

## SESSION 3

### **FUEL FABRICATION**

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# Preparation of ceramic grade $UO_2$ powder by atomization from uranyl nitrate solutions

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The thermal denitration of a nitrate solution by direct conversion to a ceramic grade uranium dioxide powder, in a furnace that combines atomization nozzle and gas stirred bed, is an attractive method because no liquid waste products are formed and it has relative simplicity.

The  $UO_2$  powder characteristics, such as size, shape, specific surface area and sinterability as a function of procedural variables were determined. This technique has been developed in the pelleting pilot plant of the IPEN/CNEN-SP and it appears to be practical and economically feasible for wet recovery of rejected  $UO_2$  powders and pellets from production process, with the recovered powder being directly mixed to the powder from the AUC reduction process.

## 1. Introduction

In the regular production of  $UO_2$  nuclear fuel pellets, about 10% of the powder used can turn as scrap. Scrap occurs as green bodies, sintered pellets and slurry of the grinding machine. The different kinds of scrap are preferably processed as uranyl nitrate in a wet chemical method, e.g. AUC [1,2] or ADU [3] precipitation and recovered as  $U_3O_8$  or powder in the process of pellet fabrication.  $U_3O_8$  produced by calcination of scrap pellets and  $UO_2$  grinding swarf is used in the fabrication of  $UO_2$  pellets with AUC powder improve to the cycle economy, to equalize different lots, to adjust the distribution of porosity and to decrease the final density [4]. The recovery of scrap by a wet chemical process always produces aqueous waste solutions with small ( $\sim 500 \mu\text{g/L}$ ) quantities of uranium [5]. This uranium should be recovered by a suitable recycling process. Therefore, in a  $UO_2$  pellet production pilot plant it would be convenient to have the direct conversion of uranyl nitrate solutions, prepared from  $UO_2$  scrap powders, to standard  $UO_2$  powder. The powder produced would then be mixed with that reduced from AUC.

The most direct and probably simplest method of converting a nitrate solution to an oxide powder is denitration. Unlike other methods, only heat is required and no waste products are formed. Water and  $NO_n$  vapors generated during thermal decomposition may be converted

back to nitric acid and recycled to prepare the uranyl nitrate solution.

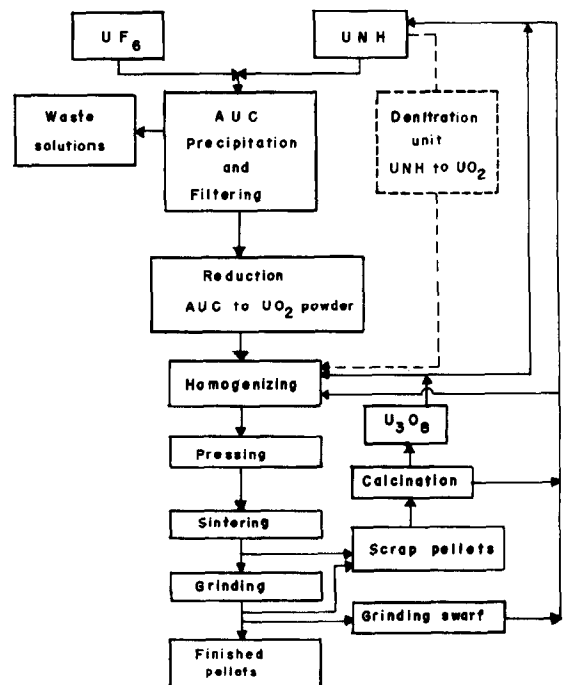


Fig. 1. Flow sheet of the  $UO_2$  pellets production.

A simple thermal denitration has been employed for the conversion of uranyl nitrate solution to  $UO_2$  for preparation of  $UF_4$ . Reviews of previous literature on the most important conversions routes of uranyl nitrate to  $UO_2$  suitable for fabrication of fuel pellets are given in ref. 6.

In continuous methods the denitration of uranyl nitrate has been carried out by addition of a concentrated aqueous solution to a hot layer of  $UO_3$  in a horizontal stirred bed and it is subsequently reduced to  $UO_2$  by hydrogen [7]. The direct reduction of uranyl nitrate solutions by a high temperature flame reactor is another special process; a concentrated uranyl nitrate solution together with a solution of formic acid is injected into a chamber at about  $300^\circ C$  using air or a  $H_2/N_2$  mixture as carrier gas; the uranium oxides  $U_3O_8$ ,  $UO_3$  are obtained [9].

