Research Article

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Optimization of medium–low-grade phosphorus rock carbothermal reduction process by response surface methodology

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Abstract: Phosphorus extraction from phosphorus rock was conducted by carbothermal reduction with silica and coke. The effects of reaction temperature, reaction time, coke excess coefficient, molar ratio of silicon–calcium, and phosphorus rock particle size on the phosphorus reduction rate were investigated by the response surface methodology (RSM). The central composite design (CCD) with five factors and five levels was used to explore the effects of variables' interactions on the phosphorus reduction rate. The results showed that there are significant interactions between reaction time and temperature; reaction temperature and molar ratio of silicon–calcium; reaction temperature

and phosphorus rock particle size; coke excess coefficient and molar ratio of silicon–calcium; and coke excess coefficient and phosphorus rock particle size. The optimum conditions in the experimental range are reaction time 92 min, reaction temperature 1340°C, coke excess coefficient 1.27, molar ratio of silicon–calcium 1.28, and phosphorus rock particle size 75–106 µm, which were derived from the quadratic statistic model. Under these conditions, the phosphorus reduction rate can reach 96.88%, which is close to the model prediction value 99.40%. The optimized carbothermal reduction conditions of phosphorus rock by the RSM are helpful to reduce the energy cost of thermal phosphoric acid process.

Keywords: phosphorus rock, carbothermal reduction reaction, response surface methodology, optimization

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1 Introduction

Yellow phosphorus is mainly obtained from phosphate ore, coke, and silica by carbothermal reduction method in the electric furnace, and the main components of the three raw materials are $\text{Ca}_5(\text{PO}_4)_3\text{F}$, C, and SiO_2 , respectively. In this process, coke is mainly used as a reducing agent and conductor, whereas silica is mainly used as a flux to form stable silicate and promote the reduction reaction of phosphate [1–3]. The main reaction equation is shown in Eq. 1:

The phosphorus obtained by carbothermal reduction process is an irreplaceable raw material to produce phosphates and their derivatives. It is an important raw material for producing food-grade, electronic-grade, and medical-grade phosphoric acid, as well as the basic raw material for agricultural chemical products [4,5]. However, in order to facilitate slag discharge, the operating temperature of yellow

phosphorus production by the electric furnace process should be about 150°C higher than the melting point of the residue, and the power consumption is 13,000–15,000 kWh per ton, which makes it a typical huge energy consumption industry [6,7]. Therefore, the development of an energy-saving technology is vital to promote the sustainable development of yellow phosphorus industry.

In China, medium- and low-grade phosphate ores are the majority of phosphorus resources. The utilization percentage of medium- and low-grade phosphorus resources is lower than expected. Effective utilization of medium- and low-grade phosphate ores is necessary to realize the sustainable development of phosphorus chemical industry [8]. Phosphoric acid prepared by wet process of medium- and low-grade phosphate requires ore dressing, and the purity of the prepared phosphoric acid is not high enough, which leads to the subsequent complicated separation process [9]. Kiln phosphoric acid process is still in the research stage due to its immature technology [10]. Medium- and low-grade phosphate ores can be directly used in the thermal process of phosphoric acid to obtain high-purity phosphoric acid. The huge energy consumption is its main disadvantage [4,11]. Therefore, reducing energy consumption is an important issue in thermal phosphoric acid process.

Many studies on thermal phosphoric acid technology have been carried out. Jiang *et al.* [12] studied the kinetics of fluorapatite carbothermal reduction reaction. After reaction at 1,250°C for 60 min, the reduction rate of fluorapatite reached about 48%. The reaction at 1,300°C for 60 min resulted in a reduction rate of 76%. Li *et al.* [13] found that a reduction rate of 98.9% with medium- and low-grade phosphate ores was approached at 1,550°C for 60 min and the reaction temperature is the most important factor that influences the reduction rate of phosphate ore. Cao *et al.* [14] added a certain amount of alkali metals to enhance the activity of carbon and the reduction rate of phosphorus rock. By adding 1.5% K_2CO_3 and reacting at 1,300°C for 60 min, the reduction rate of phosphorus rock was increased to 67%. When the reaction time was prolonged to 4 h, the reduction rate of phosphorus rock could reach 91.32%. Yang *et al.* [15] revealed that the carbothermal reduction reaction of fluorapatite promoted by Al_2O_3 mainly occurred in the low-temperature zone and at the initial stage of the reaction. The reaction was conducted at 1,250°C for 50 min, and the reduction rate of phosphorus rock can be increased from 65% to 75% by adding Al_2O_3 . Li *et al.* [16] used medium- and low-grade phosphorus rocks with high content of calcium to react at 1,300°C for 210 min, and the reduction rate of phosphorus rock could reach more than 94%. They proposed that the reduction rate of phosphate

