

MODELING CONVERSION OF AMMONIUM DIURANATE (ADU) INTO URANIUM DIOXIDE (UO₂) POWDER

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ABSTRACT

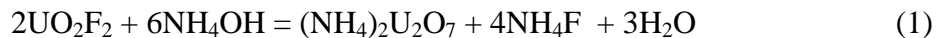
In the paper, Brandon mathematical model that describes the relationship between the essential fabrication parameters [reduction temperature (T_R), calcinations temperature (T_C), calcinations time (t_C) and reduction time (t_R)] and specific surface area of ammonium diuranate (ADU)-derived UO₂ powder products was established. The proposed models can be used to predict and control the specific surface area of UO₂ powders prepared through ADU route. Suitable temperatures for conversion of were examined with the proposed model through assessment of the sinterability of UO₂ powders.

Keywords: UO₂ powder, Ammonium diuranate (ADU), Brandon mathematical model ...

1. INTRODUCTION

The manufacture of the UO₂ nuclear fuel pellets includes the conversion of UF₆ into UO₂ powder and the fabrication of UO₂ pellets from such UO₂ powder [1-3]. In regard to the conversion of UF₆ into UO₂ powder, many dry and wet conversion methods have been developed [4-9]. In a former wet conversion, UF₆ was hydrolyzed in water to form uranyl fluoride – fluoride acid (UO₂F₂-HF) solution. Subsequently, the solution was precipitated through either an ammonium diuranate (ADU) route or an ammonium uranyl carbonate (AUC) route. These ADU and/or AUC powders are then calcinated and reduced into UO₂ powders [5-9]. The ADU-derived uranium oxide powder (or ex-ADU uranium oxide powder) possesses some characteristics different from the AUC-derived uranium oxide powder (or ex-AUC uranium oxide powder), such as particle size and **free flow ability** [7-9]. General, ex-ADU uranium oxide powder is fine and non-spherical with moderate specific surface area (SSA), having high sintering reactivity but difficulty in pressing. Thus, such powder has to be granulated in order to increase its **free flow ability** so that the pellet length can easily be controlled during pressing [1, 7-9].

Chemical reactions for ADU formation from uranyl solution, in particular, are as below



The ADU intermediate products are often contaminated with fluoride (F) ions. So, the preparation of UO_2 powder via ADU route includes two sequential steps including the calcinations of ADU precipitate into U_3O_8 powder with coincident F elimination and the reduction of the U_3O_8 into UO_2 ceramic powder [10-11]. These two steps are essential in the UO_2 pellet fabrication.

The parameters of the UO_2 preparation strongly affect the final characteristics of UO_2 powder and, therefore, have an effect on UO_2 pelletizing [6-9]. Specific surface area (SSA) of the UO_2 powder is one of the most important characteristics affecting the activity and the correspondence of the powder during UO_2 ceramic pellet fabrication. The SSA is a function of grain size, aggregation and agglomeration, morphology and structure of the powder [6-9]. Therefore, SSA is considered as the most important feature to assess sinterability of the UO_2 powder. The proposed model has been well applied for predicting a basic characteristic of nuclear fuel ceramic powder as well as for controlling the lab-scale production of the powder in our lab. In the paper, we establish a new mathematical model to describe the relationship between SSA of ex-ADU uranium oxide powder and the process parameters of the calcination and reduction that were employed for the powder fabrication. In addition, the sinterability of uranium oxide powders prepared by both ADU was tested and compared.

2. EXPERIMENTAL

The ADU powder was precipitated by the reaction of ammonium liquid with a solution containing uranyl fluoride (UO_2F_2) and fluoride acid (HF) with U:F molar ratio of 1:6. The solution is composed of the same constituents (UO_2F_2 and HF) and their molar ratio as the product of the UF_6 hydrolyzing process. Analytical grade nitrogen and hydrogen were used as pure gases during calcinations and reduction.

