Modeling the UO$_2$ ex-ADU pellet process

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Abstract

Studies on modeling uranium dioxide (UO$_2$) powder and pellet processes from ammonium diuranate (ADU)- derived uranium dioxide powder (UO$_2$ ex-ADU powder) were reported in the paper. A mathematical model describing the effect of the fabrication parameters on specific surface area (SSA) of UO$_2$ powders was built up. The Brandon model is used to describe the relationship between the essential fabrication parameters [reduction temperature (T$_R$), calcination temperature (T$_C$), calcination time (t$_C$) and reduction time (t$_R$)] and SSA of the obtained UO$_2$ powder product. Response surface methodology (RSM) based on face centered (CCF), one type of quadratic central composite design (CCD), was used to model the pellet process. The experimental studies on the UO$_2$ pellet process determined region of experimental planning as follows: conversion of ADU into UO$_2$ powder at various temperatures of 973 K, 1023 K and 1073 K and sintering of UO$_2$ pellets at temperatures of 1923 K, 1973 K and 2023 K for times of 4 h, 6 h and 8 h. On the base of the proposed model, the relationship between the technological parameters and density of the UO$_2$ pellet product was suggested to control the UO$_2$ ex-ADU pellet process as desired levels.

Key Words: UO$_2$ ex-ADU, UO$_2$ pellet process, modeling;

1. Introduction

In nuclear fuel technology for light water reactors (LWRs), uranium dioxide (UO$_2$) is the essential material for the fabrication of ceramic fuel that has been widely used in both pressurized water reactors (PWR) and boiling water reactors (BWR). Uranium in the form of UO$_2$ ceramic pellets has been used as fuel in more than three quarters of the total installed capacity of nuclear power plants [1-3].

The manufacture of the UO$_2$ nuclear fuel pellets includes the conversion of UF$_6$ into UO$_2$ powder and the fabrication of UO$_2$ pellets from such UO$_2$ powder [1-3]. In regard to the conversion of UF$_6$ into UO$_2$ powder, many wet and dry conversion methods have been developed. In a former wet conversion, UF$_6$ was hydrolyzed in water to form uranyl fluoride – fluoride acid (UO$_2$F$_2$-HF) solution. Subsequently, the solution was precipitated through either an ammonium di-uranate (ADU) route or an ammonium uranyl carbonate (AUC) route. These ADU and/or AUC powders are then calcined and reduced into UO$_2$ powders.

The parameters of the UO$_2$ preparation strongly affect the final characteristics of UO$_2$ powder [4] and, therefore, have an effect on UO$_2$ pelletizing. 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 [5-6]. Therefore, SSA is considered as the most important feature to assess sinterability of the UO$_2$ powder. In an effort to control the SSA of UO$_2$ powder, we established a mathematical model to describe the relationship between its SSA and the process parameters for the calcination and reduction that were employed for UO$_2$ powder fabrication via ADU route.

An important prerequisite for stabilizing and controlling the UO_2 pellet process is to find quantitative relationships between product characteristics and process parameters. For UO_2 pellet process the density is one of the most important product characteristics [7-8]. There are many factors affecting directly and indirectly the final density of the pellets, including technological parameters, machine, operator empowerment, process review and etc. The most important factors affecting directly the UO_2 pellet process are technological parameters, including material parameters of calcination – reduction conversion of ADU into UO_2 ceramic powder (temperature and time for calcination and reduction) and process parameters of UO_2 pellet sintering (sintering temperature and time) [7-8]. In the study, a model for the UO_2 ex-ADU pellet process was established to assess the sytematic relationship between the technological parameters and the density of UO_2 ex-ADU pellets that could apply to nuclear fuel fabrication and design. Three of the most important technological parameters including conversion temperature, sintering temperature, and sintering time were studied; and RSM based on CCF type of CCD improved by Box and Hunter was empirically used to study on and model the interactive effect of the technological parameters (independent variables) on the UO_2 pellet density (response variable). The model showed the contribution of individual parameter that controls the density of the UO_2 pellet products through those important parameters. So, the purpose of the present study is to assess the effects of the three technological parameters on the UO_2 ex-ADU pellet process, using RSM based on CCF type of CCD for designing the experiments to minimize the experimental runs, for developing the model to optimize the UO_2 ex-ADU pellet process conditions and for assessing the effect of the parameters on the pellet density to control the process.

