Preparation of U_3O_8 by Calcination from Ammonium Uranyl Carbonate Using Response Surface Methodology: Process Ptimization

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ABSTRACT: *The parameters to prepare U_3O_8 by calcination from ammonium uranyl carbonate were optimized by using response surface methodology. A quadratic equation model for the value of total uranium and U^{4+} of triuranium octaoxide was built and the effects of main factors and their corresponding relationships were obtained. The statistical analysis of the results indicated that the value of total uranium and U^{4+} of triuranium octaoxide was significantly affected by the calcination temperature and calcination time in this study range. The optimized calcination conditions were determined as follows: the calcination temperature 961.6 K, the calcination time 27.9 min, and the mass of material 37.86 g, respectively. Under these conditions, the value of total uranium and U^{4+} of triuranium octaoxide was 84.29% and 28.14%. The validity of the model was confirmed experimentally and the results were satisfactory.*

KEYWORDS: *Ammonium uranyl carbonate; Response surface methodology; Calcination; U_3O_8; Total uranium; U^{4+}.*

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INTRODUCTION

Nuclear energy is clean, effective, and sustainable new energy. At present, nuclear energy occupies the centre stage among the group of preferred energy sources. It plays an essential role in overcoming the impending global energy crisis, and in reducing energy vulnerability. In addition, nuclear energy is a promising cheaper and cleaner energy source compared to fossil fuels, with no contribution to greenhouse gases [1]. In 2005, the International Energy Agency not only endorsed the expansion of nuclear energy but also encouraged countries to speed up the process [2-3]. Uranium dioxide, one of the most important fuel pellets, which is widely used as nuclear fuel in light water reactors, it is manufactured by calcining ammonium uranyl carbonate to triuranium octaoxide, followed by its reduction to uranium dioxide using cracked ammonia at 700℃[4]. Calcination technology significantly affects the quality of the products, subsequently, determines the profitability of the products. In spite of this, earlier attempts to optimize the important calcinations process through several common techniques have not yielded desirable result [5]. These techniques either rely on the classical one parameter at a time approach that ignores the combined interactions between physicochemical parameters, or are theoretical in nature. Furthermore, these techniques also require large number of experimental data to be generated [6]. In order to produce triuranium octaoxide in an optimized pathway which considers the interaction of different process parameters [7], there is a need to adopt multivariate statistical technique.

Response Surface Methodology (RSM) is a well-established mathematical and statistical technique for analyzing the effects of several independent variables [8]. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions [9]. It deals with multivariate experimental design strategy, statistical modeling and process optimization [10]. Several literature have shown that RSM is a powerful statistical tool in process optimization; it is successfully applied to optimize the process parameters for biosorption of metals [11], and producing dyes [12] from synthetic solutions. This work focused on employing RSM technique to calcination process of ammonium uranyl carbonate.

In this study, the effects calcination temperature, calcination time, and the mass of sample on the value of total uranium and U^{4+} of triuranium octaoxide were investigated by means of Central Composite Design (CCD, a part of RSM package). RSM was used to determine the optimal condition and an empirical model correlating the decomposition rate to the three variables was then developed.

EXPERIMENTAL SECTION

Materials and thermal decomposition behavior

The ammonium uranyl carbonate used in the study was obtained from No. 272 Nuclear industry Factory, China National Nuclear Corporation. The ammonium uranyl carbonate particle size was less than 50 μm. The thermal behavior of ammonium uranyl carbonate was reported in the literature. The results show that there are two weight loss stages (stages Ⅰ and Ⅱ) in the TG curves. For the TG curves, stage Ⅰ begins at 383 K and stops at 523 K, which is attributed to the decomposition of ammonium uranyl carbonate. Stage Ⅱ relates to the temperature range of 813-863K, which is interpreted by the reduction of uranium dioxide to triuranium octaoxide[13]. As can be seen, the weight loss is very significant for ammonium uranyl carbonate at 445 K, and the lower temperature of uranium dioxide to triuranium octaoxide is 813 K, which provide basis for temperature choose to prepare triuranium octaoxide by calcination from ammonium uranyl carbonate. On the basis of these results in literature, the thermal decomposition mechanism of ammonium uranyl carbonate could be summarized by eq as follow:

$$(NH_4)_4UO_2(CO_3)_3 = 4NH_3 + UO_3 + 2H_2O + 3CO_2 \quad (1)$$

$$3UO_3 + H_2 = U_3O_8 + H_2O \quad (2)$$

Calcination experiments

The calcination experiments were carried out in a conventional tube furnace, the influence of different parameters, such as temperature, duration of calcination times, and mass of sample were studied. Initially, the furnace was preheated at 25 K/min until the target temperature was reached. Then the ammonium uranyl carbonate was weighed and placed in a ceramic reactor which was located approximately in the centre of

Table 1: Independent variables and their level used for center composite rotatable design.

Independent variables	Symbol	Coded variable levels	
		-1	+1
Calcination temperature (K)	χ_1	673	1073
Calcination time (min)	χ_2	20	60
Mass of sample (g)	χ_3	30	50

the tubular electric oven. During the reaction, the temperature was monitored by a PID (proportional–integral–derivative) temperature controller system. Several cycles of experiment were repeated. For each cycle, an experiment was performed for a fixed duration. Afterwards, the product was removed from the tubular reactor and put into a drier rapidly. They were naturally cooled to the ambient temperature. The value of total uranium and U^{4+} of triuranium octaoxide was determined using chemical analysis methods according to the EJ/T947－95.

Designation of experiment using Response surface methodology

On the basis of initial decomposition results and analysis of TG, RSM was employed to optimize the calcination conditions in order to obtain a high the value of total uranium and U^{4+} of triuranium octaoxide, and CCD was employed to design the experiments. In this study, the effects of three independent variables, χ_1 (calcination temperature), χ_2 (calcination time), and χ_3 (mass of sample), were investigated at two level using central composite design (Table 1).

The value of the total uranium and U^{4+} of triuranium octaoxide was taken as the two responses of the designed experiments. A total of 20 experiments consisting of 8 factorial points, 6 axial points, and 6 replicates at the central points were performed. The experimental data obtained from the designed experiment were analyzed by the response surface regression procedure using the following second-order polynomial equation [14-15]:

$$\gamma = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i<j}^{n} \beta_{ij} \chi_i \chi_j, \quad (3)$$

where γ is the predicated response, β_0 is a constant, β_i represents the i-th linear coefficient, β_{ii} is the i-th quadratic coefficient, β_{ij} indicates ij-th interaction coefficient, and χ_{ij} s are independent variables.

RESULTS AND DISCUSSION

Data analysis and evaluation of the model by RSM

Table 2 shows the results of the experiments conducted based on the design matrix under the defined conditions. The value of the total uranium of triuranium octaoxide was found to range from 61.25% to 85.62%, while the value of U^{4+} of triuranium octaoxide obtained range from 0.23% to 32.7%. 15-20 runs at the central point were used to determine the experimental error. According to the sequential model, the sum of squares can be obtained, and the models were selected based on the highest order polynomial where the additional terms were significant and the models were not aliased [16]. The responses of the value of the total uranium and U^{4+} of triuranium octaoxide were considered in studying the effect of process variables. The response of the value of total uranium, U^{4+} of triuranium octaoxide and the independent variables were used to develop an empirical model after excluding the insignificant terms, which is presented by Eq. (3) and (4), respectively:

$$\gamma_1 = -44.57 + 0.20\chi_1 + 1.57\chi_2 - 0.29\chi_3 - 1.03\chi_1\chi_2 + 4.07\chi_1\chi_3 + 1.21\chi_2\chi_3 - 8.13\chi_1^2 - 6.36\chi_2^2 - 1.86\chi_3^2 \quad (4)$$

$$\gamma_2 = -90.51 + 0.23\chi_1 + 1.00\chi_2 - 1.05\chi_3 - 2.09\chi_1\chi_2 + 7.01\chi_1\chi_3 - 2.36\chi_2\chi_3 - 1.18\chi_1^2 - 6.61\chi_2^2 - 6.06\chi_3^2 \quad (5)$$