The calcinations of ADU into U_3O_8 and the reduction of the U_3O_8 into UO_2 powder were carried out in an apparatus consisting of a rotary tube furnace 1300°C (Nabertherm, Germany) and hydrogen-nitrogen-steam supply system. The calcinations were carried out over a range of time and temperatures in an atmosphere of nitrogen and steam (1:1 in molar ratio). After the calcinations finished, the subsequent reduction was carried out in a reducing atmosphere of hydrogen and nitrogen gases (3:1 in molar ratio). The final product was UO_2 powder. The specific surface area (SSA) of the obtained UO_2 powder was measured by the Brunauer–Emmett–Teller (BET) method (Coulter SA 3100, USA).

Sinterability of the UO_2 powders was tested by density of UO_2 pellets prepared from the UO_2 powder samples in various conversion temperatures. Compacting of green pellets was performed with a die of 11.3 mm in diameter by using a hydraulic single acting press (Carver,

USA) and pressing at 350 MPa, lubricating on die surface with a mixture of zinc stearate and acetone. Sintering was performed in a high temperature furnace (Nabertherm, Germany) with a molybdenum heating sheet. A flow of high-purity hydrogen gas was used for a reducing atmosphere in sintering. Sintered pellet density was determined by Hydrostatic (or Archimedes) method. The resintering test was carried out to determine the thermal stability of the fuel pellets, the sintered pellets were placed into the sintering furnace and held down in the reducing medium (Ar + 7% H₂) for 24 hours at the temperature of 1700 ± 50°C. The thermal stability of the fuel pellets is estimated through the change of the average pellet diameter before and after testing or by the change of pellet density.

3. RESULTS AND DISSCUSSION

3.1. Multiple regression analysis for the establishment of Brandon equation

In order to master preparing the UO₂ powders whose properties are appropriate to the UO₂ ceramic pellet fabrication and on the basis of experimental data that describe the effects of process conditions on SSA of UO₂ powder, a statistical modeling method using Brandon multiple regression model is used [12-14]. Our experimental data also indicated that four parameters (factors) affecting SSA of UO₂ powder are in a descending order as follows: reduction temperature T_R, calcinations temperature T_C, calcinations time t_C, and reduction time t_R. Thus, we established Brandon model by determining corresponding parameters in that order. By using the method of least squares and Solver tool of Microsoft Excel, the function $f_1(T_R)$ is determined in the equation as follows:

$$f_1(T_R) = 5.2506 - 0.0023 \cdot T_R \quad (3)$$

\hat{y}_1 was calculated as follows:

$$\hat{y}_1 = \frac{y}{f_1(T_R)} = \frac{SSA(Ex.)}{f_1(T_R)} \quad (4)$$

With the same calculation, the other functions of T_C, t_C, and t_R were obtained as bellows:

$$f_2(T_C) = 3.1369 - 0.0031 \cdot T_C \quad (5)$$

$$f_3(t_C) = 0.8899 + 0.031 \cdot t_C \quad (6)$$

$$f_4(t_R) = 0.9324 - 0.0166 \cdot t_R \quad (7)$$

The corresponding independent functions \hat{y}_1 were:

$$\hat{y}_2 = \frac{\hat{y}_1}{f_2(T_C)} \quad (8)$$

$$\hat{y}_3 = \frac{\hat{y}_2}{f_3(t_C)} \quad (9)$$

$$\hat{y}_4 = \frac{\hat{y}_3}{f_4(t_R)} \quad (10)$$

All of these values are reported in Table 1.

The constant a in Brandon equation was calculated from average of y_4 to be 1.00006. Thus, Brandon function describing the effect of the process parameters on the SSA of the UO_2 powder is in the form:

$$y(SSA) = a \cdot f_1(T_R) \cdot f_2(T_C) \cdot f_3(t_C) \cdot f_4(t_R) \quad (11)$$

$$y(SSA) = 1.00006 \cdot (5.2506 - 0.0023 \cdot T_R) \cdot (3.1369 - 0.0031 \cdot T_C) \cdot (0.8899 + 0.031 \cdot t_C) \cdot (0.9324 + 0.0166 \cdot t_R) \quad (12)$$

$SSA_{(Cal.)}$ values of the UO_2 powder are shown in Table 1.