2. Experiments

2.1. Experimental methods

The ADU powder was precipitated by the reaction of ammonium hydroxide with a synthetic solution containing UO_2F_2 and HF with U:F molar ratio of 1:6. The calcination of ADU into U_3O_8 and the reduction of 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 calcination was carried out over a range of time and temperatures in an atmosphere of nitrogen and steam (1:1 in molar ratio). After the calcination 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).

Sintering was carried out with UO_2 pellets prepared from UO_2 powder samples at the various conversion temperatures. The UO_2 powder samples first were blended with 10 wt.% and 0.25 wt.% of U_3O_8 and porous former (ammonium oxalate), respectively; and then compacted green pellets in a die of 11.3 mm in diameter by using a hydraulic single acting press (Carver, USA) and pressing at 350 to 400 MPa, lubricating on die surface with a mixture of zinc stearate and acetone. Sintering was performed at temperature of 1923 K, 1973 K and 2023 K for time of 4h, 6 h and 8 h in a high temperature furnace 1800 °C (Nabertherm, Germany) with a molybdenum heating sheet. A flow of high-purity hydrogen gas was used for a reducing atmosphere in sintering.

Density, the most important characteristic of the sintered pellet, was determined by hydrostatic (or Archimed) method [4].

2.2. Modeling method

RSM based on CCF type of CCD was empirically used to model the the UO_2 pellet process. The total number of required experimental runs was: $(2^k + 2k + n_0) = 17$, where k is the number of factors (k =3), n_0 is the number of replications at the center points ($n_0 = 3$). The UO_2 pellet

density (Y, in 10^3 kg/m^3) was taken as the response variable and described in the form given in Eq. (1).

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i,j=1(i \neq j)}^{k} b_{ij} X_i X_j \qquad (1)$$

The UO$_2$ pellet process were estimated through the regression analysis and response surface plots of the independent variables (X_i) and each dependent variable (Y).

3. Results and discussion

3.1. Modeling the UO$_2$ ex-ADU powder process

Multiple regression analysis for the establishment of Brandon equation

In order to master preparing the UO$_2$ powders whose properties are appropriate to the UO$_2$ ceramic pellet fabrication and on the basis of experimental data that describe the effects of process conditions on SSA of UO$_2$ powder, a statistical modeling method using Brandon multiple regression model is used. The form of Brandon mathematical equation is as follows:

$$y = a. f_1(x_1) f_2(x_2) \dots f_j(x_j) \dots f_k \qquad (2)$$

Where, y denotes the SSA of UO$_2$ powder, $f_j(x_j)$ are the functions presenting the effect of process parameter x_j on SSA (y), and a is a constant.

In Brandon equation, the series of functions $f_j(x_j)$ are presented in a descending order of the relevance of process factors.

In order to establish Brandon equation, an experimental data set $\{y; x_1, x_2, \dots x_k\}$ is used for determining the regression function $y = f_1(x_1)$. From $f_1(x_1)$, a new data set is obtained by evaluating:

$$\hat{y}_1 = \frac{y}{f(x_1)} \qquad (3)$$

As a result, $\hat{y}_1$ is independent on x_1 but is affected by $x_2, x_3, \dots x_k$:

$$\hat{y}_1 = a. f_1(x_1). f_2(x_2) \dots f_j(x_j) \dots f_k(x_k) \qquad (4)$$

The others $f_j(x_j)$ are calculated in the same way with $f_1(x_1)$, we obtain:

$$\hat{y}_k = \frac{y_{k-1}}{f(x_k)} = \frac{y}{f_1(x_1). f_2(x_2) \dots f_k(x_k)} \qquad (5)$$

Our experimental data indicated that four parameters (factors) affecting SSA of UO$_2$ powder are in a descending order as follows: reduction temperature T_R, calcination temperature T_C, calcination 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:

$$f_1(T_R) = 5.2506 - 0.0023 \cdot T_R \qquad (6)$$

$\hat{y}_1$ was calculated as follows:

$$\hat{y}_1 = \frac{y}{f_1(T_R)} = \frac{SSA_{(Ex.)}}{f_1(T_R)} \qquad (7)$$

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

$$f_2(T_C) = 3.1369 - 0.0031 \cdot T_C \qquad (8)$$

$$f_3(t_C) = 0.8899 + 0.031 \cdot t_C \qquad (9)$$

$$f_4(t_R) = 0.9324 - 0.0166 \cdot t_R \qquad (10)$$

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

$$\hat{y}_2 = \frac{\hat{y}_1}{f_2(T_C)} \qquad (11)$$

$$\hat{y}_3 = \frac{\hat{y}_2}{f_3(t_C)} \qquad (12)$$

$$\hat{y}_4 = \frac{\hat{y}_3}{f_4(t_R)} \qquad (13)$$

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:

$$y(SSA) = a \cdot f_1(T_R) \cdot f_2(T_C) \cdot f_3(t_C) \cdot f_4(t_R) \qquad (14)$$

$$y(SSA) = 1.00006 \cdot (5.2506 - 0.0023 \cdot T_R) \cdot (3.1369 - 0.0031 \cdot T_C) \cdot (0.8899 + 0.031 \cdot t_C) \cdot (0.9324 + 0.0166 \cdot t_R) \qquad (15)$$

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

Test Brandon mathematical model by Wilcoxon's rank sum test.

The Wilcoxon rank-sum test is a nonparametric alternative to the two-sample (for example A and B) test that we wish that the data of measurements in population A is the same as that in B. We have two groups:

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

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

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

Herein, $SSA_{(Ex.)}$ is experimentally obtained SSA. The two groups are combined into one group (for example W_T) W_T of $W_{(1)}, W_{(2)}, W_{(3)}, ..., W_{(n1+n2)}$; order data in the combined group $W_{(1)} \leq W_{(2)} \leq ... \leq W_{(n1+n2)}$; and then assign ranks (as in Table 2).

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

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

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	_2_	3	_4_	_5_	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	_12_	_13_	_14_	_15_	16	_17_	_18_	19	20
W_T	4.205	4.333	4.338	4.43	4.471	4.604	4.771	5.921		
Rank	_21_	22	_23_	24	_25_	_26_	_27_	28		

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 (^oC)	t_R (hr.)	T_C (^oC)	t_C (hr.)	$SSA_{(Ex.)}(\ddot{y})$ (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

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, in reliability range from 160.35 to 245.65, so two group $SSA_{(Ex.)}$ and $SSA_{(Cal.)}$ are asserted to be the same.
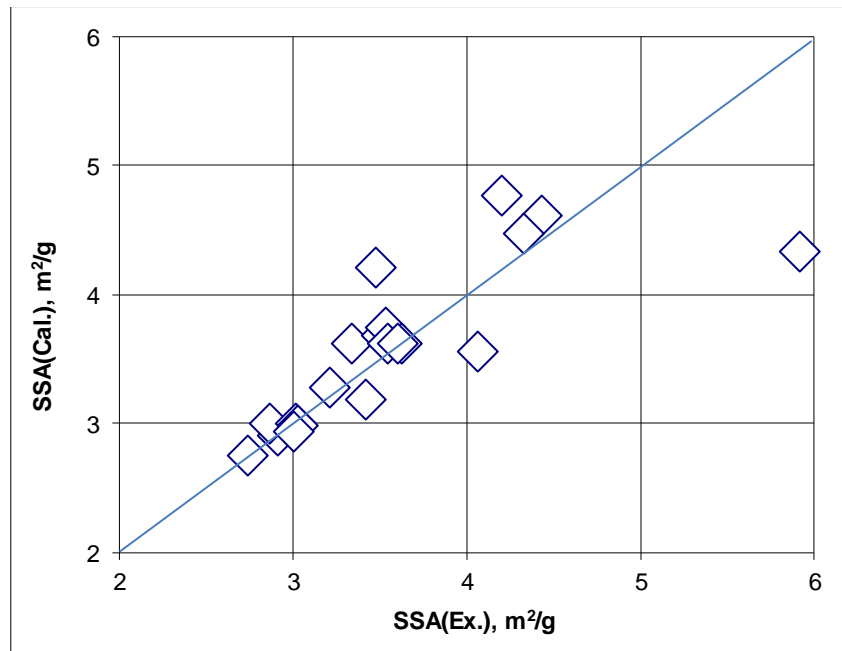

Fig. 1. The plot comparing $SSA_{(Ex.)}$ with $SSA_{(Cal.)}$ of the UO$_2$ powder.

Figure 2 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. Thus, we suppose that the Brandon mathematical model is capable to describe the effect of the factors on the SSA of the UO$_2$ powder that was obtained from the calcination and reduction of ADU.