ore decreases with the increase in the molar ratio of silicon–calcium, and the decrease in the reduction rate is more significant when the molar ratio of silicon–calcium > 2. Li *et al.* [17] studied the growth behavior and size characterization of metallic iron particles in coal-based reduction of oolitic hematite–coal composite briquettes and manifested that reduction temperature, time, and ore size fraction strongly influenced the reduction. Li *et al.* [18] studied the feasibility of potassium feldspar as a flux to reduce phosphate rock, and they found that when the coke excess coefficient increased from 1.0 to 1.05, the reduction rate of phosphate rock increased from 95% to 99.61%. In order to reduce the temperature (time) of the carbothermal reduction reaction and save energy, orthogonal experiments are mainly used by the current researchers to optimize the process conditions. When the reaction temperature is mainly in the range of 1,250–1,350°C and the reaction time is 60–120 min, the reduction rate of phosphate ore could usually reach 40–95%. From the above description, one can see that in addition to reaction temperature and time, coke excess coefficient, molar ratio of silicon–calcium, and phosphorus rock particle size are other pivotal factors to determine the reduction rate of phosphorus ore. In this paper, these five factors are chosen to study their effects on the phosphorus reduction rate.

The response surface methodology (RSM) is a relatively scientific and efficient parameter optimization method, which is widely used in chemical, agricultural, pharmaceutical, environmental, and mechanical engineering fields. This method is simple and efficient, especially for studying the interaction between several experimental factors. Compared with single-factor optimization, the response surface methodology has the advantages of fewer experiments, accurate prediction, and the ability to study the interaction between several factors at the same time [19], which makes this method better than the traditional orthogonal methodologies. In this paper, based on single-factor experiment and literature research, the response surface methodology is used to optimize the process variables (reaction temperature, reaction time, coke excess coefficient, molar ratio of silicon–calcium, and phosphorus rock particle size) of carbothermal reduction reaction of phosphorus rock to improve the energy efficiency of thermal phosphoric acid process.

2 Materials and methods

The phosphorus rock used in the experiments was from Yichang, Hubei Province. PANalytical Axios wavelength-dispersive X-ray fluorescence spectrometer was used to determine the composition of the phosphorus rock. The

Table 1: The main chemical components of the phosphorus rock (%wt)

Composition of ore	P ₂ O ₅	CaO	SiO ₂	MgO	Fe ₂ O ₃	Al ₂ O ₃	F
W (%)	19.58	42.23	25.33	7.17	1.45	1.3	1.45

main chemical components are shown in Table 1. The industrial analysis of the reducing agent coke is shown in Table 2. Silica (analytical purity) was supplied by Sinopharm Chemical Reagent Co. Ltd.

The phosphorus rock powder was mixed with coke and silica powders, which passed 200-mesh sieve evenly according to the designed ratio, pressed into several $\varnothing 15 \times 3$ mm flakes under 5 MPa, and then dried for further use. 5–6 g of dried sample was placed in a graphite crucible and heated in the LFT-1600 tube furnace, with the rate of flow of nitrogen of 80 mL min⁻¹ for 30 min. Under the protection of nitrogen, the temperature was elevated at a rate of 5°C min⁻¹ to a specified temperature. After the reaction ended, the slag was removed from the graphite crucible after cooling to room temperature. After ground through 200-mesh sieves, the residue was used for the analysis of the content of P₂O₅ and further characterization. The phosphorus rock particle size was determined using sieves with different meshes.