The Brandon mathematical model was tested by Wilcoxon's rank sum test. We have two groups:

Group $SSA_{(Ex.)}$: $X_1, X_2, X_3, \dots, X_{n1}$; distribution \hat{y}

Group $SSA_{(Cal.)}$: $Y_1, Y_2, Y_3, \dots, Y_{n2}$; distribution \hat{y}

Null Hypothesis: $SSA_{(Ex.)} = SSA_{(cal.)}$

The two groups were combined into one group and ordered data in the combined group $SSA_{(1)} \leq SSA_{(2)} \leq \dots \leq SSA_{(n1+n2)}$; and then assigned ranks (as in Table 2).

Table 2: Order of all observations in the combined sample and assign ranks of the group W_T ($SSA_{(Cal.)}$ data are underlined)

W_T	2.868	2.899	2.917	2.994	3.182	3.34	3.424	3.478	3.514	3.538
Rank	1	<u>2</u>	3	<u>4</u>	<u>5</u>	6	7	8	9	10
W_T	3.549	3.552	3.613	3.613	3.624	3.626	3.674	3.735	4.07	4.199
Rank	11	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	16	<u>17</u>	<u>18</u>	19	20
W_T	4.205	4.333	4.338	4.43	4.471	4.604	4.771	5.921		
Rank		<u>21</u>	<u>22</u>	24	<u>25</u>	<u>26</u>	<u>27</u>	28		

Thus, sum of ranks S of group \hat{y} is calculated as follows:

$$S = 2 + 4 + 5 + 12 + 13 + 14 + 15 + 17 + 18 + 21 + 23 + 25 + 26 + 27 = 222$$

Mean rank (μ_T) of distribution \hat{y} is:

$$\mu_T = \frac{n_2(n_1 + n_2 + 1)}{2} = \frac{14(14 + 14 + 1)}{2} = 203$$

And the variance is:

$$\sigma_T^2 = \frac{n_1 n_2 (n_1 + n_2 + 1)}{12} = \frac{14 \cdot 14 (14 + 14 + 1)}{12} = 473.66$$

$$\sigma_T = \sqrt{\sigma_T^2} = \sqrt{473.66} = 21.76$$

95% reliability of μ_T is: $\mu_T \pm 1.96 \cdot \sigma_T$

$$\mu_T - 1.96 \cdot \sigma_T = 203 - 1.96 \cdot 21.76 = 160.35$$

$$\mu_T + 1.96 \cdot \sigma_T = 203 + 1.96 \cdot 21.76 = 245.65$$

The sum of ranks S of group \hat{y} is 222; within reliability range from 160.35 to 245.65, so two groups, $SSA_{(Ex.)}$ and $SSA_{(Cal.)}$, are asserted to be the same. Figure 1 is the plot comparing $SSA_{(Ex.)}$ with $SSA_{(Cal.)}$ of the UO_2 powder indicating the agreement of the proposed calculation with the experimental data.