Table 3.

Characteristics of the UO$_2$ powder

Inspection items	UO$_2$ ex-ADU	Methods
SSA	$2.5 - 6.0$ m^2/g	BET
Bulk density (g/cm^3)	1.42 ± 0.11 g/cm^3	Scott Volumeter
Tap density (g/cm^3)	2.44 ± 0.16 g/cm^3	Tap densitometer
O/U	2.125 ± 0.037	Gravimetry
F content	< 50 ppm	Pyrohydrolysis

Impurities (ppm)	ICP-MS
Al	119.5
B, Cd, Cr, Co, Cu, Mo, Ta, Th, Ti, W, V	below detection
Mg	below detection
Ca	58.2
Fe	47.2
Pb	0.13
Mn	0.26
Ni	0.13
Rare Earths	< 1
Si	106.4
Zn	below detection

3.2. Modeling the UO_2 ex-ADU pellet process

The previous study [6] also shown that the densities of UO_2 ceramic pellet samples prepared from UO_2 ex-ADU powders at conversion temperatures of 973 K (700 °C) and 1023 K (750 °C) and at sintering temperature of 1973 K for 6 h were $10.21 \pm 0.27 \times 10^3$ kg/m^3 and $10.14 \pm 0.17 \times 10^3$ kg/m^3, respectively with the above conversion temperatures. Retesting sinterability of the UO_2 ex-ADU powders at conversion temperatures of 973 K, 1023 K and 1073 K (800 °C) was performed at a sintering temperature of 1973 K for 8 h, the average densities of the UO_2 ceramic pellet samples were $10.27 \pm 0.06 \times 10^3$ kg/m^3, $10.26 \pm 0.09 \times 10^3$ kg/m^3 and $10.58 \pm 0.06 \times 10^3$ kg/m^3, respectively with the above conversion temperatures. On the other hand, testing sinterability of the UO_2 ex-ADU powder at conversion temperature of 1073 K was performed at sintering temperatures of 1923 K for 8 h and 2013 K for 4 h. The average densities of the UO_2 ceramic pellet samples were $10.23 \pm 0.12 \times 10^3$ kg/m^3 and $10.46 \pm 0.11 \times 10^3$ kg/m^3, respectively with the above sintering temperatures and sintering times.

From the above experimental results, region of the experimental planning was determined and coded on CCD type of CCF as follows: conversion temperatures (X_1) of 973 K (coded level of -1), 1023 K (coded level of 0) and 1073 K (coded level of 1); sintering temperatures (X_2) of 1923 K (coded level of -1), 1973 K (coded level of 0) and 2023 K (coded level of 1); and sintering time (X_3) of 4 h (coded level of -1), 6 h (coded level of 0) and 8 h (coded level of 1). Experimental studies on effect of the sintering temperature and time, and the conversion temperature on the UO_2 pellet density were performed based on the designed matrix under the defined conditions (as in Table 4) in order to obtain the good match data for modeling the UO_2 pellet process.

The effects of the sintering temperatures and times, and the conversion temperatures on the UO_2 pellet density were studied. The results of 17 experimental runs (as in Table 4) were entered into the MODDE 5.0 software in order to fit model by multiple linear regression. The results of 17 runs based on CCD type of CCF were also given in Table 4. The regression coefficients estimated by the software are: $b_0 = 10.30$, $b_1 = 0.31$, $b_2 = 0.16$, $b_3 = 0.06$, $b_{22} = -0.10$, $b_{33} = 0.05$, $b_{12} = -0.08$ and $b_{13} = -0.03$. The probability values (p-value) of b_{11} and b_{23} coefficients were greater than 0.05, indicating insignificant confidence levels; hence, they were rejected. The accuracy and variability of the above model could be evaluated by the coefficient of determination (R^2). The R^2 for the UO_2 pellet process was calculated to be 0.996, explaining that the variability of response is at 99.6 % confidence level, and only 0.4 % of the total variations cannot be explained by the model. Moreover, the value of adjusted determination coefficient (adj. R^2) of 0.992 was also close to 1. Thus, the calculated model for the UO_2 pellet process had a good agreement with the experimental data. Final calculated equation for the pellet density which incorporates the types of coded coefficients was shown in Eq. (16).

$$Y\ (\times 10^3\ kg/m^3) = 10.30 + 0.31X_1 + 0.16X_2 + 0.06X_3 - 0.10\ X_2^2 + 0.05X_3^2 - 0.08X_1X_2 - 0.03X_1X_3 \quad (16)$$

The calculated vs. experimental plot for the UO_2 pellet density was shown in Fig. 2 (a). It could be seen that the experimental results were distributed relatively near to a straight line with good agreement of the calculated (predicted) and experimental (actual) results. This demonstrates that the fitted regression coefficient to the equation (good fit of data) and the CCD model with an experimental design can be effectively applied for controlling the UO_2 pellet process.