The quality of the model developed was evaluated based on the correlation coefficient value[17]. The R^2 values for Eq. (4) and Eq. (5) were 0.987 and 0.943, respectively, which indicated that 98.7% and 94.3% variabliity of the total variation in the total uranium and U^{4+} of triuranium octaoxide was attributed to the experimental variables studied. The R^2 of 0.987 and 0.943 for Eq. (4) and Eq. (5) was considered relatively high,

Table 2: Experimental design matrix and results.

Run	Calcination temperature χ_1 (K)	Calcination time χ_2 (min)	Mass of sample χ_3 (g)	Total uranium γ_1 (%)	U^{4+} γ_2 (%)
1	673.00	20.00	30.00	64.56	12.39
2	1073.00	20.00	30.00	84.71	28.69
3	673.00	60.00	30.00	80.11	19.6
4	1073.00	60.00	30.00	84.71	30.5
5	673.00	20.00	50.00	61.25	10.87
6	1073.00	20.00	50.00	85.51	30.73
7	673.00	60.00	50.00	78.62	14.14
8	1073.00	60.00	50.00	85.62	32.7
9	536.64	40.00	40.00	67.15	0.23
10	1209.36	40.00	40.00	84.69	28.31
11	873.00	6.36	40.00	70.44	8.78
12	873.00	73.64	40.00	85.42	31.41
13	873.00	40.00	23.18	85.25	30.31
14	873.00	40.00	56.82	83.94	28.27
15	873.00	40.00	40.00	84.31	27.58
16	873.00	40.00	40.00	84.71	28.24
17	873.00	40.00	40.00	84.39	28.52
18	873.00	40.00	40.00	84.45	29.16
19	873.00	40.00	40.00	84.53	28.89
20	873.00	40.00	40.00	84.61	29.08

indicating that there was a good agreement between the experimental value and the predicted one from this model.

Furthermore, anlysis of variance (ANOVA, also a part of RSM) was carried out to justify the adequacy of the model. The ANOVA for the quadratic model for the value of the total uranium and U^{4+} of triuranium octaoxide is presented in Table 3. The model's adequacy was tested through the lack of fit F-test, in which the residual error was compared to the pure error (Table 3). According to the software analysis, "Lack of fit F-value" of the total uranium of triuranium octaoxide of 136.86 implies that the lack of fit was significant. The "Model F-value" of the total uranium of triuranium octaoxide of 86.12 implies that the model was significant and there was only a 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" of the total uranium of triuranium octaoxide less than 0.05 indicate that the model terms are significant, whereas the values greater than 0.1 are not significant. The same, "Lack of fit F-value" of the U^{4+} of triuranium octaoxide of 51.32 implies that the lack of fit was significat. The "Model F-value" of the U^{4+} of triuranium octaoxide of 18.51 implies that the model was significant and there was only 0.01% chance that a "Model F-value" this large could occur due to noise. Values of "Prob> F" of the U^{4+} of triuranium octaoxide less than 0.05 indicates that the model terms are significant.

The checking of model adequacy is an important part of the data analysis procedure, since it would give poor or misleading results if it is an inadequate fit [18]. Multivariable linear regression was used to calculate the coefficients of the second-order polynomial equation and the regression coefficients, whose significance was

Table 3: Analysis of variance (ANOVA) for response surface quadratic model for the value of total uranium and U^{4+} of triuranium octaoxide.

