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SEMI-BATCH AND CONTINUOUS CARBOCHLORINATION OF ZIRCONIA IN A PILOT PLANT FLUIDIZED BED REACTOR: OPTIMIZATION OF OPERATING CONDITIONS *VIA* RESPONSE SURFACE METHODOLOGY

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Keywords:

Zirconia, Carbochlorination, Response surface methodology (RSM), Fluidized bed reactor (FBR)

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ABSTRACT: Zirconium tetrachloride was produced in a pilot plant fluidized bed reactor *via* the carbochlorination reaction of zirconia. Minitab software 17 was used for the design of experiment with response surface methodology (RSM) for both semi batch and continuous processes. The operating temperature (800-1200 °C), reaction time (30-90 min) and mean particle size (MPS) (70-130µm) were chosen as the range of operating conditions at semi-batch mode. Also, the ranges of operating variables at the continuous mode were chosen to be the operating temperature(1000-1400°C), chlorine concentration (3-5mol/m^3) and mean particle size (MPS) (70-130µm). The coefficients of determination (R^2) for semi-batch and continuous modes by RSM analysis were 99.54% and 99.94%, respectively. The optimal operating conditions was predicted to be the Cl_2 concentration of 3mol/m^3, temperature of 1380 °C and the mean particle size of 70µm in which the maximum chlorine conversion of 98.26% was obtained at continuous process. The optimum operating conditions for semi-batch process were found by using RSM modelling to be 1200°C, 90 min and 70 µm, in which the maximum zirconia conversion of 92.7% was obtained.

INTRODUCTION: Zirconia (Zirconium dioxide (ZrO_2)) is a crystalline oxide of zirconium [1]. Zirconium metal has unique characteristics like resistance to radiation damage [2], very low absorption cross section [3, 4], compatibility with uranium fuel [5], resistance to corrosion [6], retention of strength [7] and desirable response to alloying modifications [8]. Also, pure zirconia is used in nuclear and metallurgical industries, solid electrolytes, optical fibers and gem industries (cubic single crystals) [9].

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Nuclear-grade zirconium metal produces in the conventional process from zirconium tetrachloride by the magnesium reduction or fused salt electrolysis. Chlorination of pure ZrO_2 using chlorine in the presence of carbon at high temperature produces zirconium tetrachloride ($ZrCl_4$) [10].

$ZrCl_4$ is used as the starting material in other proposed methods for the production of zirconium as an alternative to conventional route [11]. According to the following reaction, Zirconium tetrachloride is produced using chlorination of zirconia in the presence of carbon which is really an approximation (CO_2 formation occurs simultaneously with CO) [12]:

$$ZrO_2 + 2Cl_2 + 2C \rightarrow ZrCl_4 + 2CO \quad (1)$$

This reaction is called carbochlorination, because, ZrO_2 chlorination occurs in the existence of carbon (a reducing agent) in dry conditions to make the reaction thermodynamically possible. Presence of carbon favours the formation of chlorides and decreases the oxide formation tendency by providing a low oxygen potential atmosphere. It is known that at the same high temperature, the chlorination reaction rate is slower than the carbochlorination reaction [9]. Fluidized bed reactor (FBR) is a contacting device that uses the principle of fluidization in its operation. FBR has many benefits, including uniform temperature distribution, favourable heat and mass transfer, low pressure drop, excellent particle mixing, operational flexibility and ease of solid handling [13].

Zirconia carbochlorination is a complex non-catalytic gas-solid reaction. There are some investigations that report the chlorination of zirconia. Zirconium dioxide carbochlorination on literature contains the main kinetic parameters (such as the order of the reaction with respect to reactants and activation energy) and the reaction mechanism. These investigations often hampered by the reaction complexity because involve two solid and one gaseous reacting component.

O' reilly *et al.*, [14] found that in the carbochlorination of ZrO_2 in a static bed (using excess of petroleum coke powder), the chemical reaction model controls the process in the temperature range of 1223-1373 K. The activation energy and order of reaction into Cl_2 were 230.3 kJ mol^{-1} and 0.64, respectively. Jena *et al.*, [10] studied ZrO_2 chlorination kinetics in the temperature range of 973 to 1273 K. The activation energy was found to be 18.3kJ/mol. Bicerolu and Gauvin [11] determined the kinetics of carbochlorination of ZrO_2 and the effects of temperature (1400-1950 K), chlorine concentration and carbon (graphite) content on the rate of conversion in a thermo-gravimetric analysis. They reported the activation energy and order of reaction into Cl_2 to be $94 kJ/mol^{-1}$ and 0.79, respectively. Moreover, they found that the carbon concentration range of 22-26% can result in maximum rate of process.

Landsberg *et al.*, [15] studied the kinetics of zirconium dioxide (in the form of disk pellets surrounded by a loosely packed bed of carbon powder) chlorination in the temperature range of 1120-1320 K. They found that the rate of reaction for carbothermic chlorination was first order with respect to the chlorine concentration and the activation energy was determined to be 127.7kJ/mol. The results of different studies varied based on experimental conditions, the method of sample preparation and the type of carbonaceous agent used. A survey of the literature showed that there is no published data regarding to chlorination reaction of zirconia in the presence of carbon in a pilot scale fluidized bed reactor, in spite of the fact that it is very important in the extractive metallurgy of zirconium.

The purpose of the present work was the carbochlorination of zirconia in a pilot plant fluidized bed reactor in the semi-batch and continuous mode. No attempt was made to identify the detailed mechanism of the reaction or the reaction rate. RSM was implemented for the modelling and optimizations of operating conditions while the response (reaction conversion) was affected by chlorine concentration, temperature, reaction time and mean particle size. Furthermore, the important operating parameters affecting the reactor performance were investigated by the validated model.

Experimental Section:

MATERIALS: The gases used for this study were Nitrogen (99.9% purity) and Cl_2 (99.9% purity). The powdered materials were ZrO_2 (Sooreh Co., Isfahan, Iran) (composition: Zr = 73.9%, Fe = 0.18%, Si = 0.015%, Al = 0.01% and Hf = 0.004%) and carbon (composition: fixed carbon = 95.8%, Ash = 3.2%, Volatile 0.6% and heating loss = 0.4%). The BET surface areas of ZrO_2 and carbon were determined to be $14.4 m^2/g$ and $1.5 m^2/g$, respectively (Sorptometer Kelvin 1042, ISO 9277-2010). The characterization (size and morphology) of the powdered ZrO_2 and carbon were determined by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). **Fig. 1** and **2** shows the SEM and XRD of the powdered materials in the reactor feed, respectively. The mixture of carbon / zirconia (20/80% wt) was used to prepare briquettes using laboratory hydraulic press. Then the briquettes were powdered by means of a laboratory crusher to produce particles with mean size from 70 to 130 µm.