The content of P₂O₅ in the residue was analyzed by gravimetric method with quinoline phosphomolybdate as agent. The phosphorus rock reduction rate (Y) was calculated according to Eq. 2:

$$Y = \frac{M_0 w_0 - M_1 w_1}{M_0 w_0} \quad (2)$$

where M_0 and M_1 are the mass of samples before and after the reaction and w_0 and w_1 are the mass fraction of P₂O₅ before and after the reaction, respectively.

The reaction time (A), reaction temperature (B), coke excess coefficient (C), molar ratio of silicon–calcium (D), and phosphorus rock particle size (E) were the factors and the phosphorus reduction rate (Y) was the response value in this paper.

3 Results and discussion

3.1 Single-factor investigation

The results of the single-factor investigation are displayed in Figure 1. The results in Figure 1a show that the reduction rate increases with the reaction time. When the reaction time continues to extend, the reduction rate will tend to close to

Table 2: Analysis of the industrial coke (%wt)

Fixed carbon	Ash	Volatile matter	Moisture
82.03	9.27	4.15	4.55

100% as the most phosphates had reacted out. Considering the reduction rate and economic cost, the reaction time in the RSM experiments is in the range of 30–120 min.

As shown in Figure 1b, the reduction rate increases gradually with the reaction temperature. When the temperature is above 1,300°C, the reduction rate increases slowly and becomes stable. From the point of view of thermodynamics, the increase in the temperature provided a favorable thermodynamics condition and promoted phosphorus rock reduction. Considering the reduction rate and application feasibility, the RSM experiments were conducted at 1,200–1,400°C.

Considering the effects of the amount of reduction agent coke on the reduction rate, the relation between different coke excess coefficients and the reduction rate is demonstrated in Figure 1c, which shows that the reduction rate increases with CEC. In order to study the effects of coke excess coefficient on the reduction rate comprehensively, the coke excess coefficient (CEC) was set in the range of 0.80–1.60 in the RSM experiments.

The effects of molar ratio of silicon–calcium (Si/Ca) on the reduction rate and the results are shown in Figure 1d. One can see that the reduction rate increases first and then decreases with the increase in the molar ratio of silicon–calcium (Si/Ca). In the process of phosphorus production, silica is used as a flux to reduce the reaction temperature. The melting point of slag usually depends on the value of silicon–calcium ratio. The amount of silica should not be too high to prevent side reactions from occurring. The molar ratio of silicon–calcium (Si/Ca) was set in the range of 0.80–1.60 in the RSM experiments.

The phosphorus rock particle size influences the heat and mass conduction and thereby the reduction rate. Figure 1e shows that the reduction rate increases first and then decreases with the decrease in the phosphorus rock particle size. When the phosphorus rock particle size is in the range of 75–106 µm, the reduction rate is the highest in the single-factor investigation experiments. Therefore, five different particle sizes of 0–48 µm, 48–75 µm, 75–106 µm, 106–150 µm, and 150–270 µm were chosen in the RSM experiments.

3.2 Optimization of reaction conditions by RSM

Based on the literature investigation and previous single-factor experiments, reaction time (A, 30–120 min), reaction

Figure 1: Influence of various factors on the reduction rate. (a) Fixed levels B (1,300°C), C (1.20), D (1.20), E (75–106 μm). (b) Fixed levels A (75 min), C (1.20), D (1.20), E (75–106 μm). (c) Fixed levels A (75 min), B (1,300°C), D (1.20), E (75–106 μm). (d) Fixed levels A (75 min), B (1,300°C), C (1.20), E (75–106 μm). (e) Fixed levels A (75 min), B (1,300°C), C (1.20), D (1.20).

temperature (B, 1,200–1,400°C), coke excess coefficient (C, 0.8–1.60), molar ratio of silicon–calcium (D, 0.8–1.60), and phosphate particle size (E, 0–270 μm) were chosen as factors to pursue the best reduction rate of phosphorus rock. The central composite design (CCD) with five factors and five levels was conducted by Design-Expert 8.0.6 software as shown in Table 3. The optimum conditions for phosphorus rock carbothermal reduction were obtained by the response surface methodology.

Through CCD procedure, the detailed fifty experiments with five different factors and levels were generated and are shown in Table 4. The phosphate reduction rates of 50 runs of the experiments are also displayed in Table 4, and the reduction rate was obtained in the range of 61.18% to 97.90%.