Hydrothermal and microwave denitration were studied earlier. Hydrothermal denitration involved heating hydrated thorium nitrate crystals in a steam atmosphere using a rotary tube furnace [10]. In ref. [11] the microwave denitration for preparing thorium-urania powders was investigated and in ref. [12] Koizumi reported on the

preparation of urania-plutonia powders.

This paper describes the thermal denitration of uranyl nitrate hexahydrate (UNH) solutions in a furnace that combines an atomization nozzle and a gas stirred bed. The final goal is to demonstrate the influence of procedural variables, e.g. temperature and pressure atomization, on the  $UO_2$  powder characteristics.

The procedure actually adopted for obtaining experimental  $UO_2$  pellets at Nuclear Energy Research Institute is described in fig. 1 and the direct denitration has been studied to reduce the production steps.

## 2. Experimental procedures

The uranyl nitrate-water system was investigated by previous workers [13]. Uranyl nitrate hexahydrate,  $UO_2(NO_3)_2 \cdot 6H_2O$ , decomposes in air at temperatures of  $200$  to  $500^\circ C$  to  $UO_3$  with liberation of  $NO_2$ ,  $O_2$  and water vapor:

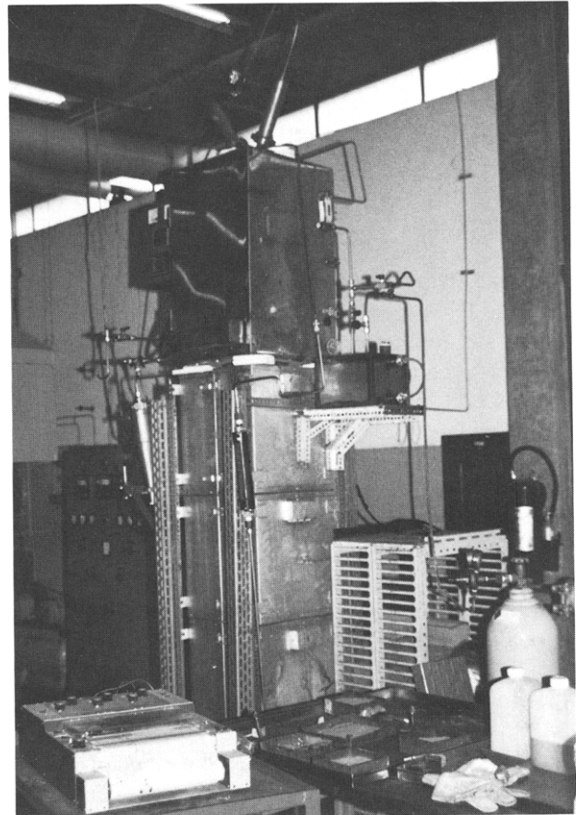
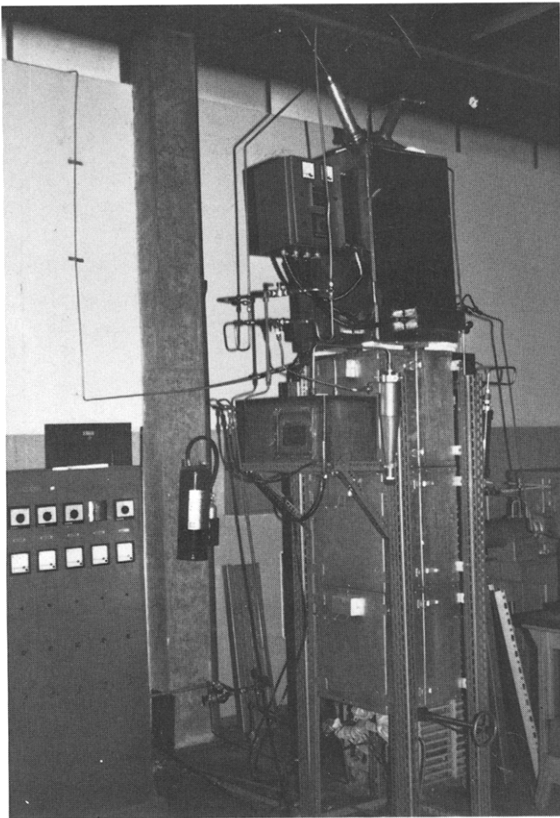
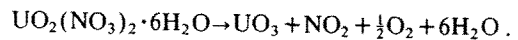


Fig. 2. Laboratory scale denitration unit.