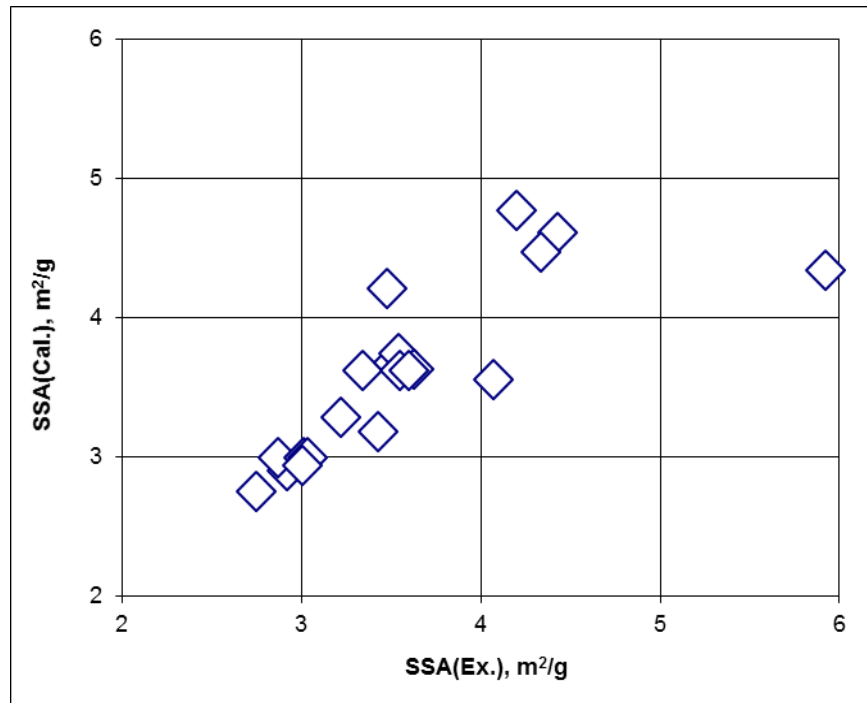


Figure 1: Comparison of $SSA_{(Ex.)}$ and $SSA_{(Cal.)}$ of the UO_2 ex-ADU powder.

Table 1: Experimental and calculated data of function $f_1(T_R)$ and \hat{y}_1 ; $f_2(T_C)$ and \hat{y}_2 ; $f_3(t_C)$ and \hat{y}_3 ; $f_4(t_R)$ and \hat{y}_4 ; and $SSA_{(Cal.)}(\hat{y})$ used to establish Brandon mathematical model

Sample	T_R (°C)	t_R (hr.)	T_C (°C)	t_C (hr.)	$SSA_{(Ex.)}(\hat{y})$ (m ² /g)	$f_1(T_R)$	\hat{y}_1	$f_2(T_C)$	\hat{y}_2	$f_3(t_C)$	\hat{y}_3	$f_4(t_R)$	\hat{y}_4	$SSA_{(Cal.)}(\hat{y})$ (m ² /g)
M1	550	5	650	4	4.430	3.986	1.111501	1.122	0.990731	1.014	0.977149	1.015	0.962329	4.604
M2	600	5	650	4	4.333	3.871	1.119465	1.122	0.997829	1.014	0.984150	1.015	0.969224	4.471
M3	650	5	650	4	5.921	3.756	1.576579	1.122	1.405276	1.014	1.386010	1.015	1.364990	4.338
M4	700	5	650	4	3.478	3.641	0.955337	1.122	0.851535	1.014	0.839861	1.015	0.827123	4.205
M5	600	2	700	3	4.070	3.871	1.051517	0.967	1.087513	0.983	1.106433	0.966	1.145851	3.552
M6	600	3	700	3	3.340	3.871	0.862915	0.967	0.892456	0.983	0.907982	0.982	0.924437	3.613
M7	600	4	700	3	3.514	3.871	0.907870	0.967	0.938949	0.983	0.955284	0.999	0.956432	3.674
M8	600	5	700	3	3.538	3.871	0.914070	0.967	0.945362	0.983	0.961809	1.015	0.947221	3.735
M9	700	3	600	5	4.199	3.641	1.153381	1.277	0.903267	1.045	0.864453	0.982	0.880119	4.771
M10	700	5	700	4	3.626	3.641	0.995990	0.967	1.030086	1.014	1.015964	1.015	1.000555	3.624
M11	700	3	700	5	3.549	3.641	0.974839	0.967	1.008211	1.045	0.964888	0.982	0.982374	3.613
M12	650	4	750	2	2.917	3.756	0.776707	0.812	0.956653	0.952	1.004993	0.999	1.006201	2.899
M13	650	4	750	3	2.868	3.756	0.763660	0.812	0.940583	0.983	0.956947	0.999	0.958097	2.994
M14	650	4	750	5	3.424	3.756	0.911705	0.812	1.122928	1.045	1.074675	0.999	1.075966	3.182

3.2. Test of sinterability of UO₂ powders

Density of the UO₂ ceramic pellets was characterized mainly on the sinterability of the UO₂ powders. The resintering test was performed to check the thermal stability of the pellets after sintering. In order to test sinterability of the UO₂ powders, these samples were prepared at various conversion temperatures of 550°C, 600°C, 650°C, 700°C and 750°C with a conversion time of 5 hours. According to our test, the conversion time of 5 hours is sufficient to eliminate fluoride down to below 100 µg per gram of the powder. Table 3 shows some characteristics of the obtained ex-ADU uranium oxide powder samples. The powder samples were compacted to obtain green pellets. Sintering of green pellets was performed using a batch type laboratory sintering furnace at a temperature of 1700°C as described in the experimental section.

