Modeling the UO_2 ex-AUC pellet process

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Abstract

Studies on modeling uranium dioxide (UO_2) powder and pellet processes from ammonium uranyl carbonate (AUC)- derived uranium dioxide powder (UO_2 ex-AUC 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. To the best of our knowledge, the Brandon model 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 Brandon model was tested with Wilcoxon's rank sum test, showing a good agreement with the experimental parameters; the model can be used to predict and control the SSA of UO_2 powder.

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 AUC into UO_2 powder at various temperatures of 773 K, 823 K and 873 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.

The studies on the modeling were implemented at Nuclear Fuel Technology Center (ITRRE).

Key Words: UO_2 ex-AUC, 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_2F_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 calcinated and reduced into UO_2 powders. The AUC process has three merits [1-3]. First, the obtained UO_2 powder possesses good flowability that simplifies the subsequent pelletizing process by eliminating fringe steps and the addition of a lubricant. Thus, the obtained UO_2 powder can be directly pressed into green (unsintered) UO_2

pellets. Second, the UO_2 powders obtained from AUC route have highly stable sinterability. Lastly, the AUC process, in case of UF_6 conversion, is capable of bringing down the fluorine content to a low level.

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 AUC route.

In general, UO_2 ex-AUC powder is spherical and possesses good fluidity that would simplify the subsequent pelletizing process by eliminating fringe steps and the addition of a lubricant; and can be directly pressed into green pellets (unsintered UO_2 pellets), prepressing and granulating might be omitted [1-3]. 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 AUC 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-AUC pellet process was established to assess the sytematic relationship between the technological parameters and the density of UO_2 ex-AUC 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-AUC 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-AUC 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 AUC powder was precipitated by the reaction of ammonium carbonate with a synthetic solution containing UO_2F_2 and HF with U:F molar ratio of 1:6. The calcination of AUC 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^oC (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; with the UO_2 ex-AUC powder, prepressing and granulating might be omitted; 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 ^oC (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-AUC 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:

$$f_1(T_R) = 1.698 + 0.0009415.T_R \quad (6)$$

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

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

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

$$f_2(T_C) = 3.023 - 0.002935.T_C \quad (8)$$

$$f_3(t_C) = 1.353 - 0.095.t_C \quad (9)$$

$$f_4(t_R) = 1.365 - 0.0896.t_R \quad (10)$$

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

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

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

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

All of these values are reported in Table 1.

The constant a in Brandon equation was calculated from average of y_4 to be 1.0000255.

Thus, Brandon function describing the effect of the process parameters on the SSA of the UO_2 powder is in the form:

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

$$y(SSA) = 1.0000255.(1.698 + 0.0009415.T_R).(3.023 - 0.002935.T_C).(1.353 - 0.095.t_C).(1.365 - 0.0896.t_R) \quad (15)$$

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

Group $SSA_{(Cal.)}$: $Y_1, Y_2, Y_3, \ldots, Y_{n2}$; 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 $W_{(1)}, W_{(2)}, W_{(3)}, \ldots, W_{(n1+n2)}$; order data in the combined group $W_{(1)} \leq W_{(2)} \leq \ldots \leq W_{(n1+n2)}$; and then assign ranks (as in Table 2).

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

$S=2+6+7+8+10+11+12+15+16+17+18+22+26+27=197$

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/gr.)	$f_1(T_R)$	$\hat{y}_1$	$f_2(T_C)$	$\hat{y}_2$	$f_3(t_C)$	$\hat{y}_3$	$f_4(t_R)$	$\hat{y}_4$	$SSA_{(Cal.)}$ ($\hat{y}$) (m^2/gr.)
M1	550	5	650	4	2.250	2.216	1.015423	1.115	0.91049	0.973	0.93575	0.917	1.02045	2.206
M2	600	5	650	4	2.420	2.263	1.069424	1.115	0.95891	0.973	0.98552	0.917	1.07472	2.252
M3	650	5	650	4	2.645	2.310	1.145034	1.115	1.02671	0.973	1.05520	0.917	1.15071	2.299
M4	700	5	650	4	2.446	2.357	1.037738	1.115	0.93050	0.973	0.95632	0.917	1.04288	2.346
M5	600	2	700	3	2.724	2.263	1.203765	0.969	1.24292	1.068	1.16378	1.186	0.98143	2.776
M6	600	3	700	3	2.573	2.263	1.137037	0.969	1.17402	1.068	1.09927	1.096	1.00280	2.567
M7	600	4	700	3	1.977	2.263	0.873658	0.969	0.90207	1.068	0.84464	1.007	0.83910	2.357
M8	600	5	700	3	1.961	2.263	0.866587	0.969	0.89477	1.068	0.83780	0.917	0.91363	2.147
M9	700	3	600	5	3.259	2.357	1.382661	1.262	1.09561	0.878	1.24785	1.096	1.13834	2.864
M10	700	5	700	4	1.905	2.357	0.808214	0.969	0.83450	0.973	0.85766	0.917	0.93529	2.037
M11	700	3	700	5	2.228	2.357	0.945249	0.969	0.97599	0.878	1.11161	1.096	1.01406	2.198
M12	650	4	750	2	2.165	2.310	0.937240	0.822	1.14054	1.163	0.98069	1.007	0.97426	2.223
M13	650	4	750	3	2.399	2.310	1.038540	0.822	1.26381	1.068	1.18335	1.007	1.17559	2.041
M14	650	4	750	5	1.242	2.310	0.537668	0.822	0.65430	0.878	0.74521	1.007	0.74033	1.678