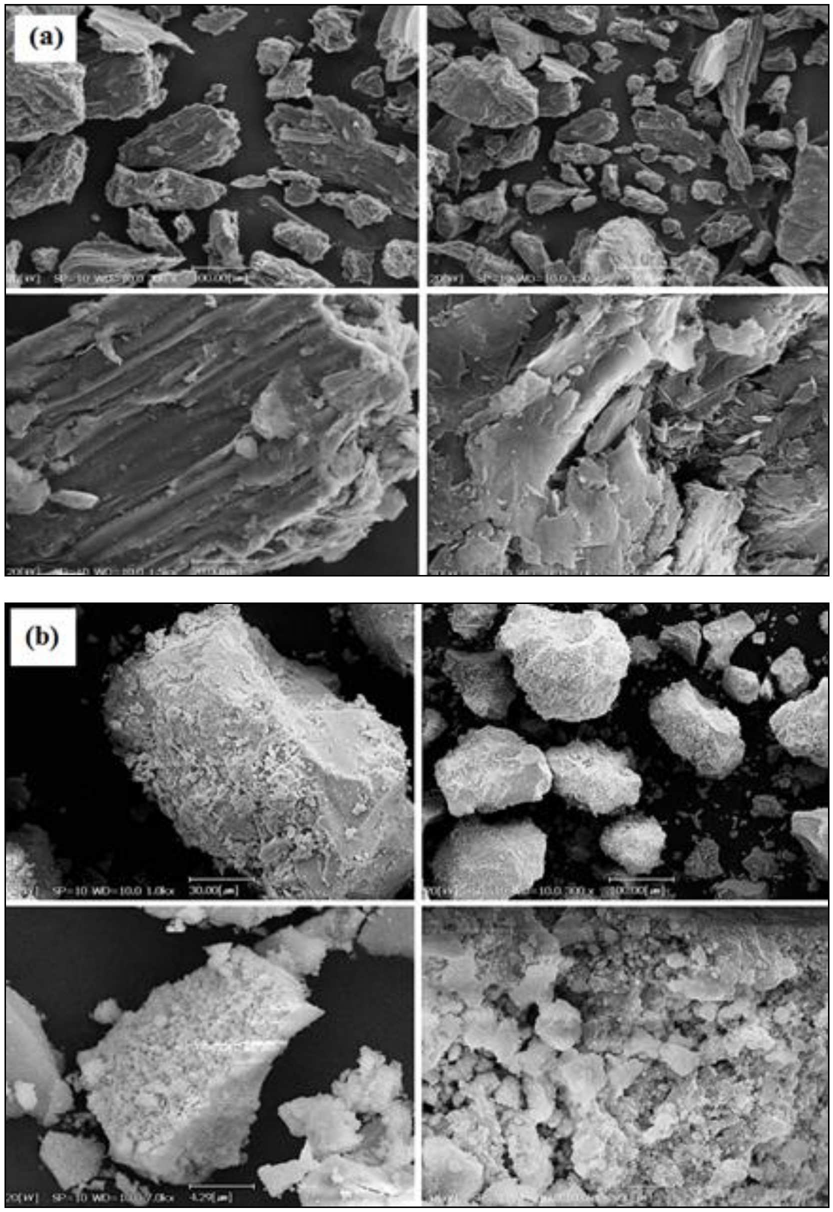
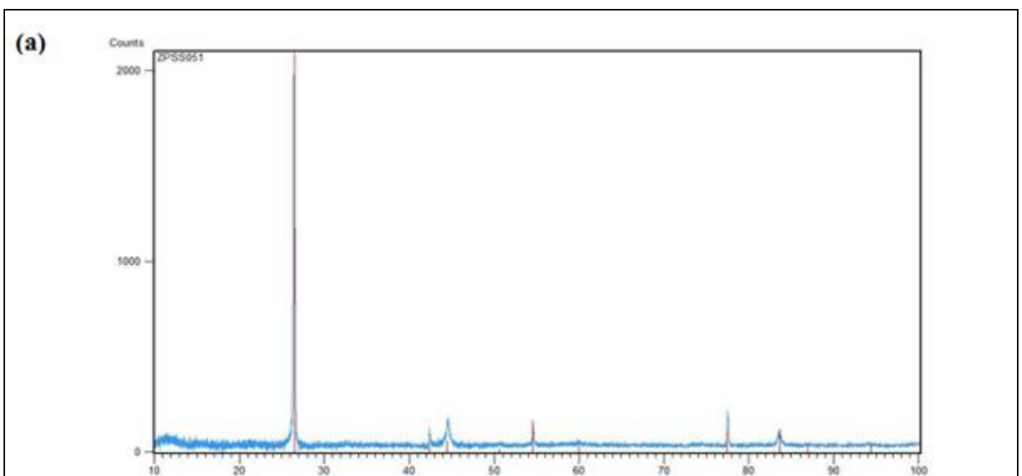
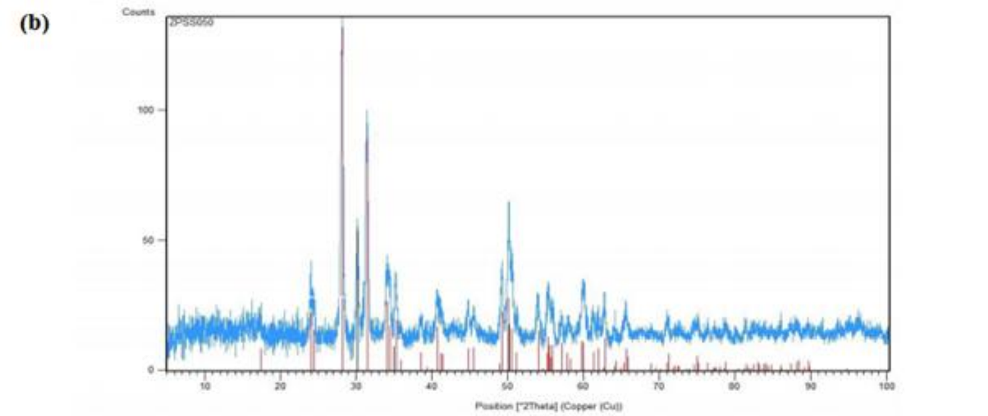


FIG. 1: THE SEM IMAGES OF (A) CARBON AND (B) ZIRCONIA



Sample Identification and Quantification

Line color	Ref.Code	Compound Name	Formula	Crystal S.
—	00-012-0212	Graphite	C	Hexagonal

