the reactor until ambient temperature. The ex-AUH UO_2 powder cooled was stabilized by nitrogen-air mixed gas.

3. Results and discussion

3.1 Characteristics of AUH powder and filtrate

3.1.1 Estimation of chemical composition of AUH powder.

In ADU process, pure UNH solution reacts with ammonia gas or ammonia water to form ADU during the precipitation process. The chemical composition of ADU is shown in Table Ⅲ [8].

As mentioned previously, since pure UNH solution reacted with ammonia gas, the chemical composition of AUH was considered to be $xUO_3 \cdot yNH_3 \cdot zH_2O$ similar to ADU.

The molar ratio of uranium to nitrogen was 1:0.16 from Table Ⅳ (EDAX), and the uranium content of AUH was 62 wt%. Based on this analysis result, the chemical composition of AUH is considered to be $UO_3 \cdot 0.16NH_3 \cdot 5.33H_2O$.

Table Ⅲ: Chemical composition of ADU

	Chemical composition	Uranium content (wt%)
Ⅰ	$UO_3 \cdot 2H_2O$	73.9
Ⅱ	$UO_3 \cdot 0.33NH_3 \cdot 1.67H_2O$	74.0
Ⅲ	$UO_3 \cdot 0.50NH_3 \cdot 1.50H_2O$	74.0
Ⅳ	$UO_3 \cdot 0.67NH_3 \cdot 1.33H_2O$	74.1

Table Ⅳ: Result of EDAX

	Normal concentration (wt%)			
	Point 508	Point 511	Point 512	Average
Oxygen	17.80	18.19	19.01	18.33
Carbon	0.65	1.43	0.67	0.92
Nitrogen	0.75	0.82	0.73	0.77
Uranium	80.80	79.56	79.59	79.98

3.1.2 Variation of mean particle size of AUH slurry with pH.

The variation of mean particle size of AUH slurry with pH is shown Fig. 3. The mean particle size of all batches tended to increase from pH 4.5 to pH 6.0 and decreased thereafter.

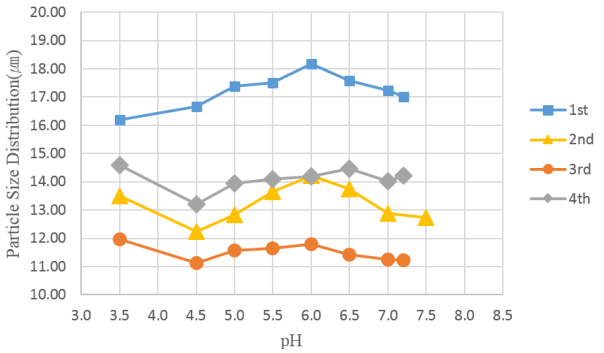

Fig. 3. Variation of mean particle size of AUH slurry with pH.

3.1.3 Particle size distribution of AUH powder.

Fig. 4 shows the particle size distribution of AUH powder of all batches. The particle size distribution of 1st and 4th batch was a mono-modal type having a peak value at the size of 16.23 ㎛, 13.7 ㎛, respectively, but that of 2nd and 3rd batch was a bi-modal type (2nd values: 2.914, 15.53 ㎛, 3rd values: 3.95, 13.85 ㎛).

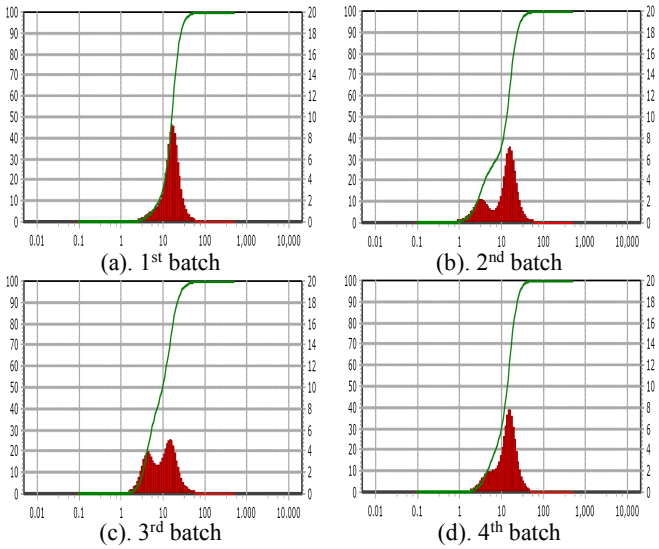

Fig. 4. Particle size distribution of AUH powder; (a) 1st, (b) 2nd, (c) 3rd, (d) 4th.