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

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	1.242	1.678	1.905	1.961	1.977	2.037	2.041	2.147	2.165	2.198
Rank	1	<u>2</u>	3	4	5	<u>6</u>	<u>7</u>	<u>8</u>	9	<u>10</u>
W_T	2.205	2.223	2.228	2.250	2.252	2.299	2.346	2.357	2.399	2.42
Rank	<u>11</u>	<u>12</u>	13	14	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	19	20
W_T	2.446	2.566	2.573	2.645	2.724	2.776	2.864	3.259		
Rank	21	<u>22</u>	23	24	25	<u>26</u>	<u>27</u>	28		

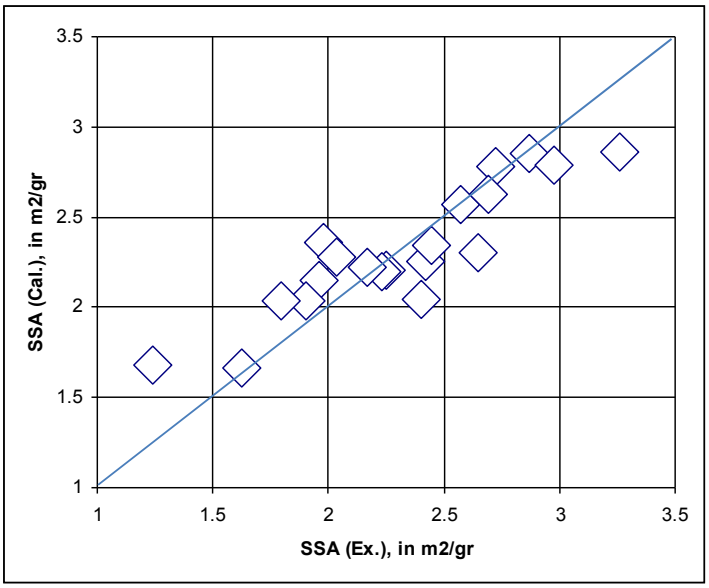

Fig. 1. The plot comparing $SSA_{(Ex.)}$ with $SSA_{(Cal.)}$ of the UO_2 powder.

Figure 1 is the plot comparing $SSA_{(Ex.)}$ with $SSA_{(Cal.)}$ of the UO_2 powder with coefficient of variation of 7.8% 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 AUC.

Table 3

Characteristics of the UO_2 powder

Inspection items	UO_2 ex-AUC	Methods
SSA	1.5 – 2.5 m^2/g	BET
Bulk density	$1.38 \pm 0.05 \times 10^3$ kg/m^3	Scott Volumeter
Tap density	$2.17 \pm 0.09 \times 10^3$ kg/m^3	Tap densitometer
O/U	2.116 ± 0.009	Gravimetry
F content	< 40 ppm	Pyrohydrolysis
Impurities (ppm)		ICP-MS
Al	104.6	
B, Cd, Cr, Co, Cu, Mo, Ta, Th, Ti, W, V	below detection	
Mg	26.6	
Ca	64	
Fe	43.5	
Pb	0.13	
Mn	0.13	
Ni	0.13	
Rare Earths	< 1	
Si	108.4	
Zn	0.13	