The best way to visualize the influence of independent variables on the response is to draw surface response plots of the model. The shapes of three-dimensional response surfaces of the regression model constructed by MODDE 5.0 software show the nature and extent of the interactive relationships between independent variables and response, as in Fig. 2 (b).

It can be seen from Eq. (16) that b_1 (of X_1) and b_2 (of X_2) linear coefficients of regression model show positive effect on Y (UO_2 pellet density), therefore its response surface had a local maximum value.

Effect of the technological parameters on the UO_2 pellet process could be assessed through the coefficients of regression model, as in Eq. (16). The b_1 (of X_1) linear coefficient is much greater than the b_{12} (of X_1X_2) and b_{13} (of X_1X_3) interactive ones; contribution of X_1 on Y would be linear and could be quantitatively calculated by $b_0 \pm 0.26$. The b_3 (of X_3) linear coefficient was the same as the b_{33} (of X_3^2) quadratic one and their sum was greater than the b_{13} (of X_1X_3) interactive coefficient; so contribution of X_3 on Y would be half linear and half quadratic; this can be seen from Fig. 2 that the sintering temperature and time had a positive effect in conversion temperature range of 973 K to 1073 K, but a trend of inefficiency in low range from 973 K to 1023 K (the contour of the sintering temperature vs. the sintering time on the UO_2 pellet density at 973 K is similar to that at 1023 K) and efficiency in higher range from 1023 K to 1073 K was observed for the influence of the conversion temperature on the UO_2 pellet process; contribution of X_3 on Y could be quantitatively calculated by $b_0 \pm 0.10$. Contribution of X_2 on Y was small because positive effect of the b_3 (of X_3) linear coefficient would be eliminated by negative effects of the b_{22} (of X_2^2) quadratic and b_{12} (of X_1X_2) interactive ones; and the contribution could be quantitatively calculated by $b_0 \pm 0.02$. Thus, the contributions of X_1, X_2 and X_3 to Y could be in order of $X_1 > X_3 > X_2$. The assessing of relationship between the X_i and Y would suggest controlling the UO_2 ex-ADU pellet process, that is necessary and important for nuclear fuel fabrication and design aspects of commercial nuclear reactors. One of characteristics of sintered UO_2 pellet products for nuclear fuel is the density achieving value of 10.30×10^3 kg/m^3 to 10.70×10^3 kg/m^3 [4]. From the proposed model, the technological parameters for the UO_2 pellet process would be calculated so that the UO_2 pellet product has a desirable density.

Otherwise, SSA of the UO_2 ex-ADU powders calculated from Eq. 15 at the conversion temperature of 973 K, 1023 K and 1073 K are 3.7 m^2/g, 3.0 m^2/g and 2.3 m^2/g, respectively [6]. It could be seen that general UO_2 powder SSA of around 2.3 m^2/g is of sinterability.

On the base of the experimental and modeling studies, a flow sheet for preparing the UO_2 ex-ADU pellet product of the density of 10.5×10^3 kg/m^3 was proposed, as in Fig. 3, and could be described as follows: the ADU was converted into UO_2 powder in rotary furnace through calcination in atmosphere of stream and N_2 mixture and reduction in atmosphere of H_2 and N_2 mixture at temperature of 1073 K for 5 h, the UO_2 powder obtained would be of the sinterability; the UO_2 pellet preparing was carried out with the stages: blending with U_3O_8 (10 wt.%) as adductive and ammonium oxalate (0.25 wt.%) as pore former, prepressing at 200 MPa pressure, granulating under 20 mesh, pressing at 350 to 400 MPa to form green pellet and sintering in high temperature furnace in H_2 and N_2 mixture at 1973 K for 7.0 h to 8.0 h; density of the UO_2 pellet product would be approximately 10.5×10^3 kg/m^3.