Source	Df	Sum of squares		Mean square		F-value		Prob > F	
		ΣU	U^{4+}	ΣU	U^{4+}	ΣU	U^{4+}	ΣU	U^{4+}
Model	9	1151.87	1570.36	127.99	174.48	86.12	18.51	<0.0001	<0.0001
Residual	10	14.86	94.27	18.49	9.43				
Lack of fit	5	14.75	92.47	2.95	18.49	136.86	51.32	<0.0001	0.0003
Pure error	5	0.11	1.80	0.022	0.36				
Cor total	19	1166.74	1664.63						

R^2=0.987 R^2_{adj} =0.976 adequate precision=27.122 >4 ; R^2=0.943 R^2_{adj} =0.893 adequate precision=14.83 >4

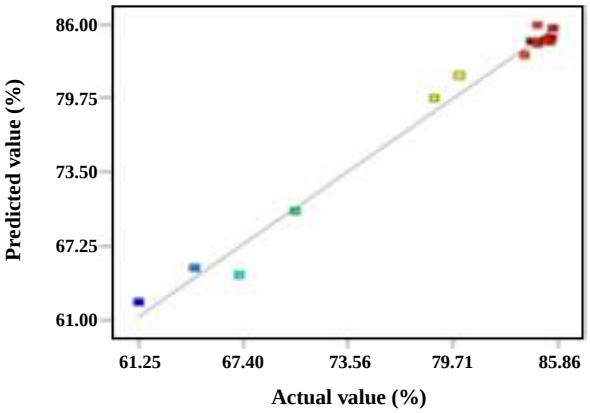

Fig. 1: Predicted vs. experimental vaule for the total uranium of triuranium octaoxide.

determined using the P-value, summarized in Table 4. In this case, χ_1, χ_2, χ_1^2, χ_2^2 and the interaction terms ($\chi_1\chi_2$) were significant to the total uranium of triuranium octaoxide, and χ_1, χ_2, χ_1^2, χ_2^2 were significant to $U^{4+}$of triuranium octaoxide, whereas the interaction terms (χ_1, χ_2, $\chi_2\chi_3$, $\chi_1\chi_3$) were insignificant to the response.

Response surface analyses

Total uranium of triuranium octaoxide

As shown in Fig.1, the predicted values were compared with the experimental values for total uranium of triuranium octaoxide. Actual response values were measured for a particular run, and the predicted values were evaluated from the model and generated by using the approximating functions. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the model developed was reasonable.

As we know, the best way to visualize the influence of the independent variables on the response is to draw surface response plots of the model [19]. The three-dimensional response surfaces which were constructed to show the effects of the calcination variables on the value of triuranium octaoxide using the fitted quadratic polynomial equation obtained from regression analysis were shown in Fig. 2 and Fig. 3. Fig. 2 shows the effect of calcination temperature and calaination time on the value of total uranium of triuranium octaoxide at the fixed mass of sample of 40 g, while Fig. 3 shows the effect of calcination temperature and mass of sample on the value of the total uranium of triuranium octaoxide, with the calcination time set at 40 min. It was observed that the value of total triuranium octaoxide significantly increased with increasing calcination temperature and calcination time, while the value of total triuranium octaoxide is seen to increase with a decrease in mass of sample within the experimental range studied. It seems that more ammonium uranyl carbonate was decomposed with increasing temperature. This can be interpreted as the thermal decomposition of ammonium uranyl carbonate is endothermic reaction and ammonium uranyl carbonate would take place acceleration reaction with the increasing temperature [13]. Moreover, it should be mentioned that, Extending the calcination time leads to a complete calcination reaction. Thereby, the total uranium of triuranium octaoxide increased with increasing calcination temperature and caicination time. Additionally, the figure reveals that the effect of the calcination temperature on the value of total triuranium octaoxide was more significant than calcination time.

Table 4: Regression coefficient of polynomial function of the value of total uranium and U^{4+}.