3.2. Modeling the UO_2 ex-AUC pellet process

With process parameters of the UO_2 pellet sintering, our study [6] also shown that the densities of UO_2 ceramic pellet samples prepared from UO_2 ex-AUC powders at conversion temperatures of 823 K (550 ^oC) and 873 K (600 ^oC) and at sintering temperature of 1973 K for 6 h were $10.25 \pm 0.06 \times 10^3$ kg/m^3 and $10.19 \pm 0.08 \times 10^3$ kg/m^3, respectively with the above conversion temperatures. Retesting sinterability of the UO_2 ex-AUC powders at conversion temperatures of 773 K (500 ^oC), 823 K and 873 K was performed at a sintering temperature of 1973 K for 8 h, the average densities of the UO_2 ceramic pellet samples were $10.38 \pm 0.11 \times 10^3$ kg/m^3, $10.49 \pm 0.07 \times 10^3$ kg/m^3 and $10.41 \pm 0.10 \times 10^3$ kg/m^3, respectively with the above conversion temperatures. On the other hand, testing sinterability of the UO_2 ex-AUC powders at the various technological parameters was performed. With the conversion temperature of 873 K and at the sintering temperature of 1923 K and time of 8 h, the average density of the UO_2 ceramic pellet samples was $9.96 \pm 0.16 \times 10^3$ kg/m^3. With the conversion temperatures of 773 K, 823 K and 873 K and at the sintering temperature and time of 2013 K

and 4 h, the average densities of the UO_2 ceramic pellet samples were 10.27± 0.16 $\times 10^3$ kg/m^3, 10.38 ± 0.14 $\times 10^3$ kg/m^3 and 10.41 ± 0.19 $\times 10^3$ kg/m^3, respectively with the about conversion temperatures. And with the conversion temperature of 873 K and at the sintering temperature of 2013 K and time of 6 h, the average density of the UO_2 ceramic pellet samples was 10.45 ± 0.16 $\times 10^3$ kg/m^3.

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 773 K (coded level of -1), 823 K (coded level of 0) and 873 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: $b_0 = 10.26$, $b_1 = 0.34$, $b_2 = 0.17$, $b_{11} = -0.26$, $b_{22} = 0.07$, $b_{12} = -0.09$ and $b_{13} = -0.06$. The probability values (p-value) of b_3, b_{33} 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 0.99, explaining that the variability of response is at 99% confidence level, and only 1% of the total variations cannot be explained by the model. Moreover, the value of adjusted determination coefficient (adj. R^2) of 0.98 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).

$$Y\ (\times 10^3\ kg/m^3) = 10.26 + 0.34X_1 + 0.17X_2 - 0.26X_1^2 + 0.07X_2^2 - 0.09X_1X_2 + 0.06X_1X_3 \quad (16)$$

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.

Table 4
Central composite rotatable design arrangement and results.

Run order	Independent variables						Responses		
	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	9.61 ± 0.26	2.69	9.55
2	1	-1	-1	2023	4	773	10.25 ± 0.16	1.59	10.27
3	-1	1	-1	1923	8	773	10.02 ± 0.21	2.10	10.05
4	1	1	-1	2023	8	773	10.44 ± 0.16	1.54	10.44
5	-1	-1	1	1923	4	873	9.36 ± 0.22	2.39	9.43
6	1	-1	1	2023	4	873	10.36 ± 0.14	1.32	10.39
7	-1	1	1	1923	8	873	9.96 ± 0.16	1.62	9.93
8	1	1	1	2023	8	873	10.50 ± 0.14	1.32	10.56
9	-1	0	0	1923	6	823	9.60 ± 0.23	2.43	9.66
10	1	0	0	2023	6	823	10.37 ± 0.16	1.53	10.34
11	0	-1	0	1973	4	823	10.15 ± 0.16	1.62	10.17
12	0	1	0	1973	8	823	10.48 ± 0.14	1.35	10.50
13	0	0	-1	1973	6	773	10.24 ± 0.13	1.26	10.26
14	0	0	1	1973	6	873	10.21 ± 0.14	1.36	10.26
15	0	0	0	1973	6	823	10.28 ± 0.16	1.51	10.26
16	0	0	0	1973	6	823	10.31 ± 0.16	1.53	10.26
17	0	0	0	1973	6	823	10.25 ± 0.14	1.36	10.26

CV is coefficient of variation.