Table 3: Characteristics of the UO₂ powder

Inspection items	UO ₂ ex-ADU	Methods
SSA	2.5 – 6.0 m ² /gr	BET
Bulk density (gr/cm ³)	1.42 ± 0.11 gr/cm ³	Scott Volumeter
Tap density (gr/cm ³)	2.44 ± 0.16 gr/cm ³	Tap densitometer
O/U	2.125 ± 0.037	Gravimetry
F content	< 50 ppm	Pyrohydrolysis
Al	119.5 ppm	ICP-MS
B, Cd, Cr, Co, Cu, Mo, Ta, Th, Ti, W, V	below detection	ICP-MS
Mg	below detection	ICP-MS
Ca	58.2 ppm	ICP-MS
Fe	47.2 ppm	ICP-MS
Pb	0.13 ppm	ICP-MS
Mn	0.26 ppm	ICP-MS
Ni	0.13 ppm	ICP-MS
Rare Earths	< 1 ppm	ICP-MS
Si	106.4 ppm	ICP-MS
Zn	below detection	ICP-MS

The densities of UO₂ ceramic pellet samples prepared from ex-ADU uranium oxide powders at conversion temperatures of 550°C, 600°C, 650°C, 700°C and 750°C were shown in Table 4. After resintered, the densities increase 0.86 ± 1.89%, 1.04 ± 1.21%, 0.30 ± 0.73%, 0.52 ± 0.54% and 0.70 ± 0.36%, respectively with the above conversion temperatures. The coefficients of variations (CVs) of the densities and the results of resinter test indicated that the UO₂ ceramic pellets prepared from the ex-ADU uranium oxide powders at the conversion temperature of 750°C were more stable than those prepared at other temperatures. The figure 2 shows the density of sintered pellet as a function of conversion temperature with and without a pore former. The experiment data show a slight increase in density with the increase of

conversion temperature in case of no pore former – ammonium oxalate. In the presence of the pore former, the density of sintered pellets has a decreasing tendency with an increase of the pore former content. In this case, the effect of conversion temperature on pellet density is not clear. It might attribute to a bad distribution of the pore former during the powder preparation. Retesting sinterability of the ex-ADU uranium oxide powders at conversion temperatures of 700°C, 750°C and 800°C was performed at a sintering temperature of 1700°C for 8 hours. The densities of the UO₂ ceramic pellet samples were also shown in Table 4 and their densities increasing by the resintering were 0.43 ± 0.19%, 0.57 ± 0.10% and 0.53 ± 0.23%, respectively. The average densities were 93.67 ± 0.53, 93.64 ± 0.80 and 96.54 ± 0.57, respectively with the above conversion temperatures. From the CVs of the densities, the resinter data and, especially, the average densities, it is apparent that the sinterability of the ex-ADU uranium oxide powder at the conversion temperature of 800°C was better than those under other conditions.