Term	Df	Regression coefficient		Standard error		Lower confidence limites		Upper confidence limites		P-value	
		ΣU	U^{4+}	ΣU	U^{4+}	ΣU	U^{4+}	ΣU	U^{4+}	ΣU	U^{4+}
Intercept	1	84.53	28.52	0.50	1.25	83.43	25.73	85.64	31.31		
χ_1	1	6.26	8.26	0.33	0.83	5.53	6.41	7.00	10.11	<0.0001	<0.0001
χ_2	1	4.26	3.83	0.33	0.83	3.53	1.98	5.00	5.68	<0.0001	0.0010
χ_3	1	-0.39	-0.45	0.33	0.83	-1.12	-2.30	0.35	1.40	0.2672	0.5985
$\chi_1\chi_2$	1	-4.10	-0.84	0.43	1.09	-5.06	-3.26	-3.14	1.58	<0.0001	0.4582
$\chi_1\chi_3$	1	0.81	1.40	0.43	1.09	-0.15	-1.02	1.77	3.82	0.0883	0.2254
$\chi_2\chi_3$	1	0.24	-0.47	0.43	1.09	-0.72	-2.89	1.20	1.95	0.5880	0.6726
χ_1^2	1	-3.25	-4.70	0.32	0.81	-3.97	-6.51	-2.54	-2.90	<0.0001	0.0002
χ_2^2	1	-2.54	-2.64	0.32	0.81	-3.26	-4.45	-1.83	-0.84	<0.0001	0.0084
χ_3^2	1	-0.19	0.61	0.32	0.81	-0.90	-1.20	0.53	2.41	0.5751	0.4708

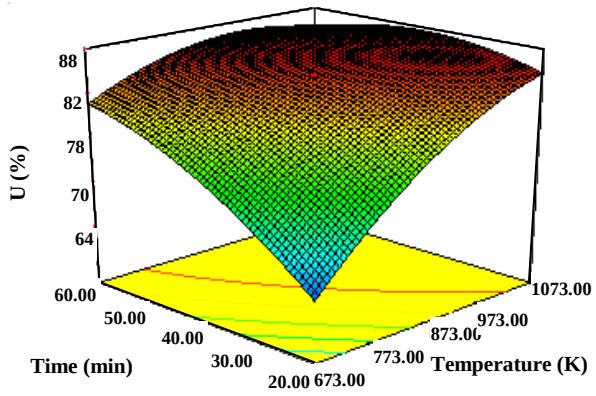

Fig. 2: Three-dimensional plot of the response surface for the total uranium of triuranium octaoxide (γ_1). As related to temperature (χ_1) and time (χ_2).

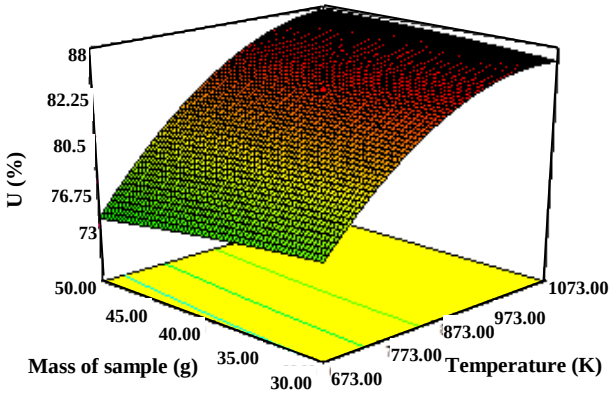

Fig. 3: Three-dimensional plot of the response surface for the total uranium of triuranium octaoxide (γ_1) As related to temperature (χ_1) and mass of sample (χ_3).

U^{4+} of triuranium octaoxide

The predicted values versus the experimental values for U^{4+} of triuranium octaoxide is shown in Fig. 4. It was found that the predicted value obtained was less close to the experimental value than that in Fig. 1. This may be attributed to the high R^2 and low standard deviation values of the model.