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 and b_{13} (of X_1X_3) interactive coefficients are positive; meanwhile the b_{11} (of X_1^2) quadratic and b_{12} (of X_1X_2) interactive coefficients are negative; so contribution of X_1 on Y was small because positive effects of the b_1 linear and b_{13} interactive coefficients would be eliminated by negative effects of the b_{11} quadratic and b_{12} interactive ones; and the contribution could be quantitatively calculated by $b_0 \pm 0.07$. The b_2 (of X_2) linear coefficient is positive and much greater than the sum of the b_{22} (of X_2^2) quadratic and b_{12} (of X_1X_2) interactive ones; so contribution of X_2 on Y would be linear and could be quantitatively calculated by $b_0 \pm 0.20$. Contribution of X_3 on Y would only be the b_{13} interactive coefficient and small; this can be seen from Fig. 2 (b) that the surfaces of the sintering temperature vs. the sintering time on the UO_2 pellet density at 773 K, 823 K and 873 K levels of the conversion temperatures are similarity; contribution of X_3 on Y could be quantitatively calculated by $b_0 \pm 0.03$. Thus, the contributions of X_1, X_2 and X_3 to Y could be in order of $X_2 > X_1 > X_3$. The assessing of relationship between the X_i and Y would suggest controlling the UO_2 ex-AUC 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-AUC powders calculated from Eq. (15) at the conversion temperature of 773 K, 823 K and 873 K are 2.7 m^2/g, 2.5 m^2/g and 2.3 m^2/g, respectively [6]. And, as shown in the previous study [6], it is apparent that 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-AUC 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 AUC 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 873 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, 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 8.0 h; density of the UO_2 pellet product would be approximate 10.5×10^3 kg/m^3.