Table 4
Central composite rotatable design arrangement and results.

| Run order | Coded level | | | Real value | | | Experimental (Actual) | | Calculated (Predicted), in 10^3 kg/m^3 |
	X_1	X_2	X_3	Sintering temperature, in K	Sintering time, in h	Conversion temperature, in K	Density, in 10^3 kg/m^3	CV, in %	
1	-1	-1	-1	1923	4	773	9.59 ± 0.12	1.30	9.60
2	1	-1	-1	2023	4	773	10.46 ± 0.10	1.00	10.44
3	-1	1	-1	1923	8	773	10.08 ± 0.15	1.50	10.07
4	1	1	-1	2023	8	773	10.60 ± 0.09	0.83	10.59
5	-1	-1	1	1923	4	873	9.77 ± 0.17	1.77	9.78
6	1	-1	1	2023	4	873	10.48 ± 0.08	0.74	10.49
7	-1	1	1	1923	8	873	10.23 ± 0.12	1.22	10.25
8	1	1	1	2023	8	873	10.65 ± 0.11	1.05	10.64
9	-1	0	0	1923	6	823	10.00 ± 0.16	1.58	9.98
10	1	0	0	2023	6	823	10.58 ± 0.12	1.10	10.60
11	0	-1	0	1973	4	823	10.06 ± 0.16	1.58	10.05
12	0	1	0	1973	8	823	10.35 ± 0.08	0.81	10.36
13	0	0	-1	1973	6	773	10.26 ± 0.10	0.98	10.29
14	0	0	1	1973	6	873	10.44 ± 0.11	1.03	10.40
15	0	0	0	1973	6	823	10.29 ± 0.12	1.16	10.30
16	0	0	0	1973	6	823	10.28 ± 0.11	1.11	10.30
17	0	0	0	1973	6	823	10.31 ± 0.12	1.15	10.30