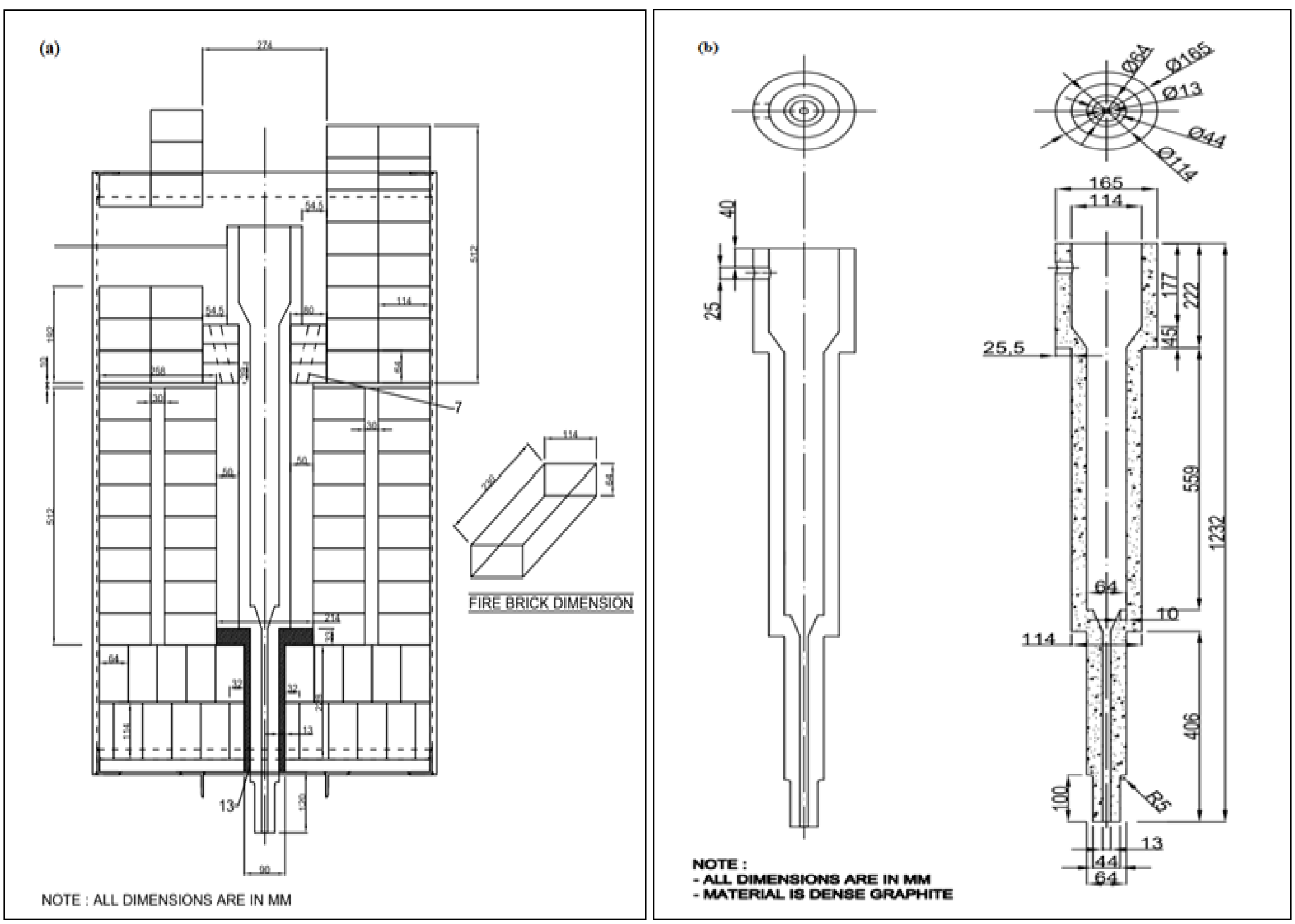


Sample Identification and Quantification

Line color	Ref.Code	Compound Name	Formula	Crystal S.
red	01-078-1807	Zirconium Oxide	ZrO_2	Monoclinic
black	00-049-1642	Zirconium Oxide	ZrO_2	Cubic

FIG. 2: THE XRD ANALYSIS OF (A) CARBON AND (B) ZIRCONIA

Apparatus and Procedure: Fig. 3 shows the schematic representation of the pilot-scale fluidized bed reactor (FBR) with its ancillary equipment used for the experimental investigation of carbochlorination of zirconia in semi-batch and continuous modes. The preheating part of the reactor vessel was 1.3 cm I.D., 6.4 cm O.D. and 40.6 cm long. The reaction section was 6.4 cm I.D., 11.4 cm O.D. and 55.9 cm long. The disengaging section was11.4 cm I.D., 16.5 cm O.D. and 15.2 cm long. A water-cooled brass clamp was used to supply power to the bottom of reactor. $ZrCI_4$ was condensed as a fluffy material in the space condenser. **Fig. 4** shows the flow sheet of the process.



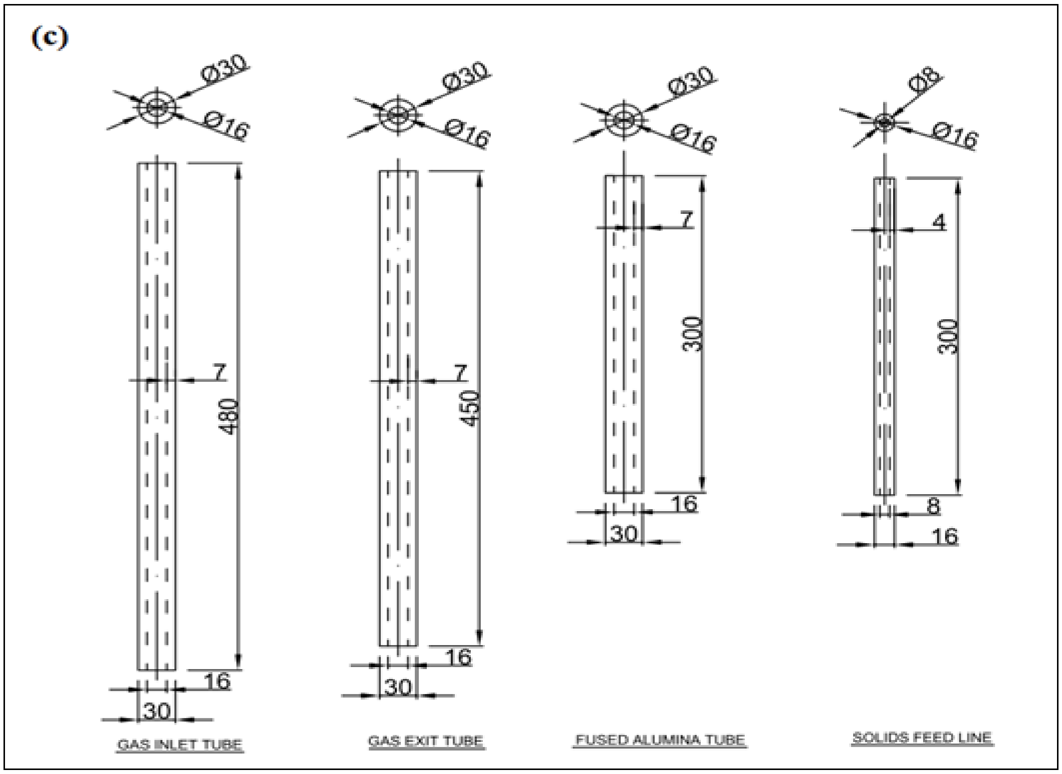
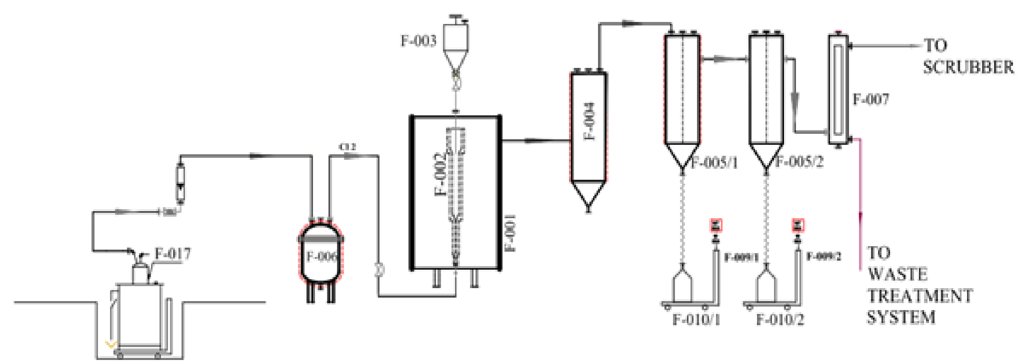


FIG. 3: SCHEMATIC REPRESENTATION OF THE PILOT-SCALE FLUIDIZED BED REACTOR (FBR) WITH ITS ANCILLARY EQUIPMENT



EQUIPMENT NUMBER	F-001	F-002	F-003	F-004	F-005/1,2	F-006	F-007	F-009/1,2	F-010/1,2	F-017
EQUIPMENT NAME	FURNACE	ELECTRO THERMAL FLUIDIZEBED	HOPPER	CYCLONE	CONDENSER	BUFFER	SCRUBBER	SCALE	SLAG TANK	CL2 CYLINDER
OPERATING TEMP.(°C)	500~1200	500~1200	AMB	500	250	100	AMB	AMB	50	38
OPERATING PRES.(barg)	ATM	ATM	ATM	0.83	0.83	1	1	----	0.83	50
MATERIAL OF CONSTRUCTION	ASTM A283GR.C	HD-GRAPHITE	ASTM A283GR.C	SS 321	SS 321	s321/ monel400	PVC	ST37/321	SS 321	ST37

FIG. 4: THE FLOW SHEET OF THE ELECTROTHERMAL FLUIDIZED BED CHLORINATION PROCESS

All experiments were carried out at the fixed Cl_2 flow rate of 2 l/min. **Table 1** shows the specifications of the pilot plant for the operation in semi-batch mode. In this case, the ranges of operating variable (temperature (T), mean particle size (MPS) and reaction time (t)) were presented in **Table 2**.