It is desirable to concentrate the solution as much as possible prior to denitration, because major amounts of energy and time are consumed to evaporate excess water. Therefore, the uranium concentration in the nitrate solution chosen for this work was close to the solubility limit

at room temperature. Uranyl nitrate (UNH) solution was prepared by dissolving  $U_3O_8$  with reagent grade 4N  $HNO_3$  to a heavy element concentration of 400 g U/L.

The preparation of  $UO_2$  powder from the UNH solution is carried out in a two step batch process. The solu-

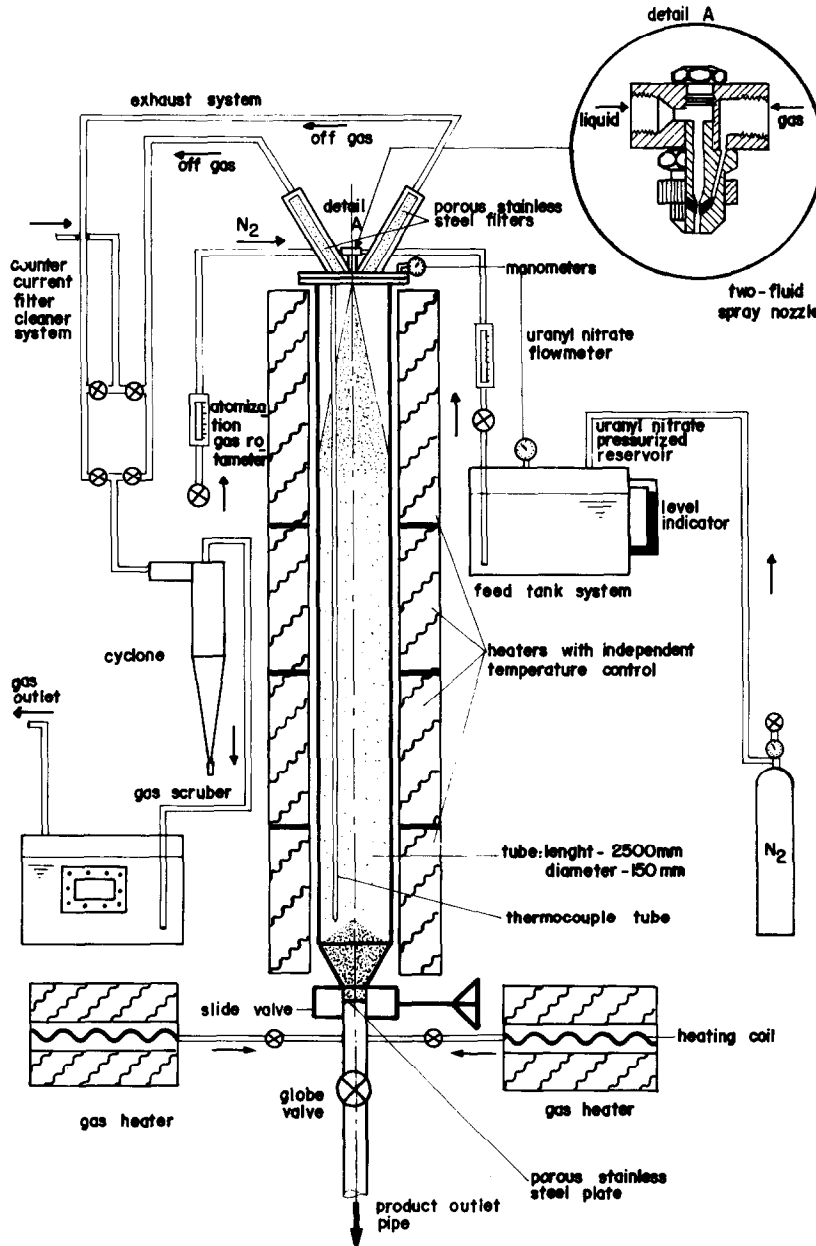


Fig. 3. Schematic drawing of the denitration furnace.

tion is sprayed into a stream of hot air/nitrogen which flows inside a cylindrical chamber to give a very reactive uranium oxide. When decomposition is complete, this oxide is then reduced to  $UO_2$  with hydrogen introduced through a porous metal distribution plate at the furnace bottom. Fig. 2 shows the denitration unit.