CV is coefficient of variation.
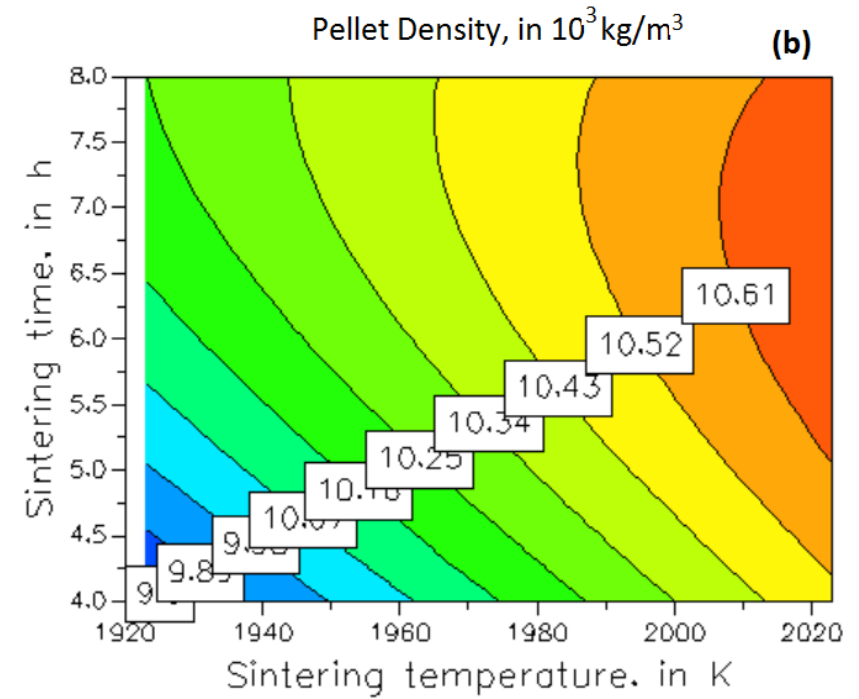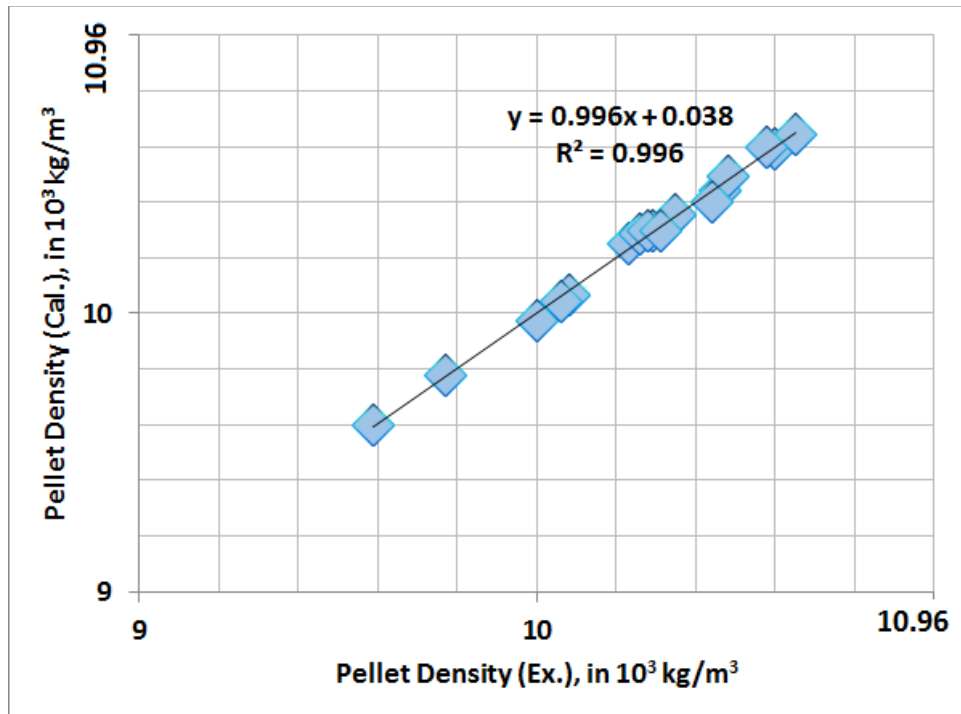
Fig. 2. Linear correlation between calculated and experimental values for the UO_2 pellet process **(a)** and contours of the sintering temperature vs. the sintering time on the UO_2 pellet density at 1073 K (b) levels of the conversion temperature **(b)**.
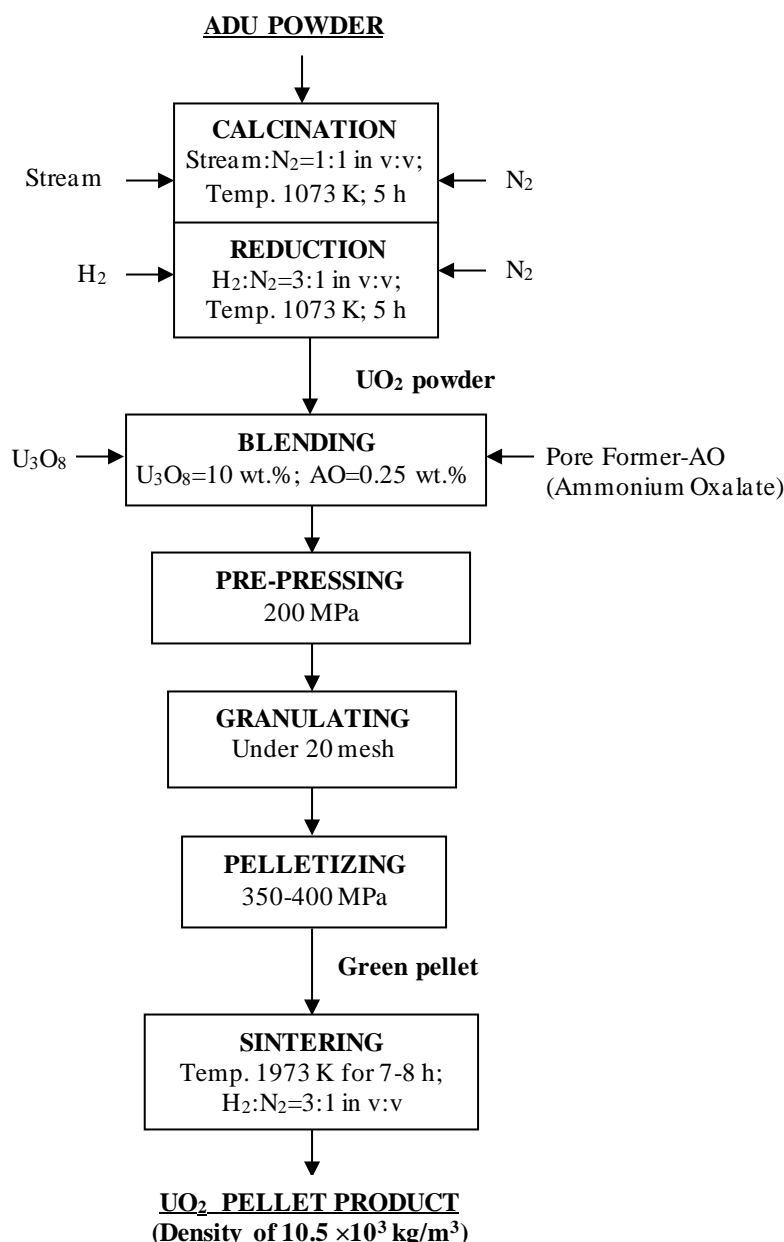
ADU POWDER

