was investigated in this report and the result was obtained as expected. The second method is longer irradiation and the third is cooling after irradiation for an appropriate time. The last two methods utilize the difference between the half-lives of ^{32}P and ^{35}S . On the basis of the experiments connected with the irradiations for 5 hr in various holes of JRR-1, the extent to which the ratio of ^{32}P to ^{35}S can be reduced by these two methods was estimated. The results are summarized in Table 5. In the table values which correspond to irradiation for 5 hr and cooling for 0 day, are the experimental values and the others are estimated values. For the purpose of reducing the ratio, selection of position and cooling are more effective than

longer irradiation. Practically, however, cooling method may be considered inadequate, because the loss of ^{35}S by decay during the cooling is not small. Selection of position and longer irradiation, though the latter must be needed to produce sufficient amount of ^{35}S , are the most reasonable methods.

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研究論文

288. Reprocessing of UO_2 -dispersed Graphite Fuel, (I)

An approach to the mechanical recovery of uranium dioxide

二酸化ウラン分散-黒鉛系燃料の再処理, (I)

機械的分離方法による二酸化ウランの回収

By Kazumi IWAMOTO* and Junichi SHIMOKAWA*

An approach to recover UO_2 mechanically from the UO_2 -graphite fuel specimen was investigated. After disintegrating an unirradiated specimen by a pulverizer, ball mill, or micron mill, the obtained powder was separated into the UO_2 and graphite phases by a heavy-media-separation method in which a zinc-bromide solution was used as the heavy medium.

The disintegration of the specimen into fine powder was essential for the mechanical separation of UO_2 .

Additional treatments such as preoxidation of the sample, addition of dispersion agent to the zinc-bromide solution, and irradiation of the solution with the ultrasonic waves, were not effective in improving the UO_2 recovery.

However, it seemed that the grinding method coupled with continuous removal of the ground particles with fluid flowing would be effective in obtaining a high UO_2 recovery.

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I. INTRODUCTION

In the fuel which is composed of a mixture of one part by weight of powdered fissionable material, the grain size of which is about 5μ or less, with 10 to 50 parts of powdered graphite, most of the fission fragments with sufficiently high kinetic energy will recoil out of the fissionable material into the surrounding graphite. In reprocessing this type of fuel, preferable advantage has to be taken of the particular property of the graphite to trap and retain fission products*. A method should be devised whereby the graphite phase can be separated from the uranium phase and the fission products only or the nuclear material only can be removed from the fuel. Separation into the two phases could be made by several potential methods such as mechanical disintegration and separation, nitric acid leaching, chloride volatilization, and electrolytic disintegration in nitric acid solution.

The investigation described in this report has been made to provide information on the mechanical recovery of UO_2 from the graphite fuel. The mixture of UO_2 particles (average size, 8μ) and graphite powder was press-molded into pellets. The ratio of the graphite to the UO_2 was selected as 50 by weight. The densities of both natural and artificial graphite pellets were 1.90 g/cm^3 and 1.63 g/cm^3 , respectively. To recover the UO_2 from

the graphite by mechanical treatments such as separations by heavy media, flotation or magnetic susceptibility, the pellets must be disintegrated preliminarily. The primary purpose of this experiment was to find what types of grinding methods were preferable for the disintegration of pellets and subsequent recovery of UO_2 .

II. EXPERIMENTAL DETAILS

The UO_2 -graphite sample pellets of 40 mm in diameter and 20 mm in length were crushed by a hammer into a size of about 3 mesh, and the crushed materials were charged to grinders. Some of the sample pellets were heated under a stream of argon to investigate the effect of heating on recovery of the UO_2 . Examined were three types of grinding methods of which brief descriptions were given in Table 1.

- (1) Pulverizer Type Nara-M3 with a replaceable screen inside (see Fig. 1).
- (2) Micron mill Type Hosokawa with sample receivers of the micron mill, micron separator, cyclone separator and filter as illustrated in Fig. 2.
- (3) Wet grinding by a ball mill, from which powder samples were taken out at fixed times.