TABLE 1: OPERATING CONDITIONS OF FBR IN SEMI - BATCH MODE

Quantity	Value
Cl_2 flow rate	2 L/min
Superficial velocity of Cl_2 in the bed	5 cm/s
Weight of C/ZnO_2 mixture	2 Kg
Weigh percent of carbon in the mixture	20%
electric current	200-250 A
Voltage	50-60 V

TABLE 2: UNCODED AND CODED LEVELS OF INDEPENDENT VARIABLES USED IN THE RSM DESIGN FOR SEMI-BATCH MODE

Coded variables	Temperature (T) (°C)	Mean particle size (MPS) (µm)	Time (t) (min)
-1	800	70	30
0	1000	100	60
1	1200	130	90

Design of Experiment: Conventionally, the classical optimization method is used by investigating the effect of one variable on the response (one-variable-at-a-time method). This optimization technique has major disadvantages like the necessity of a great deal of work (high number of required experiments) that results in increased time and expenses and the lack of investigating the interactive effects of the parameters in the process. Due to these drawbacks, the optimization is done by means of statistic methods like the response surface methodology [16-18].

Response surface methodology is one of the well-established combinations of mathematical and statistical techniques for designing and building experimental model. This methodology is useful for the evaluation of relative significance of each independent variable at minimum number of experiments. The objective is to understand the interaction among various parameters and the optimization of the operating conditions to obtain the best response, simultaneously [19]. RSM is a useful tool which has been widely applied successfully in several fields for the optimization of operating parameters in various processes [20-22].

The RSM quadratic polynomial model that includes linear, quadratic and interaction terms is as follows [23, 24]:

$$Y = A_0 + \sum_{i=1}^{k} A_i Z_i + \sum_{j=1}^{k} A_{ii} Z_i^2 + \sum_i \sum_i A_{ij} Z_i Z_j + \varepsilon \qquad (2)$$

Where A_0 is constant; A_i, A_{ii} and A_{ij} are the coefficients of the linear, quadratic and interaction parameters, respectively. Z_i represents the variables and ε is the residual associated with the experiments; k = the number of variables.

Central composite rotatable design (CCRD) (central composite design: full factorial, cube points = 8, center points in cube = 4, axial points = 6, center points in axial = 2 and α = 1) was selected as the second order symmetrical designs in RSM for 3 independent parameters with 3 levels for each one for both semi-batch and continuous. The variables were coded according to Eq. (3):

$$Z_i = \frac{X_i - X_{i,c,p}}{\Delta\zeta} \qquad (3)$$

Where X_i = the real value, $X_{i,c.p}$ = the real value at the center point and ζ= the step change in the variable X_i.

The independent variables for semi-batch process in this research were reaction time (t), reaction temperature (T) and mean particle size (MPS) in the range of 30-90 min (step size = 30), 800–1200 °C (step size = 200) and 70-130 µm (step size = 30), respectively. Zirconia conversion was response variable (dependent variable). Also, the independent variables for continuous mode were Chlorine concentration (C), reaction temperature (T) and mean particle size (MPS) in the range of 3-5 mol/m^3 (step size = 1), 1000-1400 °C (step size = 200) and 70-130 µm (step size = 30), respectively. Chlorine conversion was selected as the response variable.

The levels of independent parameters (coded and uncoded) are shown in **Table 2** (semi-batch mode) and **Table 3** (continuous mode). **Table 4** and 5 illustrate the design of experiments which were according to the coded levels in CCRD which leads to 20 experimental runs for each process mode. The implementation of RSM was performed by Minitab software (version 17).

TABLE 3: UNCODED AND CODED LEVELS OF INDEPENDENT VARIABLES USED IN THE RSM DESIGN FOR CONTINUOUS MODE

Coded variables	Temperature (T) (°C)	Mean Particle Size (MPS) (µm)	Cl_2 concentration (C) (mol/m^3)
-1	1000	70	3
0	1200	100	4
1	1400	130	5

Analysis of variance (ANOVA), R^2 and Adj. R^2 were used for the evaluation of the mathematical models. The optimum operating conditions were obtained through the first derivative of the mathematical functions for zirconia and chlorine conversion in the semi-batch and continuous processes, respectively.

TABLE 4: CENTRAL COMPOSITE ROTATABLE DESIGN FOR ZIRCONIA CONVERSION AND OBSERVED RESPONSES IN SEMI-BATCH MODE

Number of experiments	MPS	t	T	X_{ZrOz} (Experimental) (%)	X_{ZrOz} (RSM Predicted) (%)
1	-1	1	-1	67.0	64.2
2	0	0	0	57.5	57.3
3	0	0	0	57.9	57.3
4	1	-1	-1	15.5	13.3
5	-1	-1	1	35.5	36.7
6	1	1	1	87.5	88.2
7	0	0	0	57.1	57.3
8	1	-1	1	29.2	30.8
9	1	1	-1	62.4	60
10	0	0	0	58.6	57.3
11	-1	1	1	91.8	92.7
12	-1	-1	-1	20.8	18.9
13	0	1	0	72	74.5
14	-1	0	0	59	60.4
15	0	0	0	56.4	57.3
16	1	0	0	54.2	55.4
17	0	0	-1	38.8	47
18	0	0	0	57.0	57.3
19	0	0	1	75.5	70
20	0	-1	0	23	23.1

TABLE 5: CENTRAL COMPOSITE ROTATABLE DESIGN FOR Cl_2 CONVERSION AND OBSERVED RESPONSES IN CONTINUOUS MODE

Number of experiments	MPS	C	T	XCl_2 (Experimental) (%)	XCl_2 (RSM Predicted) (%)
1	0	-1	0	83.2	83.1
2	0	0	0	79.5	79.7
3	0	0	1	94.3	94.9
4	0	1	0	73.7	74.5
5	0	0	0	78.4	79.7
6	-1	0	0	81.9	82.0
7	0	0	-1	32.4	32.6
8	1	0	0	77.3	77.9
9	1	-1	1	94.4	94.2
10	0	0	0	80.8	79.7
11	1	1	-1	23.4	23.1
12	0	0	0	79.4	79.7
13	-1	1	1	95	97.4
14	-1	-1	-1	40.1	40.1
15	1	-1	-1	36.8	36.7
16	-1	-1	1	98.2	98.1
17	-1	1	-1	27.7	27.5
18	1	1	1	90.1	89.7
19	0	0	0	78.6	79.7
20	0	0	0	81.3	79.7

RESULTS AND DISCUSSION:

Fitting the Model and Analysis of Experimental Data: The least squares technique was used for the experimental data in **Table 4** and **5** to determine the coefficients in Eq. (2) which were summarized in **Table 6** and **7** for semi-batch and continuous modes, respectively.