↓

CALCINATION
Stream:N_2=1:1 in v:v;
Temp. 1073 K; 5 h

Stream →   ← N_2

REDUCTION
H_2:N_2=3:1 in v:v;
Temp. 1073 K; 5 h

H_2 →   ← N_2

↓ **UO_2 powder**

BLENDING
U_3O_8=10 wt.%; AO=0.25 wt.%

U_3O_8 →   ← Pore Former-AO
(Ammonium Oxalate)

↓

PRE-PRESSING
200 MPa

↓

GRANULATING
Under 20 mesh

↓

PELLETIZING
350-400 MPa

↓ **Green pellet**

SINTERING
Temp. 1973 K for 7-8 h;
H_2:N_2=3:1 in v:v

↓

UO_2 PELLET PRODUCT
(Density of 10.5 $\times 10^3$ kg/m^3)

Fig. 3. Flow sheet of the UO_2 pellet process from the UO_2 ex-ADU powder.

Table 5 indicated various mechanical and physical characteristics of the pellet product and American Society for Testing and Materials (ASTM) international standards are used to determine some important characteristics of the UO_2 pellet products, including ratio of O/U, average grain size, porosity, resintering and etc.

Table 5

Inspection items	The pellet	Methods
Density, in 10^3 kg/m^3	10.52 – 10.58	ASTM C373-88 (Hydrostatic) [9]
Ratio of O/U	1.998 ± 0.003	ASTM C696-99 (Gravimetry) [10]
Average grain size, in μm	31.4 ± 2.3	ASTM E 112-96 (Metallo-graphy) [11]
Hardness, in Hv	749 ± 122	Vicker
Porosity, in % (volume)	3.96 ± 0.79	ASTM C373-88 [9]
Resintering, in %	0.53 ± 0.23	[8]
Content of F, in ppm	6	ASTM C696-99 (Pyrohydrolysis) [10]
Content of Cl, in ppm	20.5	ASTM C696-99 (Pyrohydrolysis) [10]

Content of C, in ppm	99	ASTM C776-06 [10]
Impurities, in ppm		ASTM C776-06 (ICP-MS) [10]
Al	114.2	
Ca+Mg	54.5	
Cr, Co, Th, B, Cd	below detection	
Fe	44.9	
Ni	0.13	
Si	102.3	
Rare Earths	< 1	

Conclusions

we proposed a mathematical model describing the effect of the fabrication parameters on SSA of UO_2 powders. To the best of our knowledge, the Brandon model as presented in equation (15) is used for the first time to describe the relationship between the essential fabrication parameters [(reduction temperature (T_R), calcination temperature (T_C), calcination time (t_C) and reduction time (t_R)] and SSA of the obtained UO_2 powder product. The proposed model was tested with Wilcoxon's rank sum test, showing a good agreement with the experimental parameters. The proposed model was well applied for roughly predicting SSA of UO_2 powders that is fabricated by means of calcination and reduction of ADU at our institution.

Modeling the UO_2 ex-ADU pellet process, using RSM based on CCD type of CCF was proposed. The quadratic mathematical model for the pellet density was shown a good agreement with the experimental data. The technological parameters for the UO_2 pellet process could be calculated from the proposed model so that the UO_2 pellet product has the desirable density level. And the flow sheet for preparing the UO_2 ex-ADU pellet product of the density of 10.5 $\times 10^3$ kg/m^3 was established.

Acknowledgments

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