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The Brandon mathematical model describing the effect of calcination and reduction parameters on specific surface area of ex-ADU UO_2 powders

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Abstract: The report “Brandon mathematical model describing the effect of calcination and reduction parameters on specific surface area of UO_2 powders” [14] has built up a mathematical model describing the effect of the fabrication parameters on SSA (Specific Surface Area) of ex-AUC (Ammonium Uranyl Carbonate) UO_2 powders. In the paper, the Brandon mathematical model that 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 ex-ADU (Ammonium Di-Uranate) UO_2 powder product has established. The proposed model was tested with Wilcoxon’s rank sum test, showing a good agreement with the experimental parameters. The proposed model can be used to predict and control the SSA of ex-ADU UO_2 powders.

Keywords: *UO_2 powder, Ammonium Di-Uranate (ADU), Brandon mathematical model.*

I. INTRODUCTION

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 dry and wet conversion methods have been developed [4-9]. 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 [5-9]. The ex-ADU UO_2 powder possesses some characteristics different from the ex-AUC UO_2 powder, such as particle size and flowability [7-9]. The flowability and the particle size of the ex-AUC UO_2 powder are better than those of the ex-ADU UO_2 powder, so press feed preparation stage (pre-pressing and granulation) might be omitted for UO_2 ceramic pellet preperated from the ex-AUC UO_2 powder [1, 7-9].

Chemical reactions for ADU formation from uranyl solution, in particular, are as below [6]:

$$2UO_2F_2 + 6NH_4OH = (NH_4)_2U_2O_7 + 4NH_4F + 3H_2O \quad (1)$$

$$2UO_2F_2 + 6NH_3(gas) + 3H_2O = (NH_4)_2U_2O_7 + 4NH_4F \quad (2)$$

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: the calcination of ADU precipitate into U_3O_8 powder with

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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. In report [14], we built a mathematical model to describe the relationship between its SSA and the process parameters for the calcination and reduction for the ex-AUC UO_2 powder, the equation was:

$$y(SSA) = 1.0000255.(1.69 + 0.0009415.T_R).(3.023 - 0.002935.T_C).(1.353 - 0.095.t_C).(1.365 - 0.0896.t_R) \qquad (3)$$

In the paper, we would establish 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.

II. EXPERIMENTAL SECTION

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 calcination and reduction.

The calcination 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. Figure 1 shows a sketch of our apparatus. 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).

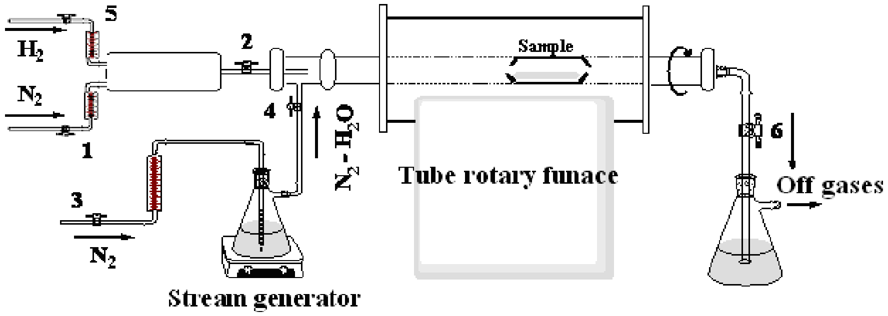

Fig. 1. Experimental setup, 1. N_2 flow for reduction; 2. Valve of H_2 and N_2 mixture flow for reduction; 3. N_2 flow for calcination; 4. Valve of N_2 and H_2O (stream) mixture flow for calcination; 5. H_2 flow for reduction; 6. Valve for gases out;

III. RESULTS AND DISCUSSION

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:

$$y = a.f_1(x_1)f_2(x_2)\dots f_j(x_j)\dots f_k(x_k) \qquad (3)$$

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 [12-14].

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:

$$\hat{y}_1 = \frac{y}{f(x_1)} \qquad (5)$$

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

$$\hat{y}_1 = a.f_1(x_1).f_2(x_2)\dots f_j(x_j)\dots f_k(x_k) \qquad (6)$$

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

$$\hat{y}_k = \frac{y_{k-1}}{f(x_k)} = \frac{y}{f_1(x_1).f_2(x_2)\dots f_k(x_k)} \qquad (7)$$

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:

$$f_1(T_R) = 5.3107 - 0.0024.T_R \qquad (8)$$

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

$$\hat{y}_1 = \frac{y}{f_1(T_R)} = \frac{SSA_{(Ex.)}}{f_1(T_R)} \qquad (9)$$

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

$$f_2(T_C) = 3.023 - 0.0029.T_C \qquad (10)$$

$$f_3(t_C) = 0.8507 + 0.0333.t_C \qquad (11)$$

$$f_4(t_R) = 0.9511 - 0.0121.t_R \qquad (12)$$

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

$$\hat{y}_2 = \frac{\hat{y}_1}{f_2(T_C)} \qquad (13)$$

$$\hat{y}_3 = \frac{\hat{y}_2}{f_3(t_C)} \qquad (14)$$

$$\hat{y}_4 = \frac{\hat{y}_3}{f_4(t_R)} \qquad (15)$$

All of these values are reported in Table I.

The constant a in Brandon equation was calculated from average of y_4 to be 0.999813.