The three-dimensional display of the response surface plot of the U^{4+} of triuranium octaoxide as function of the calcination temperature, calcination time, and mass of sample were shown in Fig. 5 and Fig. 6, respectively. Fig. 5 shows the effect of calcination temperature and calaination time on the value of U^{4+} of triuranium octaoxide, and Fig. 6 shows the effect of calcination temperature and mass of sample on the value of U^{4+} of triuranium octaoxide. As seen from Fig. 5 and Fig. 6, the value of U^{4+} of triuranium octaoxide increased abruptly with the increase of calcination temperature and then underwent a smooth increase after 973 K, while the value of U^{4+} of triuranium octaoxide decreased with increasing mass of sample within the experimental range studied. Those attributed to reduction reaction of uranium trioxide. As a result of endothermic reaction, reduction reaction of uranium trioxide would take place acceleration with the increasing temperature [13]. In addition, reduction reaction of uranium trioxide

Table 5: Model valid of the response surface of decomposition rate of cobalt oxalate.

Variables			Response			
			ΣU		U^{4+}	
Calcination temperature, (K)	Calcination time, (min)	Mass of sample, (g)	Predicted (%)	Experimental (%)	Predicted (%)	Experimental (%)
961.6	27.8	37.86	84.29	84.17	28.14	29.06

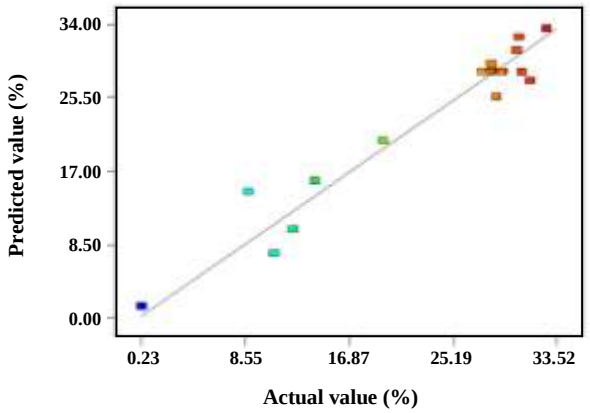

Fig. 4: Predicted vs. experimental vaule for U^{4+} of triuranium octaoxide.

isgas-solid phase reaction. therefore, the diffusion of gas became difficult with increasing mass of the sample, resulting in decrease in concentration of U^{4+} in triuranium octaoxide.

Optimal conditions and verification of the model

Thus, based on the above model, the optimal condition for the value of total uranium and U^{4+} of triuranium octaoxide at 961.6 K, 27.9 min, and 37.86 g and the value of total uranium and U^{4+} of triuranium octaoxide were 84.29% and 28.14%, respectively. In order to confirm the optimized conditions, the accuracy of the model was validated with experiments under conditions of optimum. An experiment was carried out with parameters as suggested by the model. The conditions used in the confirmatory experiment were as follows: Calcination temperature 962 K, calcination time 28 min and mass of sample 37.86 g. In this scenario, a value of total uranium and U^{4+} of triuranium octaoxide of 84.17% and 29.06%, respectively, are obtained, which concurred with the model prediction. The model is considered as fitting the experimental data very well in these experimental conditions, with an error margin of only 0.15% and 0.32%, respectively. Therefore, the model is acceptably valid.

Experimental on pilot-scale

Through RSM results and its experimental validation, it has been demonstrated that calcination temperature and calcination time were the most critical factor for a value of total uranium and U^{4+} of triuranium octaoxide. Based on these results calcination experiment of ammonium Uranyl carbonate on pilot-scale was supplemented in Fig. 7 under the optimal conditions. The output power of the rotary kiln was 24kW and the handling capacity of the reactor was about 200kg per hours.

We could see obviously from Fig. 7 that a value of total uranium and U^{4+} of triuranium octaoxide higher than the former technology. Product quality was improved significantly using response surface methodology.