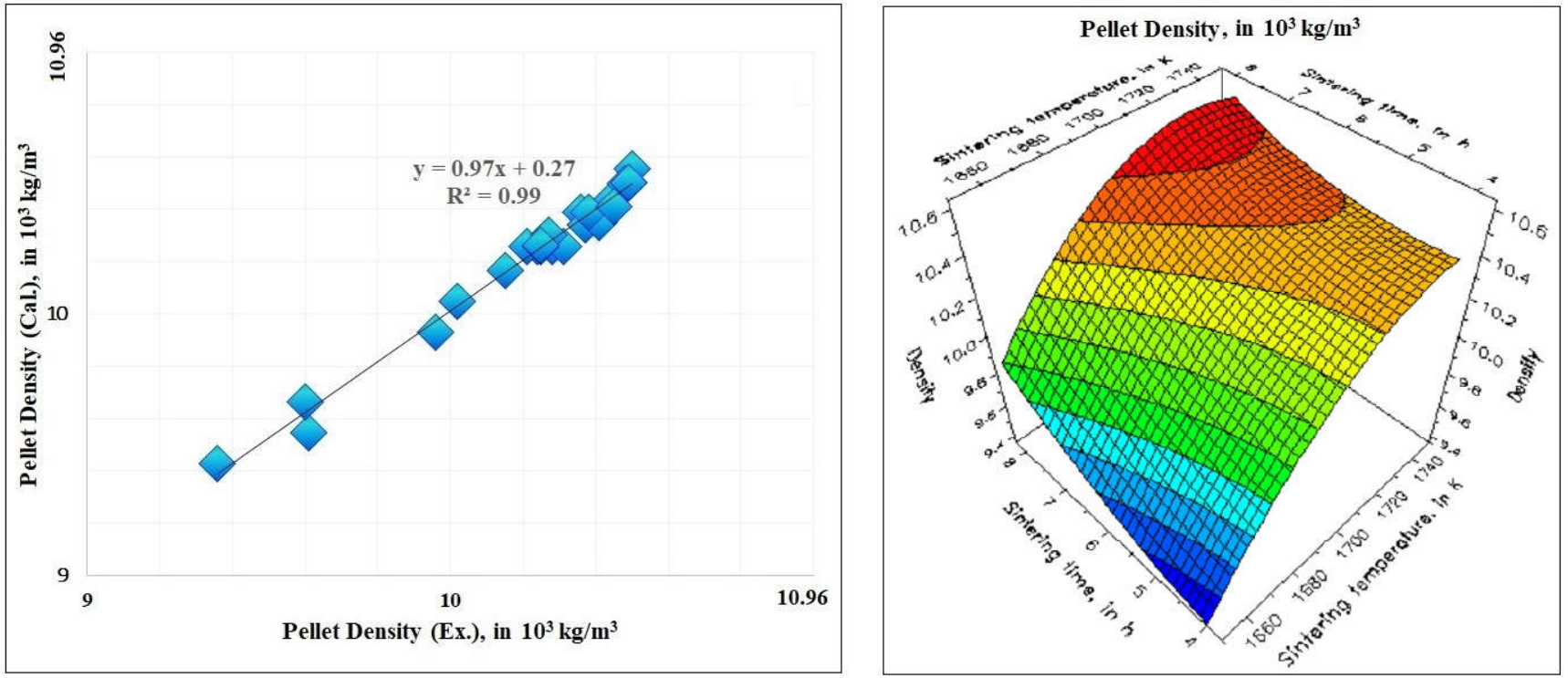

Fig. 2. Linear correlation between calculated and experimental values for the UO_2 pellet process **(a)** and response surface for the UO_2 pellet density (Y) as related to sintering temperature (X_1) and sintering time (X_2) at 873 K levels of the conversion temperature **(b)**.

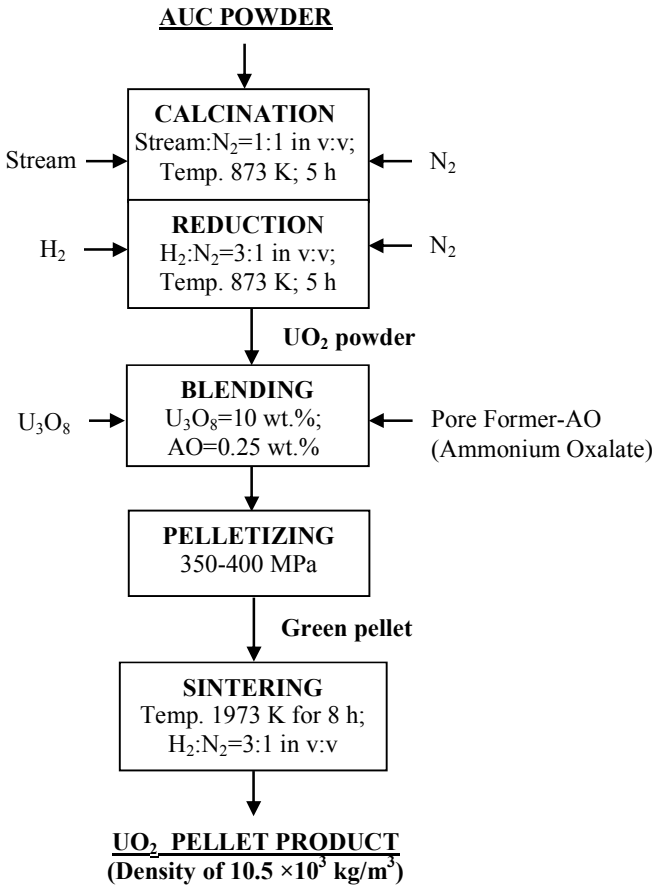

Fig. 3. Flow sheet of the UO_2 pellet process from the UO_2 ex-AUC powder.

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

Characteristics of the UO_2 pellet prepared from UO_2 ex-AUC powder.

Inspection items	The pellet	Methods
Density, in 10^3 kg/m^3	10.49 ± 0.07	ASTM C373-88 (Hydrostatic) [8-9]
Ratio of O/U	1.999 ± 0.003	ASTM C696-99 (Gravimetry) [10]
Average grain size, in μm	31.5 ± 2.5	ASTM E 112-96 (Metallo-graphy) [11]
Hardness, in Hv	637 ± 106	Vicker
Porosity, in % (volume)	4.74 ± 1.08	ASTM C373-88 [9]
Resintering, in 10^3 kg/m^3	0.07 ± 0.03	[8]
Content of F, in ppm	7	ASTM C696-99 (Pyrohydrolysis) [10]
Content of Cl, in ppm	15	ASTM C696-99 (Pyrohydrolysis) [10]

Content of C, in ppm	76	ASTM C776-06 [10]
Impurities, in ppm		ASTM C776-06 (ICP-MS) [10]
Al	100	
Ca+Mg	60.8	
Cr, Co, Th, B, Cd	below detection	
Fe	41.7	
Ni	0.13	
Si	104.5	
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 AUC at our institution.

Modeling the UO_2 ex-AUC 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-AUC pellet product of the density of 10.5×10^3 kg/m^3 was established.

Acknowledgments

Authors would like to acknowledge the financial support from the National Science and Technology Program, code KC.05-17/11-15, Vietnam Ministry of Science and Technology.

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