3.1.4 Variation of uranium content in AUH filtrate with pH and time.

The filtrate uranium content of every batch is shown in Table Ⅴ. The filtrate uranium content of 1st, 3rd, and 4th batch is 0.01ppm, and that of 2nd batch is 2.70ppm. Compared with AUC and ADU filtrate, the filtrate

uranium content of AUH process is reduced by up to 50 to 100,000 times.

Table Ⅴ: Uranium content of AUH filtrate

Batch no.	Uranium content (ppm)
1	0.01
2	2.70
3	0.01
4	0.01

3.2 Characteristics of ex-AUH UO_2 powder

3.2.1 Particle shape of UO_2 powder.

Fig. 4 shows the SEM image of ex-AUH UO_2 powder. The particle shape of ex-AUH UO_2 powder looks like a skein and is close to spherical. Also, its particle includes a number of very small pores.
Fig. 5 and Fig. 6 show the SEM images of ex-AUC UO_2 and ex-ADU UO_2 powder. The particle size of ex-AUC UO_2 powder is approximately 30 ㎛, and the particle shape is close to spherical. On the other hand, the particle size of ex-ADU UO_2 powder is less than 1 ㎛, and its particles form irregular agglomerates.

3.2.2 Particle size distribution of UO_2 powder.

The particle size distribution of ex-AUH UO_2 of every batch is shown in Fig. 7. The particle size distribution of 1st, 2nd, and 4th batch was a mono-modal type having a peak value at the size of 14.05㎛, 13,23㎛, and 12.36㎛, respectively. However, that of 3rd batch was a bi-modal type (values: 3.4, 12.2㎛).

Fig. 8 compares the particle size distribution of ex-AUC UO_2 and ex-ADU UO_2 powder and shows that the size distribution of ex-AUC UO_2 powder is a normal mono-modal type having a peak value at the size of 28 ㎛ [9], but that of ex-ADU UO_2 powder is a bi-modal type (values: 0.5, 5㎛) [9].

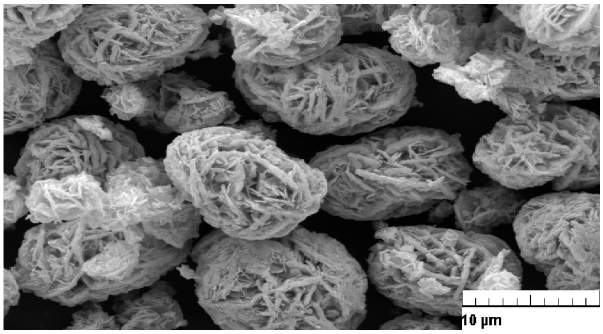

Fig. 4. SEM image of ex-AUH UO_2 powder.

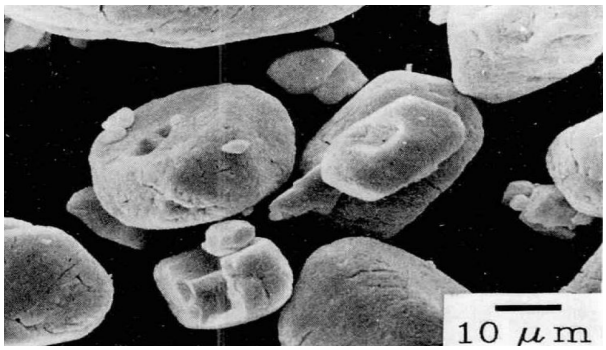

Fig. 5. SEM image of ex-AUC UO_2 powder.

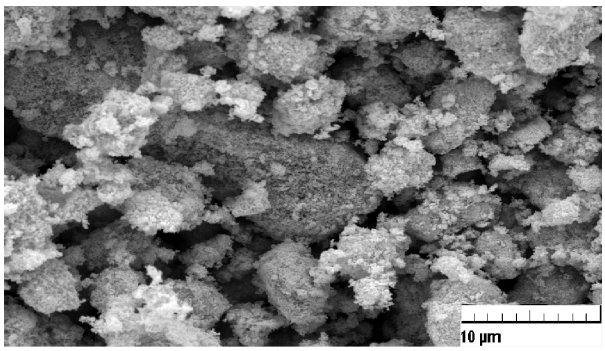

Fig. 6. SEM image of ex-ADU UO_2 powder.

3.2.3 Other properties of UO_2 powders.

Other properties (specific surface area, apparent density, and O/U ratio) of UO_2 powders prepared from wet reconversion processes are shown in Table Ⅵ [10].

As mentioned previously, since the particle of ex-AUH UO_2 powder includes a number of very small pores, it is considered to have a larger specific surface area than ex-AUC UO_2 and ex-ADU UO_2 powder do.