* This property of the graphite was applied to the fuel of the proposed Semi-Homogeneous Reactor, which has been developed at Japan Atomic Energy Research Institute.

Table 1 Experimental conditions of size reduction

Grinder	Pulverizer	Ball mill	Micron mill
Type	Nara-M3	180 mm ϕ $\times$ 180 mm ϕ	Hosokawa
Specification and performances	Replacement of screen (1mm ϕ or 0.25 mm ϕ aperture size) was done. One stage and two stages operations were carried out. Powder samples were taken at product receiver and bag-filter receiver. (see Fig. 1)	Wet grinding was performed in 1 l of water. Two types of loading of balls were done: ① 60 pieces of 25 mm ϕ ceramic balls in runs numbered C1XX; ② 42 pieces of 30 mm ϕ ceramic balls in runs numbered C2XX. Powder samples were taken at fix times.	The mill composed of two stages grinding. An opening of valve in line was controlled. Micron mill grinding system was consisted of micron mill, micron separator, cyclone separator, fan and bag filter. Four powder samples were collected. (Fig. 2)

Grinder		Pulverizer	Ball mill	Micron mill
Type		Nara-3M	180 mm ϕ $\times$ 180 mm ϕ	Hosokawa
Feeds to grinders	Coarse size reduction	By hammar	By hammar	By Nara-M3
	Type of raw sample pellets	Both natural and artificial graphite- UO_2 pellets (wt. ratio 50 : 1) Unirradiated by thermal neutron	Natural graphite- UO_2 pellet (wt. ratio 50 : 1) Unirradiated by thermal neutron	Natural graphite- UO_2 pellet (wt. ratio 50 : 1) Unirradiated by thermal neutron
	Heat treatment history of sample pellets	(1) None (2) 1,000°C, 54 hr (3) 1,200°C, 47 hr	(1) None (2) 1,000°C, 54 hr	(1) None

A: Bag filter S: Screen
PP: Powder sample from pulverizer
FP: Powder sample from bag filter

Fig. 1 Grinding by pulverizer

M: Micron mill MS: Micron separator
C: Cyclone B: Blower
V: Valve F: Bag filter
MP: Powder sample from micron mill
SP: Powder sample from micron separator
CP: Powder sample from cyclone separator
FP: Powder sample from bag filter

Fig. 2 Grinding by micron mill

The following three methods were used to determine the size distribution of the ground particles: (1) Microscopic method, (2) Sedimentation method by an autobalance, (3) Sedimentation method using a labeled nuclide. Neglecting the small amount of the UO_2 in the powder sample, the apparent size distribution of the graphite particles were obtained by the method (1) or (2). To determine the apparent size of the UO_2 particles, the powder samples were irradiated with thermal neutrons and were settled in a sedimentation tube. The γ activity of ^{239}Np at the bottom of the tube was measured by a scintillation counter instead of measuring the weight of UO_2 settled. This method would give only the apparent size of the UO_2

particles. Some of the results obtained are shown in Table 2 and Fig. 3, and will be discussed in Chap. III.

Separation of the ground powder sample into the UO_2 and graphite phases was carried out by heavy-media-separation method. A zinc-bromide solution was selected as the heavy medium, because the density should lie between the densities of the UO_2 and graphite. The zinc-bromide solution dispersed with sample powders were centrifugalized until the graphite and UO_2 phases were separated. The amounts of UO_2 in both phases were analyzed to determine the total recovery of UO_2 and the UO_2 content in the recovered UO_2 phase.