3.3 Quadratic regression fitting and the result of variance analysis

The experimental results were fitted to various models (linear, interactive (2FI), quadratic, and cubic) to get regression equation. Three different tests, namely the sequential model sum of squares, lack-of-fit tests, and model summary statistics, were conducted in this paper to determine the adequacy of various models to represent the maximum reduction rate of phosphorus rock, and the results are listed in Table 5. The fit summary output indicated that the quadratic polynomial model was significant for the present system as shown in Table 5, while the interaction of two factors (2FI) and the linear model were suggested to be insignificant. As

Table 3: Factors and coding levels of response surface analysis

Factor	Coded	Coding level				
		$-\alpha$	Low (−1)	Central (0)	High (+1)	$+\alpha$
Reaction time (min)	A	30	56	75	94	120
Temperature (°C)	B	1,200	1,258	1,300	1,342	1,400
CEC	C	0.8	1.03	1.20	1.37	1.60
Si/Ca	D	0.8	1.03	1.20	1.37	1.60
Phosphorus rock particle size (μm)	E	150–270	106–150	75–106	48–75	0–48

Table 4: Conditions and results of fifty CCD experiments

Run	Variables					Response
	Time (min)	Temperature (°C)	Carbon excess coefficient	Molar ratio of silicon–calcium	Phosphorus rock particle size (μm)	Reduction rate (%)
	A	B	C	D	E	Y
1	56	1,342	1.37	1.03	106–150	87.09
2	56	1,342	1.03	1.37	106–150	94.62
3	75	1,300	1.20	1.20	0–48	71.56
4	56	1,258	1.37	1.03	106–150	74.65
5	94	1,342	1.03	1.37	106–150	97.46
6	75	1,300	1.20	1.20	75–106	90.52
7	56	1,342	1.37	1.03	48–75	88.05
8	94	1,258	1.03	1.03	106–150	82.26
9	75	1,300	1.20	1.20	75–106	93.22
10	75	1,300	1.20	1.20	75–106	92.46
11	94	1,342	1.03	1.37	48–75	93.79
12	120	1,300	1.20	1.20	75–106	92.34
13	75	1,300	0.80	1.20	75–106	82.58
14	75	1,400	1.20	1.20	75–106	97.80
15	94	1,258	1.37	1.03	48–75	82.35
16	75	1,300	1.20	1.20	75–106	92.73
17	94	1,342	1.37	1.03	48–75	93.85
18	94	1,342	1.37	1.37	48–75	97.90
19	94	1,258	1.03	1.37	48–75	77.60
20	56	1,258	1.03	1.37	106–150	74.62
21	75	1,300	1.20	1.20	75–106	92.08
22	94	1,342	1.03	1.03	106–150	86.75
23	94	1,342	1.03	1.03	48–75	84.63
24	56	1,258	1.37	1.37	106–150	75.78
25	75	1,300	1.20	1.20	150–270	81.63
26	56	1,258	1.03	1.37	48–75	69.40
27	94	1,258	1.37	1.03	106–150	87.20
28	30	1,300	1.20	1.20	75–106	77.56
29	56	1,342	1.03	1.03	48–75	78.23
30	56	1,258	1.03	1.03	48–75	61.18
31	56	1,258	1.37	1.37	48–75	77.56
32	94	1,258	1.37	1.37	106–150	85.13
33	56	1,258	1.03	1.03	106–150	67.16
34	94	1,258	1.03	1.37	106–150	87.65
35	75	1,300	1.20	1.20	75–106	90.06
36	75	1,200	1.20	1.20	75–106	61.49
37	56	1,342	1.37	1.37	106–150	94.24
38	94	1,342	1.37	1.03	106–150	90.75
39	75	1,300	1.20	1.20	75–106	91.81
40	56	1,342	1.03	1.03	106–150	81.36
41	75	1,300	1.20	1.20	75–106	90.45
42	75	1,300	1.60	1.20	75–106	95.37
43	75	1,300	1.20	1.60	75–106	93.59
44	56	1,342	1.37	1.37	48–75	95.73
45	94	1,258	1.37	1.37	48–75	85.76
46	94	1,342	1.37	1.37	106–150	97.53
47	56	1,342	1.03	1.37	48–75	88.82
48	56	1,258	1.37	1.03	48–75	74.64
49	94	1,258	1.03	1.03	48–75	71.5
50	75	1,300	1.20	0.80	75–106	75.53