### 2.1. Description of the apparatus

A schematic diagram of the apparatus used in the UNH decomposition study is shown in fig. 3. The furnace consists of a vertical 150 mm diameter stainless steel tube with a porous gas distribution plate at the bottom. In the upper part of the reaction tube is the atomization nozzle and a sintered porous metal filter to remove the particles carried up by the fluidizing gas. The 2 500 mm high furnace is heated with a radiation heater divided into 4 heating elements, each one controlled by an on-off temperature controller actuated by a thermocouple in the furnace. The off-gases having passed through the metal filter and through a cyclone, are then transferred to the absorption washer. The sintered metal filters when clogged with powder blown up from the reaction tube, are blown back with a short time  $N_2$  pressure blast.

The solution is fed into the furnace from the  $N_2$  pressurized upper reservoir; flow rate was measured by a rotameter in the line. The fluidization gas ( $N_2$  or  $H_2$ ) pre-heater is an integral part of the furnace as shown in fig. 3.

The nozzle is of the two fluid type, as shown in fig. 3

(detail A). The UNH solution is fed through the 0.8 mm diameter central hole, and by a current of compressed nitrogen, introduced through the concentric external hole.

### 2.2. Operating characteristics

The properties of the powders can be controlled within the restraints imposed by dimensions of the denitration chamber, type of nozzle, decomposition time and temperature, as well as the pressure of the atomizing gas. The effect of the operating temperature is important both in relation to the chemical composition of the product and to particle size control.

In this work the decomposition reaction at 300, 400, 500 and 600 °C in the upper section of the furnace was first studied, maintaining the other three heating zones at 600 °C. The denitration temperature was measured by a thermocouple positioned a little below the spray nozzle.

The atomization gas was nitrogen and the fluidizing gas was preheated air or hydrogen.

The flow rate of the uranyl nitrate solution containing 400 g U/L for all experiments was maintained constant at 50  $cm^3/min$ , the pressure being  $2.5 \times 10^5$  Pa.

Subsequently the influence of the atomization gas pressure in the range of 2 to  $5 \times 10^5$  Pa on the powder properties was investigated.

Two procedures were adopted for the decomposition. In the first there were two steps: (a)  $U_3O_8$  was produced in the atomization furnace with air as fluidizing gas; (b)

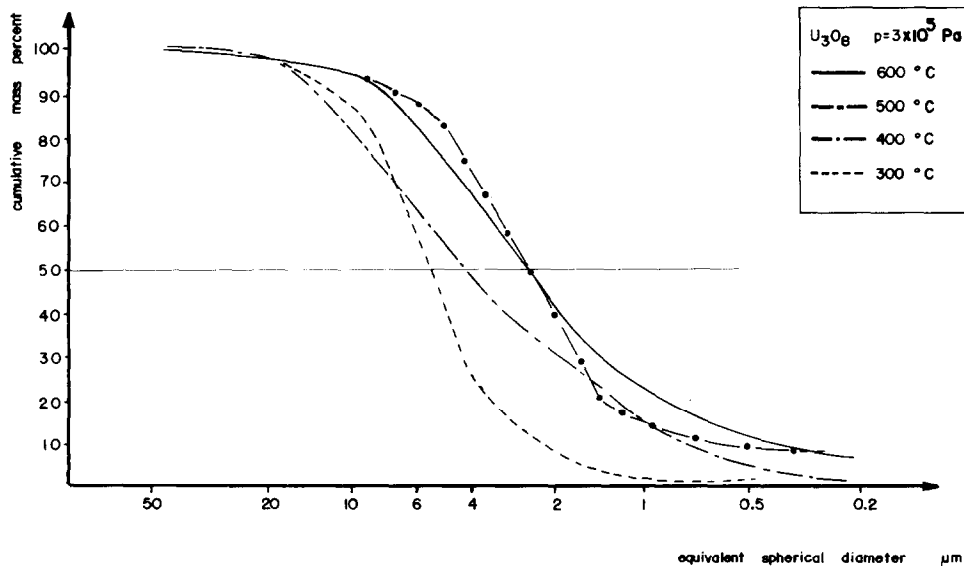


Fig. 4. Variation of  $U_3O_8$  particle size distribution with the denitration temperature.