Table 2 Description on samples

Sample No.	Pellets		Grinding		$\mu_p^{(2)}$	$\mu_u^{(3)}$	UO ₂ content (%)
	Graphite	Heat treat.	Type of grinder	Conditions of grinding			
A1P ⁽¹⁾	Art.	None	Pulverizer	1 mm ϕ screen, one stage	54	...	2.62
A1F	"	"	"	"	33	...	2.48
A2P	"	"	"	0.25 mm ϕ screen, one stage	20	...	2.70
A2F	"	"	"	"	15	8.0	2.52
B1P	Nat.	"	"	0.25 mm ϕ screen, one stage	36	5.6	3.39
B1F	"	"	"	"	18	...	3.87
B2P	"	"	"	0.25 mm ϕ screen, two stages	30	4.8	3.57
B2F	"	"	"	"	17	...	3.64
D1P	"	1,000°C	"	0.25 mm ϕ screen, one stage	32	...	3.10
D1F	"	54 hr	"	"	30	...	4.13
D2P	"	1,200°C	"	0.25 mm ϕ screen, one stage	31	...	3.14
D2F	"	47 hr	"	"	29	...	4.56
D3P	"	"	"	0.25 mm ϕ screen, two stages	33	...	3.25
D3F	"	"	"	"	29	...	4.55
C111	"	None	Ball mill ⁽⁴⁾	16 hr	23	6.3	2.23
C112	"	"	"	44 "	"	5.9	2.14
C211	"	"	"	1 "	...	...	2.20
C212	"	"	"	24 "	26	5.8	2.20
C213	"	"	"	44 "	25	5.3	2.20
C121	"	1,000°C	"	1 "	...	7.2	2.20
C122	"	54 hr	"	16 "	23	...	2.20
C123	"	"	"	59 "	22	...	2.20
C221	"	1,200°C	"	1 "	26	7.3	2.14
C222	"	47 hr	"	16 "	26	...	2.14
C223	"	"	"	59 "	23	6.9	2.14
M1A	"	None	Micron ⁽⁵⁾ mill (SP)	...	...	...	2.75
M2B	"	"	" (CP)	...	...	...	1.93
M3C	"	"	" (MP)	...	...	...	3.16
M4C	"	400°C 5 hr	" (MP)	...	...	...	3.16

- (1) "P" shows a sample powder in a product receiver. "F" shows a sample powder captured by a bag filter.
 (2) Weight mean diameter (μ) of the powder. (3) Weight mean diameter (μ) of UO₂ in the powder.
 (4) Ball mill was used in two ways. See Table 1. (5) See Fig. 2.

(1) Ground powder of graphite (before separation), average size, 23 μ

(2) UO₂ in ground powder (before separation), average size, 6.3 μ

(3) UO₂ in graphite phase (after separation), average size, 5.4 μ

Fig. 3 Particle size distribution of sample C111

III. EXPERIMENTAL RESULTS AND DISCUSSION

Effect of the density of the zinc-bromide solution on separation of the UO_2 and graphite phases was investigated using sample B2P. Results obtained are illustrated in Fig. 4. Properties of the zinc-bromide solution are given in Table 3. With increase in the density of the solution, UO_2 recovery decreased, while both UO_2 content in the recovered UO_2 phase

Fig. 4 Effect of density of zinc-bromide solution on UO_2 separation

and DF_g increased. Here, the term DF_g is one of the measures of the separation and defined as

$$\frac{(\text{wt. of graphite/wt. of } \text{UO}_2)_{\text{raw material}}}{(\text{wt. of graphite/wt. of } \text{UO}_2)_{\text{recovered } \text{UO}_2 \text{ phase}}}$$

From these results, the density of the zinc-bromide solution was chosen as 2.55 g/cm^3 in further experiments to investigate whether or not the powder samples obtained by the three types of grinding would be preferable for the recovery of UO_2 .

Table 3 Properties of zinc-bromide solution

Run No.	Density (g/cm^3)	Viscosity (c.p.)	Surface tension (dyne/cm)	Remarks
E1	2.17	12	—	
E2	2.27	17	70	
E3	2.35	22	69	
E4	2.44	35	68	
E5	2.60	80	65	
E6	2.66	—	59	
F1	2.43	—	67	Saturated with HMP
F2	2.45	—	52	Saturated with sodium oleate
F3	2.34	21	47	Ditto

Table 4 gives the results obtained for the recovery of UO_2 from the ground powder samples by the zinc-bromide solution of density 2.55 g/cm^3 . They will be discussed in the following.