TABLE 6: REGRESSION COEFFICIENTS AND ANOVA OF PREDICTED SECOND-ORDER POLYNOMIAL MODEL FOR ZIRCONIA CONVERSION AT SEMI-BATCH MODE

Source	Degree of freedom	Effect	Coefficient	SE Coefficient	Adj SS	Adj MS	t-value	f-value	p-value
Model	11				8285.08	753.19		48.94	0.000
constant			57.30	1.52			37.81		
blocks	2				10.84	5.42		0.35	0.714

Linear	3				7976.00	2658.67		172.74	0.000
MPS	1	-5.06	-2.53	1.24	64.01	64.01	-2.04	4.16	0.076
t	1	51.34	25.67	1.24	6589.49	6589.49	20.69	428.14	0.000
T	1	23.00	11.50	1.24	1322.5	1322.50	9.27	85.93	0.000
Square	3				244.57	81.52		5.30	0.026
MPS^2	1	1.24	0.62	2.39	1.02	1.02	0.26	0.07	0.803
t^2	1	-16.96	-8.48	2.39	193.13	193.13	-3.54	12.55	0.008
T^2	1	2.34	1.17	2.39	3.66	3.66	0.49	0.24	0.639
2-Way Interactions	3				58.75	19.58		1.27	0.348
MPS×t	1	0.67	0.34	1.39	0.91	0.91	0.24	0.06	0.814
MPS×T	1	-0.18	-0.09	1.39	0.06	0.06	-0.06	0.00	0.951
t×T	1	5.37	2.69	1.39	57.78	57.78	1.94	3.75	0.089
Error	8				123.13	15.39			
Lack of fit	5				121.74	24.35		52.74	0.004
Pure Error	3				1.39	0.46			
Total	19				8408.21				

TABLE 7: REGRESSION COEFFICIENTS AND ANOVA OF PREDICTED SECOND-ORDER POLYNOMIAL MODEL FOR Cl_2 CONVERSION AT CONTINUOUS MODE

Source	Degree of freedom	Effect	Coefficient	SE Coefficient	Adj SS	Adj MS	t-value	f-value	p-value
Model	11				11289.9	1026.35		1302.4	0.000
constant			79.738	0.343			232.51		
blocks	2				1.8	0.92		1.16	0.360
Linear	3				9936.3	3312.11		4202.94	0.000
MPS	1	-4.180	-2.090	0.281	43.7	43.68	-7.45	55.43	0.000
C	1	-8.560	-4.280	0.281	183.2	183.18	-15.25	232.45	0.000
T	1	62.320	31.160	0.281	9709.5	9709.46	111.00	12320.93	0.000
Square	3				1122.2	374.06		474.67	0.000
MPS^2	1	0.445	0.223	0.542	0.1	0.13	0.41	0.17	0.692
C^2	1	-1.855	-0.927	0.542	2.3	2.31	-1.71	2.93	0.125
T^2	1	-32.055	-16.027	0.542	689.5	689.52	-29.58	874.97	0.000
2-Way Interactions	3				42.6	14.19		18.00	0.001
MPS×C	1	-0.525	-0.262	0.314	0.6	0.55	-0.84	0.70	0.427
MPS×T	1	-0.274	-0.138	0.314	0.2	0.15	-0.44	0.19	0.673
C×T	1	4.575	2.287	0.314	41.9	41.86	7.29	53.12	0.000
Error	8				6.3	0.79			
Lack of fit	5				1.1	0.21		0.12	0.977
Pure Error	3				5.2	1.74			
Total	19				11296.1				

The significance of model coefficients was determined by absolute p-value and t-value which were listed in **Table 6** and **7**. A high t value and a small p-value for any of the terms in the model would be an indication of more significant influence on the response variables. Model terms with $p < 0.001$, $0.001 \leq p < 0.05$ and $p \geq 0.05$ are highly significant, significant and insignificant, respectively. In the semi-batch mode, the second-order polynomial model was determined for zirconia conversion as the function of independent parameters as follows:

$$X_{ZrO_2} = 57.30 - 2.53\,MPS + 25.67\,t + 11.50\,T + 0.62\,MPS^2 - 8.48\,t^2 + 1.17\,T^2 + 0.34\,MPS \times t - 0.09\,MPS \times T + 2.69\,t \times T \qquad (4)$$

The results showed that linear terms of temperature and time were highly significant ($p < 0.001$) while mean particle size (MPS) was insignificant ($p \geq 0.05$). The quadratic term of time was significant ($0.001 \leq p < 0.05$) while the quadratic terms of temperature and MPS were insignificant ($p \geq 0.05$). Linear interaction between time and temperature (t×T) was significant, but the linear interactions between time and MPS (t×MPS) and between temperature and MPS (T×MPS) were insignificant. The fitted model (Eq. (4) was verified *via* ANOVA which has been shown in **Table 6**. Predicted values (RSM) versus experimental (observed) values in the semi-batch mode have been presented in **Fig. 5**.

The R^2 and Adj. R^2 were 99.54% and 96.52%, respectively.

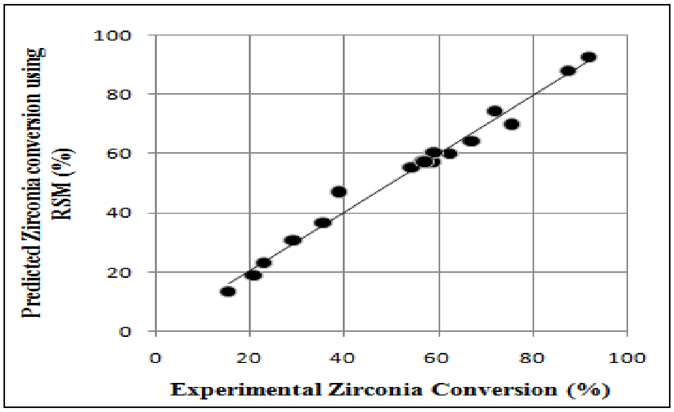


FIG. 5: PREDICTED VALUES (RSM) VERSUS EXPERIMENTAL (OBSERVED) VALUES OF ZIRCONIA CONVERSION IN SEMI-BATCH MODE

In the continuous mode, the second-order polynomial model was determined for chlorine conversion as a function of independent parameters in Eq. (5):

$$X_{Cl_2} = 79.738 - 2.090\,MPS - 4.280\,C + 31.160\,T + 0.223\,MPS^2 - 0.927\,C^2 - 16.027\,T^2 - 0.262\,MPS \times C - 0.138\,MPS \times T + 2.287\,C \times T \quad (5)$$

According to the obtained results from the ANOVA in **Table 7**, all linear terms of temperature, concentration and MPS were highly significant ($p < 0.001$). The quadratic term of temperature was highly significant while the quadratic terms of other variables were non-significant.

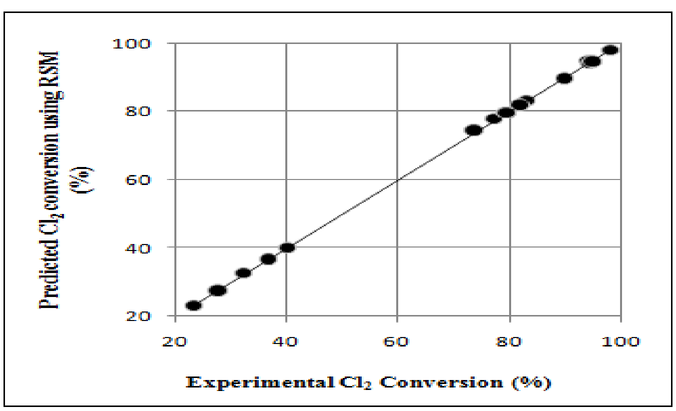


FIG. 6: PREDICTED VALUES (RSM) VERSUS EXPERIMENTAL (OBSERVED) VALUES OF CHLORINE CONVERSION IN CONTINUOUS MODE

Linear interaction between Cl_2 concentration and temperature was significant, but the linear interactions between other variables were non-significant. ANOVA (**Table 7**) verified the fitted model and the R^2 and Adj. R^2 were determined to be 99.94% and 99.87%, respectively. **Fig. 6** shows the predicted values (RSM) versus experimental (observed) values in the continuous mode.