Table 1  
The effect of the operating temperature and pressure on the  $UO_2$  particle size

UO <sub>2</sub> run	P ( $\times 10^5$ Pa)	T (°C)	Mean diameter ( $\mu$ m)	Mass percent		
				< 2 $\mu$ m	2 $\leq x \leq$ 10	> 10 $\mu$ m
3	3	600	6.0	12	75	13
4	3	500	6.6	17	58	25
5	3	400	6.2	12	65	23
6	3	300	6.4	6	70	24
7	4	600	6.8	5	70	25
8	4	500	5.8	4	76	20
9	4	400	4.4	7	79	14
10	4	300	5.2	4	84	12
11	5	600	5.0	2	81	17
12	5	500	5.5	5	77	17
13	5	400	5.4	4	80	16
14	5	300	6.7	5	69	26
17	2	400	9.0	10	58	32
18	2	500	6.2	3	77	20

The obtained  $U_3O_8$  was reduced to  $UO_2$  in an  $H_2$  atmosphere muffle furnace.

In the second the material was reduced to  $UO_2$  directly in a single step process, using in the atomization furnace an  $H_2$  fluidizing atmosphere (fig. 3).

### 3. Results and discussion

Fig. 4 shows the effect of the denitration temperature on the particle size distribution of  $U_3O_8$  powder, for a fluidization gas pressure of  $3 \times 10^5$  Pa. The mean particle size appears to become smaller with the increase of the UNH decomposition temperature.

A probable explanation for this phenomenon is the rapid vaporization of water and nitrate, producing frac-

ture in the particles. Nevertheless, the results indicate that for higher gas pressures this dependence becomes unnoticable. At high pressures a large number of drops concentrate at the bottom and wall of the reaction tube, increasing the possibility for agglomeration. The maximum fluidization gas pressure depends upon the ability of the fluidized bed to distribute the spray droplets. Besides, lower temperature tends apparently to promote agglomeration of particles with this type of feed.

The particle size distributions were measured using an X-ray monitored sedimentation technique.

In the reduction of  $U_3O_8$  powder in a muffle furnace at  $600^\circ C$  with hydrogen, the variation of particle size with the denitration parameter is even less pronounced, as shown in fig. 5. Moreover it was observed that mean particle size became larger, probably due the formation of granules during the reduction process.

In order to determine the effect of the operating temperature and pressure on the particle size of the product, several runs were carried out and the results are summarized in table 1.

Fig. 6 illustrates the variation in the bulk density of the  $UO_2$  powder for different denitration conditions. It is seen from fig. 6 that at a denitration temperature higher than  $500^\circ C$  the difference falls into a band of  $\pm 0.2$  g/cm<sup>3</sup>, indicating a less pronounced influence of the denitration parameters on the results. This conclusion may be checked too by plotting the specific surface area of  $UO_2$  and  $U_3O_8$  powder in terms of the denitration temperature and fluidization gas pressure, fig. 7. When this is done, it is seen that the BET values exhibit a dependence more noticeable with the denitration temperature than with pressure. This effect is similar to the particle size distribution.

The porosity distribution of  $UO_2$  powders obtained from  $U_3O_8$  in different denitration conditions is shown in fig. 8. In fig. 8A it is evident that for high temperatures smaller pores are formed during the denitration. Nevertheless, it should be noted in fig. 8B that larger pores (around 1  $\mu$ m) are formed at  $600^\circ C$  and  $5 \times 10^5$  Pa.

Table 2  
The variation of the apparent and final density of the  $UO_2$  powder with the denitration temperature

UO <sub>2</sub> run	P ( $\times 10^5$ Pa)	T (°C)	$D_A$ (g/cm <sup>3</sup> )	$D_F$ (g/cm <sup>3</sup> )	OPF (%)	CPF (%)	Bulk density (g/cm <sup>3</sup> )	BET (cm <sup>2</sup> /g)
3	3	600	2.81	9.90	71.3	3.2	0.58	4.9
6	3	300	3.75	9.93	62.2	3.6	1.16	3.4
7	4	600	2.34	9.85	76.2	2.4	0.71	4.4
10	4	300	2.85	10.07	71.7	2.3	0.65	3.7
11	5	600	3.88	9.36	58.6	6.0	0.65	2.6
14	5	300	3.77	9.05	59.7	5.9	1.49	2.3