Table 4 Experimental results

Run No.†	Recovery of UO_2		Remarks	
	Content of UO_2 (%)	Recovery (%)	Grinding method	Pre-treatment
A1P	78	56	Pulverizer	None
A1F	54	20	"	"
A2P	82	58	"	"
A2F	39	38	"	"
B1P	80	65	"	"
B1F	67	27	"	"
B2P	71	51	"	"
B2F	45	33	"	"

† Run No. corresponds to the sample No. given in Table 2.

Run No.	Recovery of UO_2		Remarks	
	Content of UO_2 (%)	Recovery (%)	Grinding method	Pre-treatment
D1P	84	51	Pulverizer	Heating of sample pellet
D1F	66	38	"	"
D2P	87	50	"	"
D2F	91	30	"	"
D3P	86	36	"	"
D3F	72	26	"	"
C111	57	44	Ball mill	None
C112	46	18	"	"
C211	43	41	"	"
C212	61	36	"	"
C213	46	21	"	"
C121	39	48	"	Heating of sample pellet
C122	53	42	"	"
C123	37	18	"	"
C221	54	52	"	"
C222	56	40	"	"
C223	29	18	"	"
M1A	97	80	Micron mill	None
M2B	96	79	"	"
M3C	95	46	"	"
M4C	86	50	"	"
F1	73	47	Pulverizer	Dispersion media was added.
F2	71	52	"	"
F3	46	53	"	"
H0	80	37	"	None
H1	96	38	"	Irrad. by ultrasonic wave
H2	91	42	"	"
H3	90	43	"	"
H4	90	43	"	"
I1	92	46	"	Heating of sample powder
I2	98	25	Ball mill	None
I3	91	29	"	Heating of sample powder
I4	81	14	"	"

(1) For the powder obtained by a pulverizer

Data for the recovery of UO_2 from the unheated ground-powder samples obtained by the pulverizer are given for runs A1P to B2F in Table 4. In both cases of the natural and artificial graphite samples, the product-powder

samples (with letter P in sample numbers) showed higher UO_2 recovery and UO_2 content than the powder samples (with letter F) collected in the bag filter. The former showed about 60% UO_2 recovery and about 80% UO_2 content, but these results were not satisfactory for fuel reprocessing.

(2) For the powder obtained by a ball mill

Only the natural graphite pellets were ground by the ball mill. Data for the separation of ground powder samples taken out at fixed times are given for runs C111 to C223 in Table 4. It is noted that recovery of UO_2 decreased with increase of grinding time. This may suggest that the batch ball-milling would tend to associate the ground graphite and UO_2 particles rather than promoting their ultimate separation. Therefore, the batch ball-milling seems to be undesirable for disintegration of this type of pellets. Preheating of the charging pellets did not seem to influence the recovery of UO_2 . Maximum

recovery obtained was 52% for run C221.

The particle size distribution of the UO_2 varied considerably with the general tendency as shown in Fig. 3, namely the weight fraction of UO_2 particles having larger sizes decreased in the separated graphite phase.

Photographs, by an electron microscope, of the powder samples of the raw material, the recovered UO_2 phase and graphite phase are shown in Plate 1 (1)~(3). It is seen from these photographs that the UO_2 particles remaining in the graphite phase are "twisted" with graphite particles. Therefore "twisted" UO_2 particles should be segregated beforehand in order to obtain a higher UO_2 recovery.

Plate 1 Electron-microscopic photographs of powder samples

(3) For the powder obtained by a micron mill

A micron mill was used to obtain finer powder than that obtained by a pulverizer or a ball mill. The feed material to the micron mill was the powder obtained by the pulverizer. The powder samples SP, CP and MP obtained from the mill (see Fig. 2) were tested; their data are given for runs M1A to M4C in Table 4. The runs M1A and M2B showed a 97% UO_2 content and 80% recovery in the UO_2 phase, and these values were the highest of all the runs tested. These results seem to be due to the grinding mechanism of the micron mill; when using this mill, segregation of the "twisted" UO_2 from the graphite particles further proceeded providing a continuous removal of the ground particles under air sweeping. It is suggested that the grinding method coupled with continuous

removal of the ground particles would be very effective in obtaining a higher recovery and large content of the UO_2 , although the problem of radioactive contamination seems to be rendered more difficult.