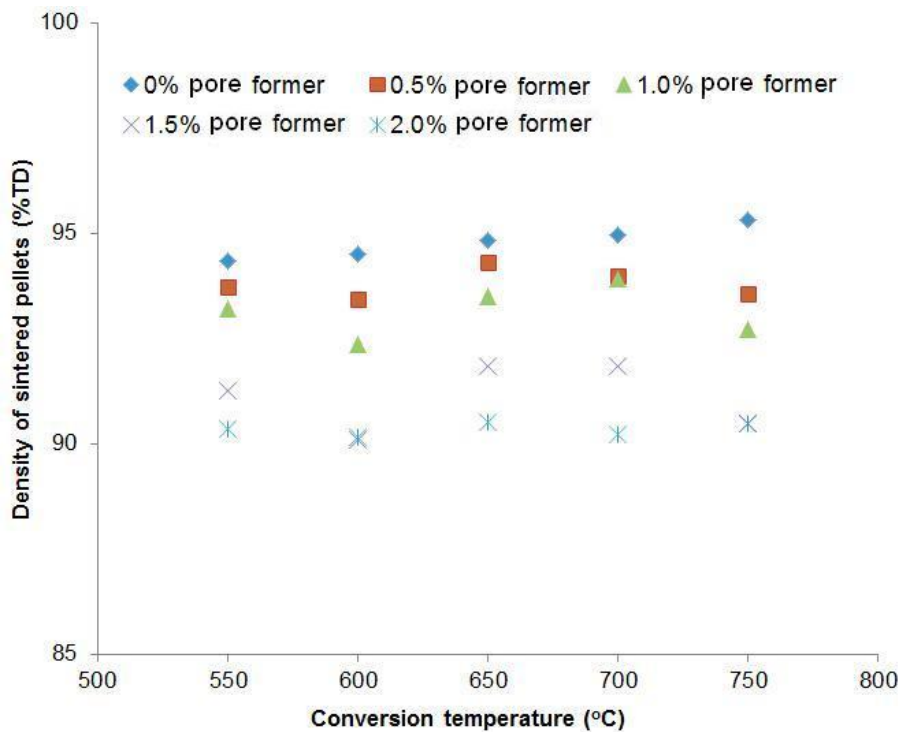


Figure 2: Plot of the ADU- derived UO₂ pellet density vs. the conversion temperatures.

Table 4: Density test data of the ceramic pellets prepared from ex-ADU uranium oxide powders at various conversion temperatures

S.N	Density test data of the ceramic pellets prepared from the ex-ADU uranium oxide powder samples at various conversion temperatures (%TD)							
	Conversion temperatures (Sintering temperature -1700°C and time-6 hours)					Conversion temperatures (Temperature -1700°C and time-8 hours)		
	550°C	600°C	650°C	700°C	750°C	700°C	750°C	800°C
1	92.44	92.20	93.58	92.72	92.51	94.60	93.63	96.29
2	94.50	87.89	92.51	99.80	92.20	93.40	93.63	96.87
3	93.56	93.16	84.13	84.87	92.61	93.43	93.42	96.51
4	93.93	92.85	87.17	92.64	91.88	94.32	93.83	96.62
5	92.84	91.84	92.86	94.28	92.68	93.62	93.86	96.44
6	93.73	75.33	95.00	92.70	92.36	93.49	90.62	98.89
7	94.29	92.24	92.32	92.37	92.79	94.55	94.12	96.35
8	92.75	92.49	92.02	91.77	93.19	92.92	94.32	97.03
9	88.85	91.16	90.78	90.61	92.42	93.41	93.62	96.82
10	92.63	91.54	89.32	92.88	90.89	93.81	93.70	96.46
11	92.97	92.86	90.79	93.71	91.57	93.32	93.57	96.47
12	92.88	93.30	90.76	93.82	91.50	93.25	93.50	96.57
13	93.41	92.45	91.65	91.34	90.58	94.25	94.23	96.31
14	93.11	92.70	92.52	93.66	91.83	93.66	93.77	96.24
15	92.84	93.13	88.52	92.92	91.33	93.34	93.62	96.33
16	94.22	93.11	94.33	93.44	91.36	94.38	94.14	96.5
17	93.33	93.33	94.56	93.21	91.11	93.52	93.75	96.52
18	92.46	94.72	94.25	93.54	91.25	92.87	94.17	96.43
19	94.89	94.50	94.65	94.55	95.84			96.14
20	94.80	94.30	95.28	94.61	96.14			96.12
21	94.82	94.02	94.94	93.86	94.01			95.59
22	94.21	93.17	94.32	94.12	94.23			96.45
23	94.17	93.07	94.15	93.5	93.58			96.40
24	94.59		93.53	93.57	92.83			96.68
CV	5.53%	4.22%	3.00%	2.62%	1.54%	0.57%	0.85%	0.59%

S.N = Serial number

SSAs of ex-ADU uranium oxide powders calculated by the equation (12), were shown in Table 5. The SSA of the ex-ADU uranium oxide powder at conversion temperature of 800°C was 2.4 m²/g. Thus, the proposed models can be used to explain why conversion temperatures of the ADU-derived UO₂ powders were 800°C.