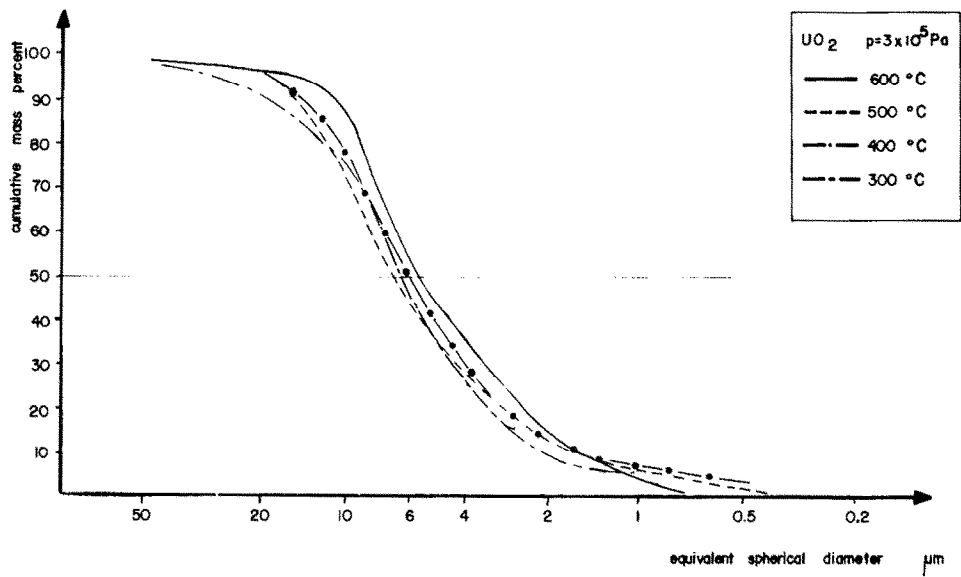


Fig. 5. Effect of denitration temperature on the  $UO_2$  particle size distribution.

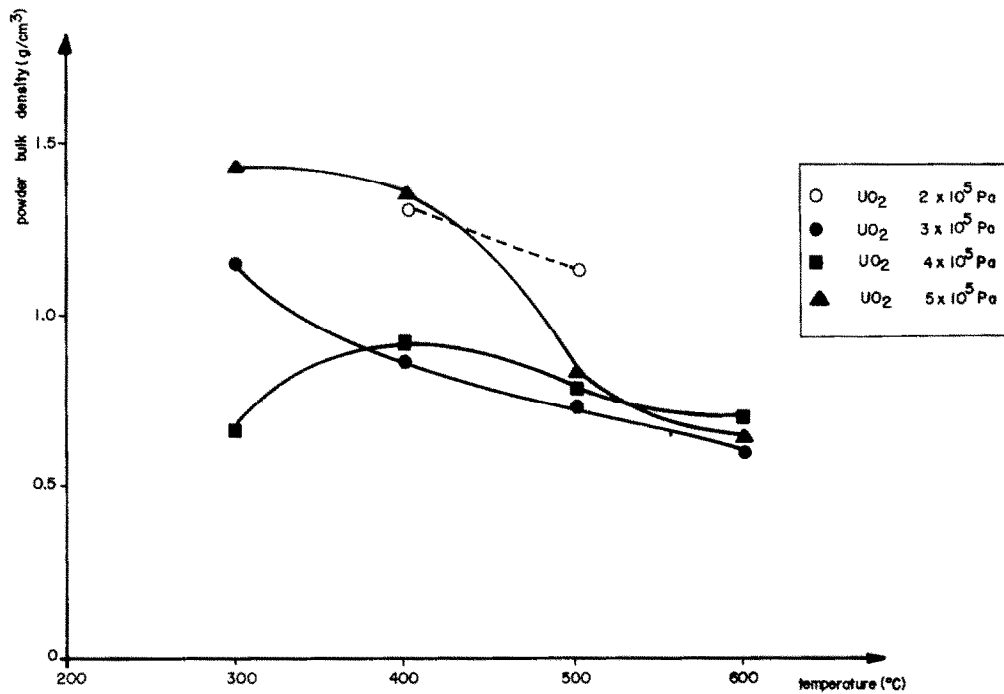


Fig. 6. Variation of the  $UO_2$  bulk density with the denitration temperature and atomization gas pressure.

The effect of the denitration parameters on the apparent ( $D_A$ ) and final density ( $D_F$ ), open (OPF) and closed (CPF) pore volumes fraction of  $UO_2$  powders are sum-

marized in table 2. The results indicate a reduction of the open pore volume with the increase of fluidization gas pressure at temperatures of 300 and 600  $^{\circ}C$ . It is probably