(4) For the powder obtained by other treatments

(a) Effect of preheating sample pellets on the grinding performance and separation by zinc-bromide solution was examined. Sample pellets were heated under a stream of argon for 54 hr at $1,000^\circ\text{C}$ and for 47 hr at $1,200^\circ\text{C}$. These preheated samples were ground by the pulverizer or by the ball mill (see Table 2). Only a little difference was found in particle-size distribution between the heated and unheated ground powders under the same grinding conditions.

Data obtained by the separation treatment are given for runs D 1 P to D 3 F and C121 to

C223 in Table 4. As seen from these results, no substantial effect was observed.

(b) Effect of the oxidation of UO_2 in the pellet or powder into U_3O_8 on the separation was also tested expecting that volume change of the UO_2 will contribute to the detachment of "twisted" UO_2 particles from the graphite particles. Oxidation treatments at 500°C for both the sample pellets and ground powder are summarized in Table 5. Separations obtained are given for runs I 1 to I 4 in Table 4. Although the UO_2 content reached as high as 98%, the oxidation did not give any effect on the recovery of UO_2 . The oxidation treatment would be effective only in aggregating UO_2 particles of larger size.

Table 5 Oxidation treatment of sample powder and pellet

Run No.	Sample material		Oxidation treatments (under oxygen)
	Sample No.	Type of sample	
I 1	B1 P	Powder	Heated at 500°C for 6 hr.
I 2	B1 P	"	None, sample powder B1 was ground by a ball mill.
I 3	I 2	"	Sample powder I 2 was heated at 500°C for 6 hr.
I 4	B	Pellet	Heated at 500°C for 6 hr, and ground by a ball mill for 72 hr.

(c) Effect of addition of dispersion agent on the separation was tested. Sodium oleate or hexa-metha-sodium phosphate was added to the zinc-bromide solution dispersed with graphite and UO_2 particles. Results for the recovery of UO_2 are given for runs F 1 to F 3 in Table 4. Comparison of runs E 4 with F 1 and F 2, or E 3 with F 3 reveals that addition of dispersion agent is not effective for improving the recovery of UO_2 .

(d) Zinc-bromide solution and 99% ethyl-alcohol solution, both dispersed with graphite and UO_2 particles, were irradiated with ultrasonic waves, expecting that an appropriate irradiation would detach "twisted" UO_2 particles from the graphite particles. Conditions of the irradiation applied are summarized in Table 6. The results obtained for runs

H 0 to H 4 in Table 4 show that irradiation tested is not effective in improving the recovery of UO_2 .

Table 6 Irradiation by ultrasonic wave

Run No.	Sample powder	Irradiation conditions
H 0	B 3	Unirradiated
H 1	B 3	500 kc for 30 min, sonic pressure, 3.8 bar, in ZnBr soln.
H 2	B 3	500 kc for 30 min, sonic pressure, 3.8 bar, in alcohol
H 3	B 3	30 kc for 1 hr, sonic pressure, 13 bar, in ZnBr soln.
H 4	B 3	30 kc for 1 hr, sonic pressure, 13 bar, in alcohol

IV. CONCLUSIONS

The approach to recover UO_2 mechanically from the graphite- UO_2 samples ground by the pulverizer, ball mill and micron mill was investigated. The recovery of UO_2 was not satisfactory in all cases except in the runs for the powder samples obtained by the micron mill. The latter runs gave an 80% UO_2 recovery and 97% UO_2 content in the recovered UO_2 phase, and these were the highest of all the runs tested. Additional treatments, such as preoxidation of the sample, addition of dispersion agent to the zinc-bromide solution, and irradiation of the zinc-bromide solution with ultrasonic waves, were not effective in improving the UO_2 recovery. However, the grinding method coupled with continuous removal of the ground particles under fluid flowing would be effective in obtaining a higher UO_2 recovery.

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