CONCLUSIONS

This research was carried out to determine optimum conditions for preparation of U_3O_8 by caicination from ammonium uranyl carbonate. The effects of operating parameters on calcination temperature, calcination time, and mass of sample were optimized using RSM. A quadratic model was developed to correlate the calcination variables with the total uranium and U^{4+} of triuranium octaoxide, respectively. This study showed that response surface methodology was an approving approach to optimize conditions for achieving suitable value of total uranium and U^{4+} of triuranium octaoxide. The experimental and predicted values were very close, which reflected the correctness and applicability of RSM. The value of the adjusted determination coefficient was 0.976 and 0.893, respectively, showing a relatively high significance. By RSM to optimize experiments, the optimal condition was found to be at 961.6 K, 27.9 min, and 37.86 g, respectively. Under these conditions, the predicted value of total uranium and U^{4+} of triuranium

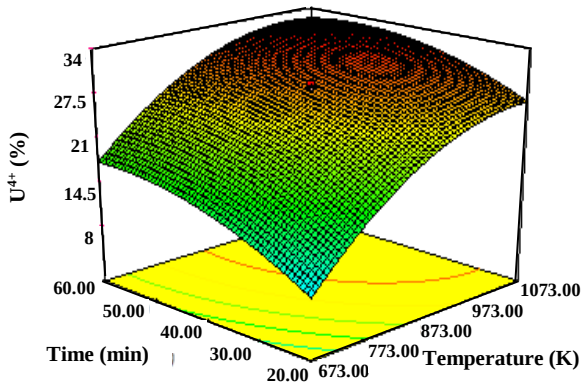

Fig. 5: Three-dimensional plot of the response surface for U^{4+} of triuranium octaoxide (γ_2). As related to temperature (χ_1) and time (χ_2).

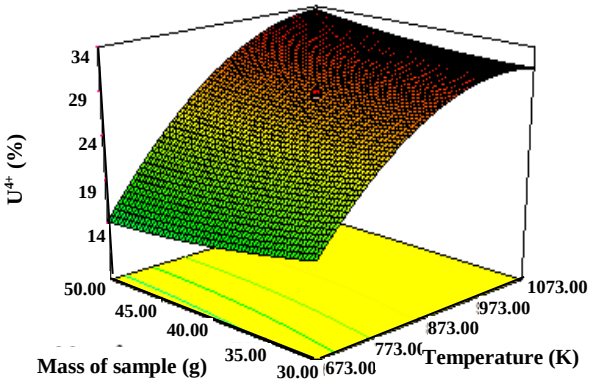

Fig. 6: Three-dimensional plot of the response surface for U^{4+} of triuranium octaoxide (γ_2). As related to temperature (χ_1) and mass of sample (χ_3).

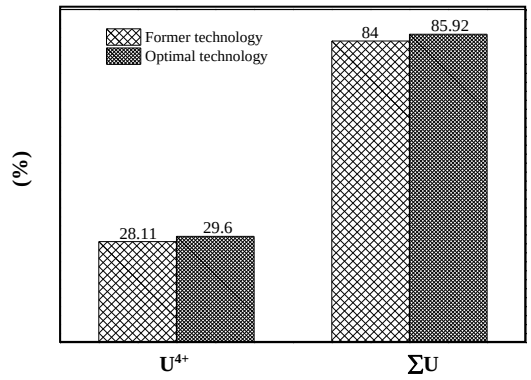

Fig. 7: The value of total uranium and U^{4+} of triuranium octaoxide under former technology and optimal technology.

octaoxide of 84.29% and 28.14% was in good agreement with the actual experimental values (84.17% and 29.06%). Compared with former technology, a value of total uranium and U^{4+} of triuranium octaoxide were improved using response surface methodology.

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Nomenclature

χ_1	Calcination temperature
χ_2	Calcination time
χ_3	Mass of sample
χ_{ij}	Independent variables

Greek symbol

β_0	Constant
β_i	Linear coefficient
β_{ij}	Interaction coefficient
β_{ii}	Quadratic coefficient
γ_1	Value of total uranium of triuranium octaoxide
γ_2	Value of $U^{4+}$of triuranium octaoxide

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