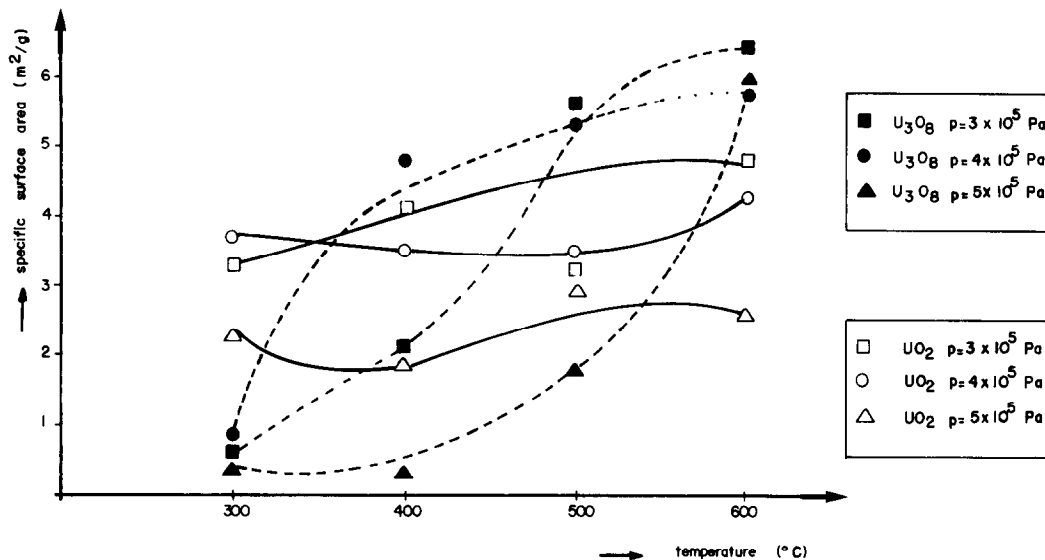


Fig. 7. The specific surface area of  $UO_2$  and  $U_3O_8$  powder for different UNH denitration temperatures.

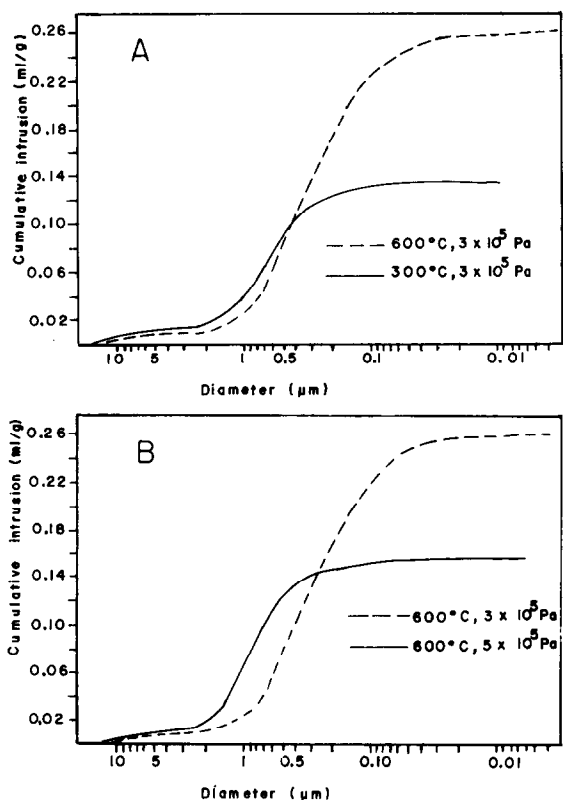


Fig. 8. The porosity distribution of  $UO_2$  powders. (A)  $3 \times 10^5$  Pa atomization pressure and at variable temperature, (B) 600°C and different gas atomization pressures.

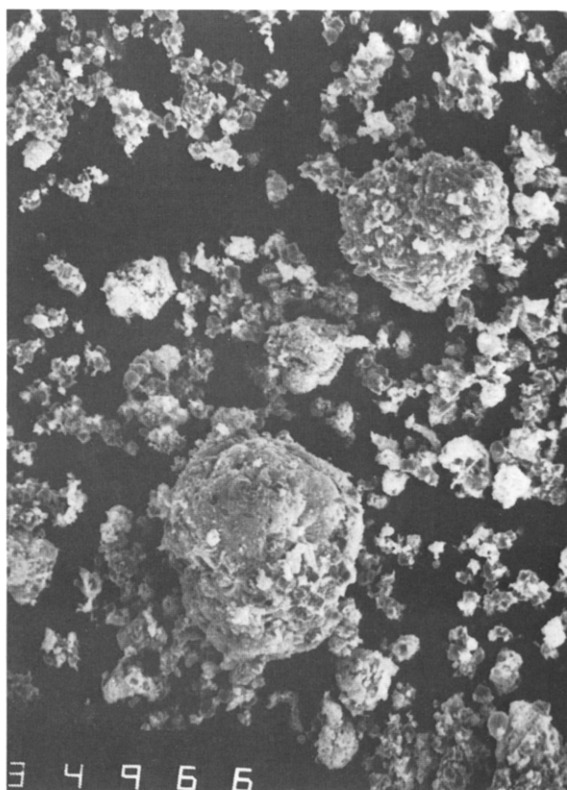


Fig. 9. SEM photometer of  $UO_2$  powder.