Optimization: The optimum zirconia conversion of 92.7% in semi-batch mode was determined by RSM at 70µm, 1200 °C, and 90 min. RSM predictions in the continuous mode showed that the maximum Cl_2 conversion of 98.26% was achieved at the optimal operating conditions of 70 µm, 1380 °C and 3mol/m^3. The precision of the modelling Cl_2 conversion was accredited with triplicate experiments at the optimum operating conditions giving the average conversion of 98 ± 2%. **Fig. 7** and **8** show the optimal operating condition for zirconia and Cl_2 conversion based on coded variables, respectively.

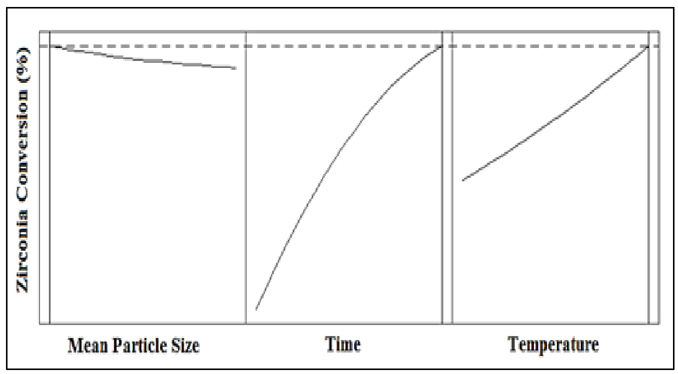


FIG. 7: OPTIMUM OPERATING CONDITIONS ACCORDING TO THE CODED VARIABLES BASED ON RSM FOR SEMI-BATCH MODE

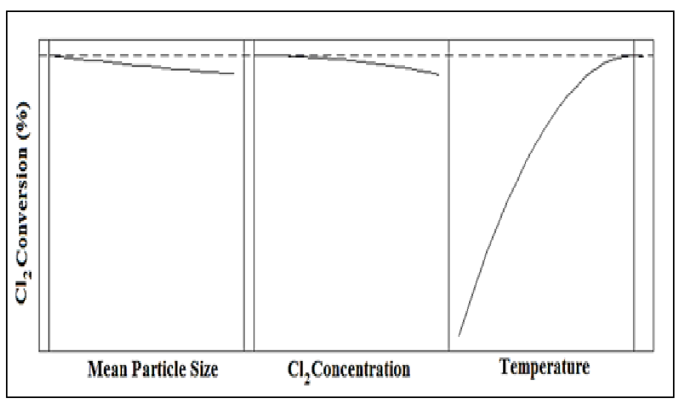


FIG. 8: OPTIMUM OPERATING CONDITIONS ACCORDING TO THE CODED VARIABLES BASED ON RSM FOR CONTINUOUS MODE

Response Surface Analysis:

Semi-Batch Mode: Fig. 9 shows the effects of mean particle size and reaction temperature on zirconia conversion at the fixed reaction time (60 min). The trend of **Fig. 9** illustrates that decreasing

MPS from 130 µm (code = 1) to 70µm (code = −1) increases the conversion due to the availability of larger surface area for reaction. But it is necessary to realize that there is a limit in the reduction of particle size due to the lack of bubbling fluidization and excessive entrainment in the reactor.

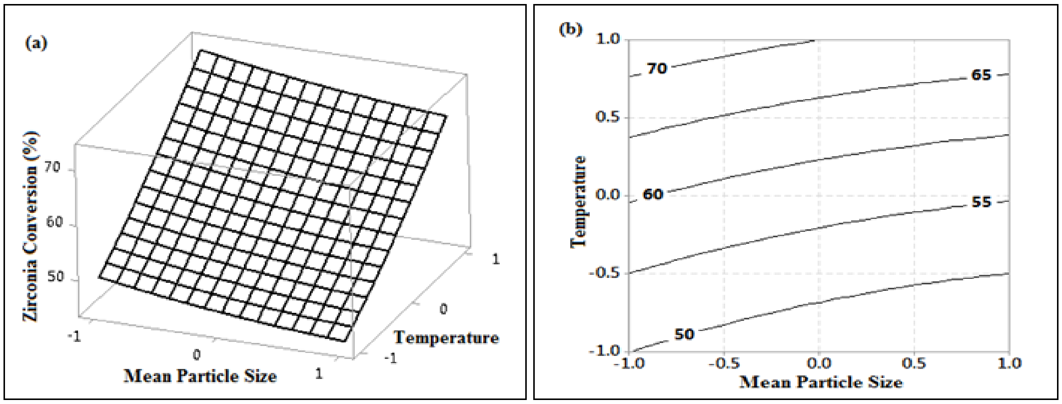


FIG. 9: THE EFFECTS OF MEAN PARTICLE SIZE AND TEMPERATURE (CODED VALUES) ON ZIRCONIA CONVERSION AT THE FIXED REACTION TIME OF 60 min IN SEMI-BATCH MODE, (A) RESPONSE SURFACE PLOT, (B) CONTOUR PLOT

As indicated in **Table 6**, MPS has a negative linear effect on zirconia conversion ($p > 0.05$), due to the increase of reaction surface area by the decreased zirconia particle size. Temperature is an important operational parameter and it is necessary to establish the optimum temperature for the process. As summarized in **Table 6**, the temperature has positive linear ($p < 0.001$) and quadratic ($p > 0.05$) effects, while the interaction of temperature MPS showed insignificant influence on zirconia conversion ($p = 0.951$). Increasing temperature causes higher reaction rate and consequently results in higher zirconia consumption and enhance zirconia conversion.

Fig. 10 depicts the effects of reaction time and MPS on zirconia conversion at 1000 °C. Increasing the chlorination time from 30 min (code = −1) to 90 min (code = 1) was found to be directly proportional to the amount of reacted zirconia.

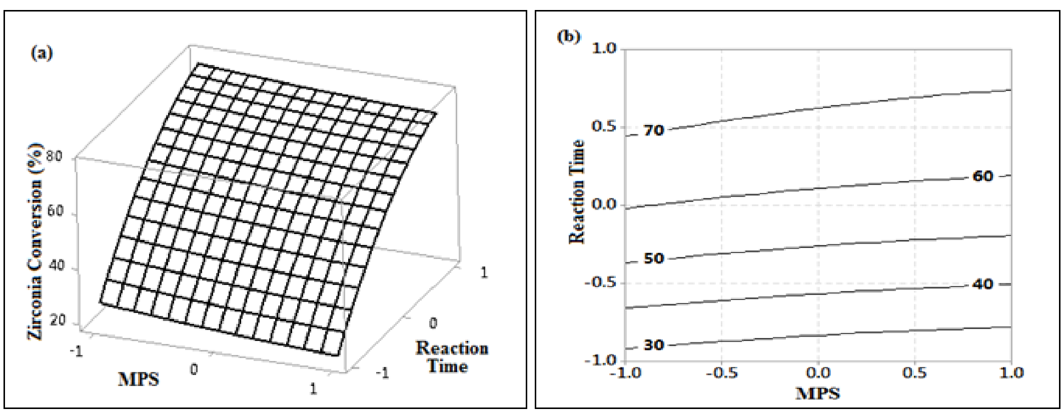


FIG. 10: THE EFFECTS OF MEAN PARTICLE SIZE AND REACTION TIME (CODED VALUES) ON ZIRCONIA CONVERSION AT THE TEMPERATURE OF 1000 °C IN SEMI-BATCH MODE, (A) RESPONSE SURFACE PLOT, (B) CONTOUR PLOT

Table 6 shows a positive linear effect of reaction time ($p < 0.001$) on the response variable at low levels of time. Also, at higher levels of chlorination reaction times, the quadratic negative effect becomes significant ($0.001 \leq p < 0.05$) which results in increasing the zirconia conversion by lower slope in comparison with lower levels of time. Moreover, interaction between MPS and time had no significant effect on conversion ($p = 0.814$).