Table 5: The SSA of the UO₂ powders calculated by Brandon equations

Conversion temperature	The SSA of the UO ₂ powders ex-ADU (m ² /g)
500°C	6.905
550°C	6.055
600°C	5.244
650°C	4.471
700°C	3.735
750°C	3.037
800°C	2.377

4. CONCLUSION

In this paper, we proposed a mathematical model describing the effect of the fabrication parameters on SSA of uranium oxide powders prepared via ADU route. The Brandon model as presented in equation (12) is used to describe the relationship between the essential fabrication parameters [reduction temperature (T_R), calcinations temperature (T_C), calcinations time (t_C) and reduction time (t_R)] and SSA of the obtained ex-ADU uranium oxide powder product. Testing sinterability of the UO₂ powder was performed and the proposed models were used to explain that conversion temperatures of the ammonium diuranate- derived UO₂ powders were 800°C.

REFERENCES

- [1] Ronald A. Knief, “*Nuclear Engineering: Theory and Technology of Commercial Nuclear Power*”, Hemisphere Publishing Corporation (1992).
- [2] D. Olander, “Nuclear fuels – Present and future”, *J. Nucl. Mater.*, 389 (2009) 1–22.
- [3] Nuclear Fuel Cycle Information System, “*A Directory of Nuclear Fuel Cycle Facilities*”, IAEA-TECDOC-1613 (2009).
- [4] M. C. Lee, C. J. Wu, “Conversion of UF₆ to UO₂: A quasi-optimization of the ammonium uranyl carbonate process”, *J. Nucl. Mater.*, 185 (1991) 190-201.
- [5] C. T. Huang, “Dry-ADU process for UO₂ production”, *J. Nucl. Mater.*, 199 (1992) 61-67
- [6] B. Ayaz, A. N. Bilge, “The possible usage of ex-ADU uranium dioxide fuel pellets with low-temperature sintering”, *J. Nucl. Mater.*, 280 (2000) 45-50.
- [7] H. Assmann, “Microstructure and Density of UO₂ for Light Water Reactors as Related to Powder Properties”, *Ceramic Powders*, Amsterdam (1983) 707 – 7117.
- [8] P. Balakrishna, C. K. Asnani, “Uranium Dioxide Powder Preparation, Pressing, and

- Sintering for optimum Yield”, Nuclear Technology, 127 (1999) 375 – 381.
- [9] Y. W. Lee, M. S. Yang, “Characterization of HWR fuel pellets fabricated using UO_2 powders from different conversion processes”, J. Nucl. Mater., 178 (1991) 217-226.
- [10] N. Lindman, “The kinetics of the elimination of fluorine from uranyl fluoride/uranium dioxide pellets”, J. Nucl. Mater., 66 (1977) 23-36.
- [11] Z. X. Song, X. W. Huang, “Defluorination Behavior and Mechanism of Uranium Dioxide”, J. of Radioanalytical and Nucl. Chemistry, 237 (1998) 81-84.

MÔ HÌNH HÓA QUÁ TRÌNH CHUYỂN HÓA CỦA URANI DIURANATE (ADU) THÀNH BỘT UO_2

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TÓM TẮT

Báo cáo này trình bày về mô hình toán học Brandon mô tả mối quan hệ giữa các thông số chế tạo cần thiết [nhiệt độ khử (T_R), nhiệt độ phân hủy (T_C), thời gian phân hủy (t_C) và thời gian khử (t_R)] với diện tích bề mặt riêng của sản phẩm bột UO_2 được điều chế từ amoni diuranate (ADU). Các mô hình đề xuất có thể được sử dụng để dự đoán và kiểm soát diện tích bề mặt riêng của bột UO_2 chuẩn bị thông qua phương pháp ADU. Nhiệt độ thích hợp cho quá trình chuyển hóa đã được kiểm tra với các mô hình được đề xuất thông qua đánh giá khả năng thiêu kết của bột UO_2 sản phẩm.

Từ khóa: bột UO_2 , Amoni diuranate (ADU), Brandon mô hình toán học ...