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

$$y(SSA) = a.f_1(T_R).f_2(T_C).f_3(t_C).f_4(t_R) \qquad (16)$$

$$y(SSA) = 0.999813.(5.3107 - 0.0024.T_R).(3.023 - 0.0029.T_C).(0.850 + 0.0333.t_C).(0.9511 + 0.0121.t_R) \qquad (17)$$

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

Table I. 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.)	$SSA_{(Ex.)}(\ddot{y})$ (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	4.430	3.991	1.110081	1.138	0.975467	0.984	0.991429	1.012	0.980	4.519
M2	600	5	650	4	4.333	3.871	1.119436	1.138	0.983687	0.984	0.999783	1.012	0.988	4.383
M3	650	5	650	4	5.521	3.751	1.471992	1.138	1.29349	0.984	1.314656	1.012	1.300	4.247
M4	700	5	650	4	3.478	3.631	0.957942	1.138	0.841777	0.984	0.855551	1.012	0.846	4.112
M5	600	2	700	3	4.070	3.871	1.051489	0.993	1.058902	0.951	1.113930	0.975	1.142	3.563
M6	600	3	700	3	3.340	3.871	0.862893	0.993	0.868976	0.951	0.914134	0.987	0.926	3.607
M7	600	4	700	3	3.514	3.871	0.907846	0.993	0.914246	0.951	0.961757	1.000	0.962	3.651
M8	600	5	700	3	3.538	3.871	0.914047	0.993	0.920490	0.951	0.968325	1.012	0.957	3.695
M9	700	3	600	5	4.199	3.631	1.156526	1.283	0.901423	1.017	0.886181	0.987	0.897	4.678
M10	700	5	700	4	3.626	3.631	0.998705	0.993	1.005746	0.984	1.022203	1.012	1.010	3.588
M11	700	3	700	5	3.549	3.631	0.977497	0.993	0.984388	1.017	0.967743	0.987	0.980	3.620
M12	650	4	750	2	2.917	3.751	0.777721	0.848	0.917124	0.917	0.999809	1.000	1.000	2.916
M13	650	4	750	3	2.868	3.751	0.764657	0.848	0.901718	0.951	0.948578	1.000	0.949	3.021
M14	650	4	750	5	3.424	3.751	0.912896	0.848	1.076529	1.017	1.058325	1.000	1.059	3.233

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 II).

Table II. 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	2.916	2.917	3.021	3.233	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	3.563	3.588	3.607	3.62	3.626	3.651	3.695	4.07	4.112
Rank	11	12	13	14	15	16	17	18	19	20
W_T	4.199	4.247	4.333	4.383	4.43	4.519	4.678	5.521		
Rank	21	22	23	24	25	26	27	28		

Thus, sum of ranks S of group ŷ is calculated as follows:

$$S=2+4+5+12+13+14+15+17+18+20+22+24+26+27=219$$

Mean rank (μ_T) of distribution ŷ 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 219, in reliability range from 160.35 to 245.65, so two group *SSA(Ex.)* and *SSA(Cal.)* are asserted to be the same. 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.

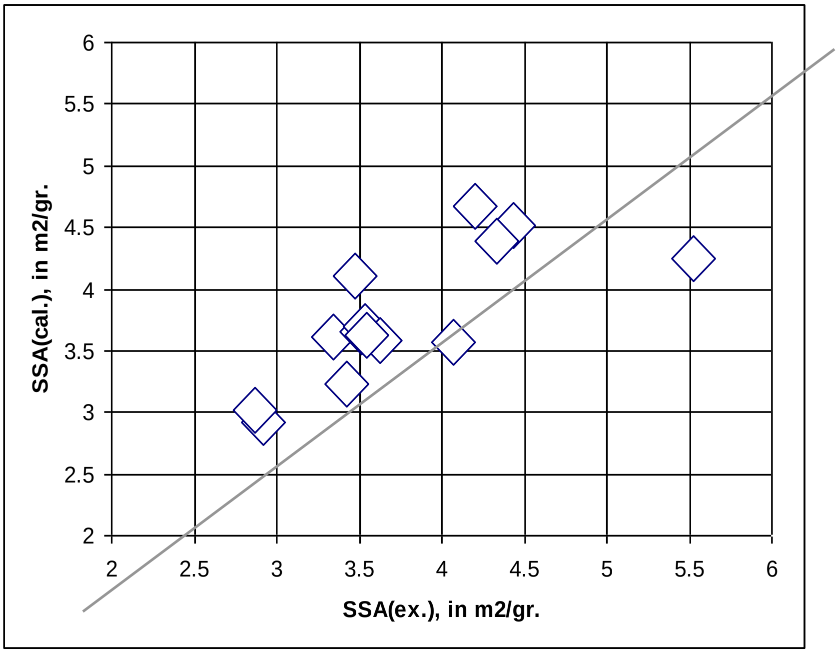

Fig. 2. Comparison of $SSA_{(Ex.)}$ and $SSA_{(Cal.)}$ of the ex-ADU UO_2 powder.

IV. CONCLUSIONS

In this paper, we proposed a mathematical model describing the effect of the fabrication parameters on SSA of the ex-ADU UO_2 powders. To the best of our knowledge, the Brandon model as presented in equation (17) 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 ex-ADU 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 the ex-ADU UO_2 powders that is fabricated by means of calcination and reduction of ADU at our institution.

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