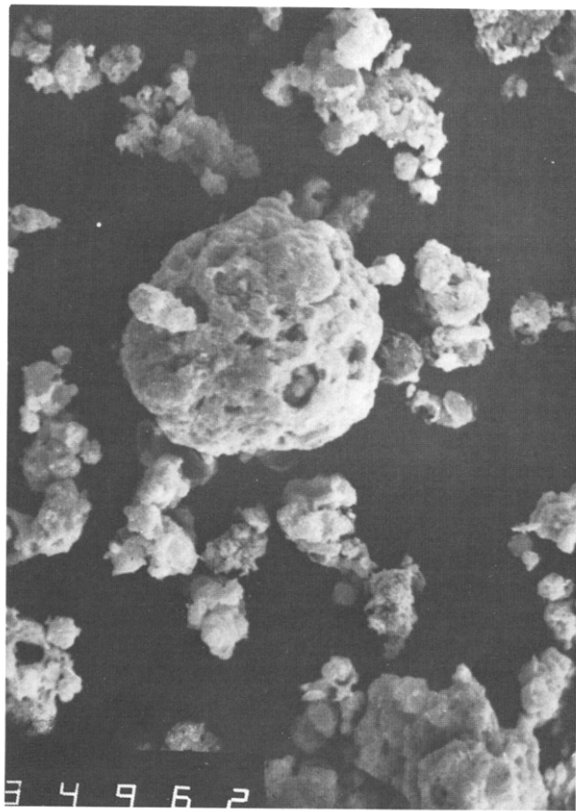


Fig. 10. The surface character of  $UO_2$  powder.

a consequence of the high specific surface area of  $U_3O_8$  powders (fig. 7) obtained at high pressure. The pore size distributions were measured by a Hg porosimeter.

Finally, SEM photographs were taken for the  $UO_2$  powders, from which the surface microreliefs and morphology were observed (fig. 9 and 10). Fig. 9 shows a particle distribution with coarse particles, which probably resulted from cementing together of clusters of finer particles. A close inspection of the particle size showed that the microreliefs depend on its size, because most of the coarse particles have caverns and the cavern depth and diameter increase as the particle size increases.

It is interesting to note that the  $UO_2$  powders reduced directly in a single step showed higher specific surface area (about  $6 \text{ m}^2/\text{g}$ ) than when the  $U_3O_8$  is reduced in a muffle furnace.

Stainless steel 304L proved to be unsatisfactory as a material of construction, due to the contamination of the  $UO_2$  powder mainly by Fe, Cr and Ni. Stainless steel 304L is not adequate for this operating temperature, Incoloy alloy is the most readily available of the satisfactory materials.

#### 4. Conclusions

This process has been developed on a laboratory plant scale mainly for recovering the  $UO_2$  scrap powder produced during the  $UO_2$  pellets fabrication.

It was found that  $UO_2$  powder characteristics are all strongly dependent on the denitration conditions. The  $UO_2$  powder prepared by UNH atomization has desirable properties. It has a surface area varying between 2 and  $5 \text{ m}^2/\text{g}$ , bulk density of approximately  $1 \text{ g}/\text{cm}^3$  and the mean particle size about  $6 \mu\text{m}$ . Hass [6] mentioned that simple thermal denitration produces uranium oxides with extremely poor characteristics for fabrication of  $UO_2$  fuel pellets. Therefore, the results obtained in this paper indicate a promising technique considering the corresponding easy operation, ability to completely confine the process materials, no waste solution and giving a product with reasonable physical parameters.

The spray nozzle used in all experiments was of the two fluid type with 0.8 mm diameter for the liquid hole; however further experiments are still necessary to observe the efficiency of other nozzles.

The maximum UNH solution flow rate depends upon the dimension of the furnace and transfer heat to the spray zone. It was observed that for this unit a feed rate higher than  $50 \text{ cm}^3/\text{min}$  implied a considerable decrease at the upper section temperature.

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