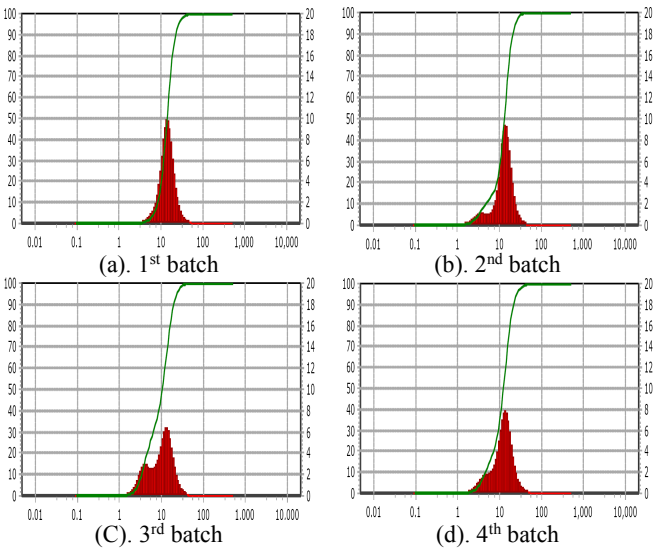

Fig. 7. Particle size distribution of ex-AUH UO_2 powder; (a) 1st, (b) 2nd, (c) 3rd, (d) 4th.

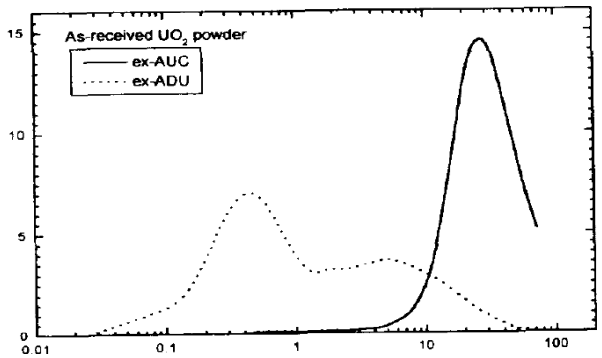

Fig. 8. Particle size distribution of ex-AUC UO_2 and ex-ADU UO_2 powder.

Table Ⅵ: Other properties of UO_2 powder

Properties	ex-AUH	ex-AUC	ex-ADU
Specific surface area (㎡/g)	6.93	5.00	3.00
Apparent density (g/㎤)	1.50	2.30	1.41
O/U ratio	2.19	< 2.15	< 2.14

3.2.4 ex-AUH UO_2 powder performance test.

The powder performance test was carried out to confirm whether it could be applied as UO_2 powder of nuclear grade for PWR or not.

The average results of 20 sintered pellets per batch are shown in Table Ⅶ. Both 1st and 2nd batch did not meet the specifications of sintered pellet for PWR. However, both 3rd and 4th batch met the specifications.

In case of 1st batch, the sinterability of powder decreased due to the reduction of the high temperature. In case of 2nd batch, the powder does not meet the specifications because the bottom heater of PFBR did not normally operate. In comparison to ex-ADU UO_2, ex-AUH UO_2 powder does not require the powder pretreatment processes.

Table Ⅶ: Results of ex-AUH UO_2 powder performance test

Batch no.	Sintered Density (g/㎤)	Rate of increase of re-sintered density (%)	Crystal grain size (㎛)
1	9.64	2.14	-
2	10.27	1.13	9.68
3	10.41	0.48	10.34
4	10.42	0.61	8.32
Spec.	10.30 ~ 10.58	≤ 1.0 % TD†	≥ 5.00

† Theoretical density

4. Conclusion

The results of the experiments described in this report lead to the following conclusions:

1) The unit processes of AUH wet reconversion process are simplified to crystallization, L/S separation, and fluosolids reduction. Especially, AUH wet reconversion process does not require additional unit processes such as filtrate treatment, waste treatment, methanol recovery, exhaust gas treatment, incineration, and so on.
2) Based on the analysis result of AUH, the chemical composition of AUH is considered to be $UO_3 \cdot 0.16NH_3 \cdot 5.33H_2O$.
3) By using the crystallization reactor, AUH powder, crystalline intermediate with large specific surface area, mono-modal distribution of particle size, and spherical shape is obtained.
4) The filtrate uranium content of AUH process is reduced by up to 50 to 100,000 times compared to that of AUC and ADU filtrate. Also, the handling of AUH powder is easy in subsequent processes after crystallization because the flowability is good compared to that of ADU powder.
5) As the result of the powder performance test, ex-AUH UO_2 powder prepared by using the PFBR meets the specifications; sintered density, a rate of increase of re-sintered density, and grain size.

Accordingly, we have come to the conclusion that the process in this report described could be applied to a manufacturing process of nuclear grade for PWR.

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