The explained results for increasing reaction time and temperature are also obvious in **Fig. 11** that illustrates the effect of reaction time and temperature on the zirconia conversion at the fixed MPS of 100 µm.

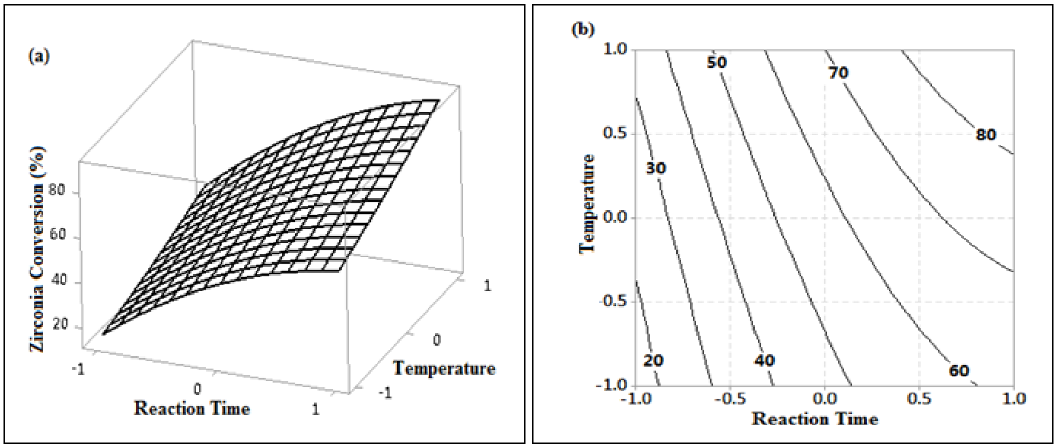


FIG. 11: THE EFFECTS OF REACTION TIME AND TEMPERATURE (CODED VALUES) ON ZIRCONIA CONVERSION AT THE FIXED MPS OF 100 µm IN SEMI-BATCH MODE, (A) RESPONSE SURFACE PLOT, (B) CONTOUR PLOT

ANOVA in **Table 6** showed that the interaction between time and temperature is non-significant ($p > 0.05$). The interaction between different parameters for the carbochlorination reaction of zirconia was illustrated in **Fig. 12**.

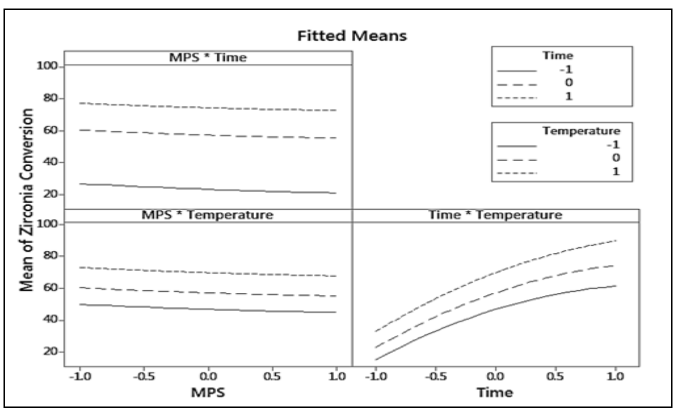


FIG. 12: INTERACTION PLOTS FOR ZIRCONIA CONVERSION BASED ON RESPONSE SURFACE METHODOLOGY

Continuous Mode: The interactions among operating variables (T, C and MPS) were investigated by drawing the Cl_2 conversion against two independent variables (x and y coordinates), and the other variable was kept constant at zero level according to Eq. (5).

The effect of inlet gas (Cl_2) concentration and reaction temperature on the Cl_2conversionwas depicted in **Fig. 13** at the fixed MPS of 1000 µm. Increasing temperature and inlet Cl_2 concentration cause higher reaction rate and consequently results in higher Cl_2 consumption. At constant temperature, if the inlet chlorine concentration increases from 3 mol/m^3 (coded = -1) to 5 ml/m^3 (coded = 1), higher zirconia consumption is obtained but at the same time the chlorine conversion is decreased which is the consequence of excess amount of chlorine in the reactor.

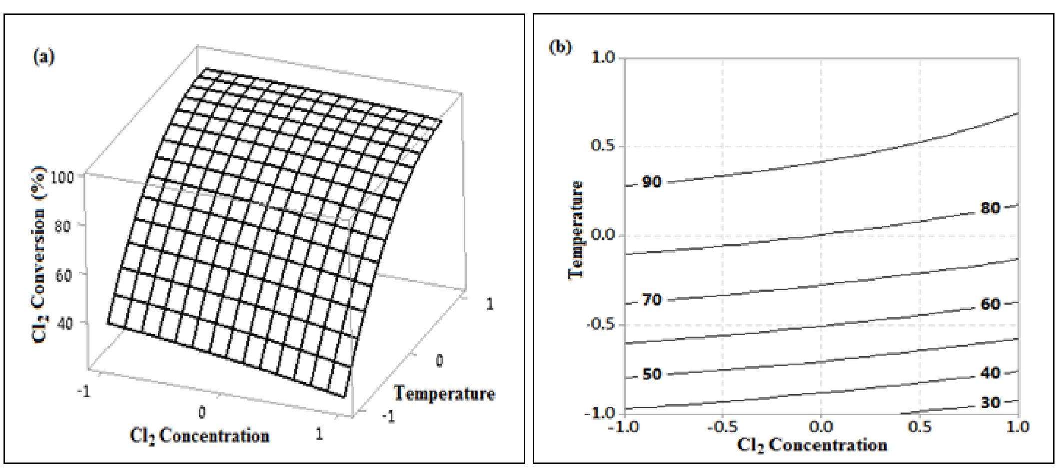


FIG. 13: THE EFFECTS OF Cl_2 CONCENTRATION AND REACTION TEMPERATURE (CODED VALUES) ON Cl_2 CONVERSION AT THE FIXED MPS OF 100 µm IN THE CONTINUOUS MODE, (A) RESPONSE SURFACE PLOT, (B) CONTOUR PLOT

Table 7 shows that Cl_2 concentration in the reactor feed has highly significant negative linear effect and non-significant negative quadratic effect on the Cl_2 conversion. This effect may also be explained due to the reaction rate with respect to chlorine (about 0.7) in which the increase in reaction rate is not considerable and a high amount of inlet Cl_2 leaves the reactor unreacted. Also, the model analysis verified that the dependency of the Cl_2 conversion to the interaction between Cl_2 concentration and temperature (C×T) is highly significant. The effect of reaction temperature and time on the Cl_2 conversion at the fixed Cl_2 concentration of 4 ml/m^3 has been shown in **Fig. 14**. Increasing temperature from 1000 °C (coded = -1) to 1400 °C (coded = 1) increases the Cl_2 conversion due to the increased reaction rate.

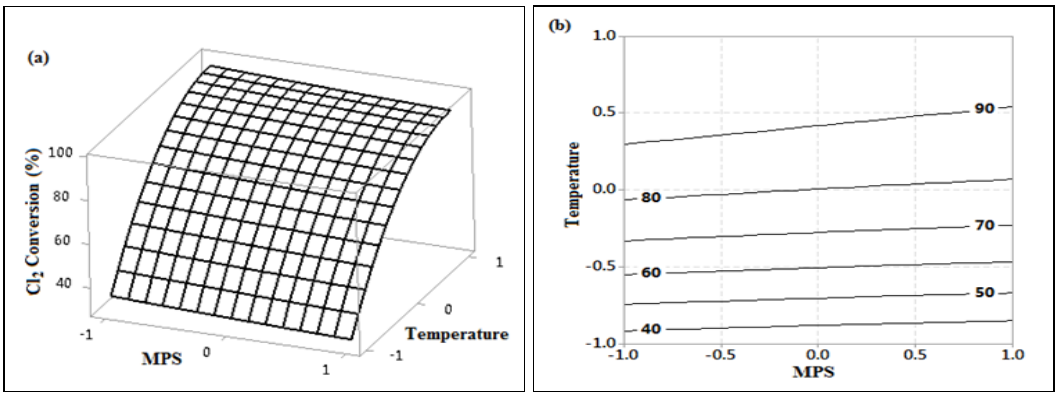


FIG. 14: THE EFFECT OF REACTION TEMPERATURE AND MPS ON THE Cl_2 CONVERSION AT THE FIXED Cl_2 CONCENTRATION OF 4 ml/m^3 IN THE CONTINUOUS MODE, (A) RESPONSE SURFACE PLOT, (B) CONTOUR PLOT

Table 7 shows that temperature has a highly significant linear positive effect and a highly significant quadratic negative effect at the higher levels of temperature which results in minor changes to the conversion by increasing the reaction temperature. Increasing the Mean particle size of powdered feeds from 70 µm (coded = -1) to 130 µm (coded = 1) results in decreased conversion similar to the semi-batch mode. In this case MPS had a highly significant linear negative effect and a non-significant quadratic positive effect (**Table 7**). The interaction between MPS and temperature was also insignificant ($p = 0.673$). The Trends of MPS and Cl_2 concentration on Cl_2 conversion at the fixed reaction temperature of 1200 °C which is depicted in **Fig. 15** are similar to the above explained influences of these two parameters. Also, the interaction between MPS and Cl_2 concentration was insignificant for Cl_2 conversion ($p = 0.427$).

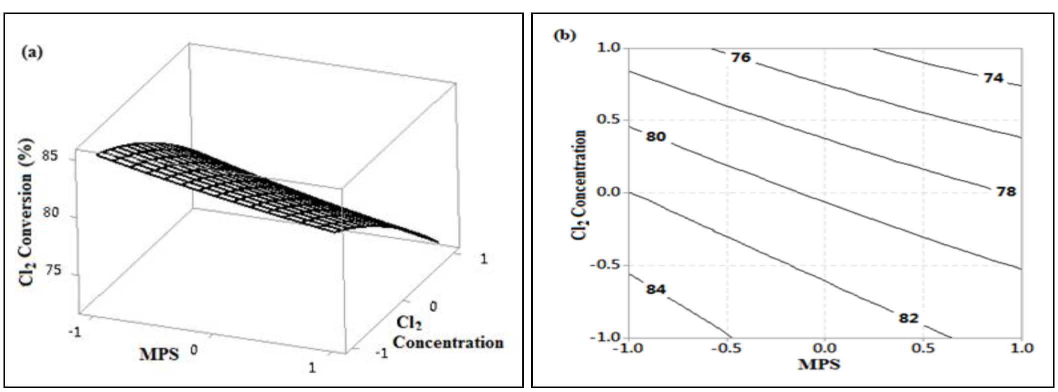


FIG. 15: THE EFFECT OF MPS AND Cl_2 CONCENTRATION ON Cl_2 CONVERSION AT THE FIXED REACTION TEMPERATURE OF 1200 °C IN THE CONTINUOUS MODE, (A) RESPONSE SURFACE PLOT, (B) CONTOUR PLOT

The overall interaction between different operating parameters on the mean reaction conversion has been shown in **Fig. 16**. **Fig. 17** shows the XRD analysis of the produced $ZrCl_4$ in the carbochlorination process.

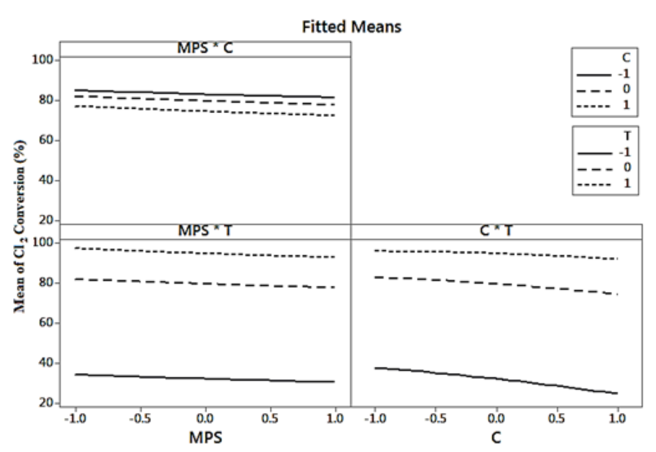
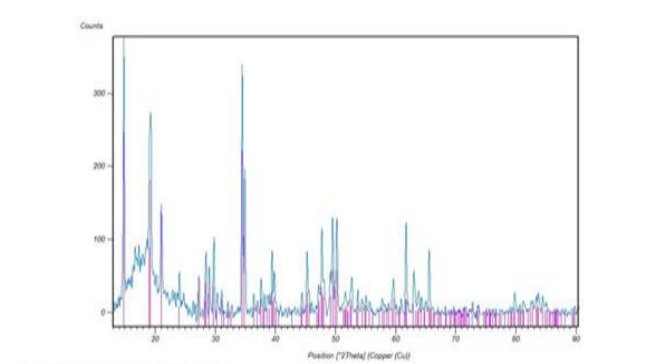


FIG. 16: INTERACTION PLOTS FOR CHLORINE CONVERSION BASED ON RESPONSE SURFACE METHODOLOGY IN CONTINUOUS MODE



Sample Identification and Quantification

Line color	Ref. Code	Compound Name	Formula	Crystal S.
—	01-072-1054	Zirconium Chloride	$ZrCl_4$	Monoclinic

FIG. 17: XRD OF THE PRODUCED $ZrCl_4$ IN THE FLUIDIZED BED REACTOR

CONCLUSION: The optimal conditions for carbochlorination of zirconia in a pilot plant fluidized bed reactor were investigated in semi-batch and continuous mode. Optimization of this process was carried out *via* RSM and experimental investigation. RSM showed that the data were appropriately fitted to second-order polynomial model. In the continuous method, all linear parameters (MPS, C and T), quadratic term of temperature and linear interaction between Cl_2 concentration and temperature were significant parameters on the reaction conversion. The obtained results indicated that higher temperature and reaction time as well as lower MPS, increases reaction conversion in the semi-batch mode. In the continuous method, linear terms of temperature and time, the quadratic term of time and the linear interaction between time and temperature were significant parameters.

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CONFLICT OF INTEREST: There is no any conflict of interest.

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