Table 5: Fit summary output as the sequential model sum of squares, lack-of-fit tests, and model summary statistics

Source	Sum of squares	df	Mean square	F-value	p-value prob > F	Remarks
Sequential model sum of squares						
Mean vs total	3.61×10^5	1	3.61×10^5			
Linear vs Mean	3.59×10^3	5	7.19×10^2	32.55	<0.0001	
2FI* vs linear	2.91×10^2	10	29.08	1.45	0.2004	
Quadratic vs 2FI*	6.24×10^2	5	1.205×10^2	63.34	<0.0001	Suggested
Cubic vs quadratic	42.70	15	2.85	2.76	0.0324	Aliased
Residual	14.42	14	1.03			
Total	3.65×10^5	50	7.31×10^3			
Lack-of-fit tests						
Linear	9.62×10^2	37	26	18.68	0.0003	
2FI	6.71×10^2	27	24.9	17.86	0.0003	
Quadratic	47.4	22	2.15	1.55	0.29	Suggested
Cubic	4.68	7	0.67	0.48	0.82	Aliased
Pure error	9.74	7	1.39			
Source	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	Remarks
Model summary statistics						
Linear	4.70	0.787	0.763	0.737	1.200×10^3	
2FI	4.48	0.851	0.785	0.792	9.48×10^2	
Quadratic	1.40	0.988	0.979	0.958	1.94×10^2	Suggested
Cubic	1.01	0.997	0.989	0.970	1.36×10^2	Aliased

* 2FI means two-factor interaction.

shown in Table 5, linear and interactive (2FI) models exhibit lower R^2 , adjusted R^2 , predicted R^2 , and also high p -values as compared to quadratic model. Cubic model was found to be aliased. Therefore, the quadratic model including linear, interactive, and quadratic terms was chosen to describe the effects of process variables on the reduction rate of phosphorus rock.

Furthermore, the analysis of variance (ANOVA) was used to evaluate the adequacy of the model equation. ANOVA evaluations of the model, including its variables and their interactions, are given in Table 6. As can be seen from Table 6, the effects of the reaction time (A), reaction temperature (B), coke excess coefficient (C), molar ratio of silicon to calcium (D), and phosphorus rock particle size (E) on the reduction rate of phosphorus rock (Y) are all significant because their prob > F -values for phosphorus rock reduction rate (Y) are all lower than 0.05 (p value < 0.05), indicating that these factors are significant [20–22]. In addition, the interactions A–B, B–D, B–E, C–D, and C–E are also significant because their prob > F -values are also below 0.05. In the analysis of variance, the larger the F -value of the variable(s) and their interaction item is, the greater influence of those item(s) on the response value is [23]. Therefore, the sequence of the effect of various factors on the

phosphorus rock reduction rate (Y) is as follows: B > A > D > C > E. The effect order of the interaction items on the reduction rate (Y) is CE > AB > CD > BD > BE.

The data shown in Table 4 were regressed by Design-Expert 8.0.6, and the derived quadratic polynomial model equation includes the reaction time (A), reaction temperature (B), coke excess coefficient (C), molar ratio of silicon to calcium (D), phosphorus rock particle size ϵ , and the reduction rate of phosphorus rock (Y). Combined with ANOVA results in Table 6 and removing insignificant items from the model, the obtained quadratic polynomial model equation is as follows:

$$Y = 9.166 + 3.56A + 6.99B + 2.81C + 3.35D - 1.55E \\ - 1.56AB + 1.15BD + 0.80BE - 1.205CD + 1.57CE \quad (3) \\ - 1.19A^2 - 2.13B^2 - 0.48C^2 - 1.206D^2 - 2.67E^2$$

Figure 2 shows the relationship between the predicted and actual reduction rates of phosphorus rock. As can be seen from the diagram, most of the actual values are close to the predicted values, and a few of the actual values fall on both sides of the predicted values symmetrically, indicating that the model fits the actual responses well. Table 5 gives the $R^2 = 0.988$, which means the model can explain 98.8% of the variation of

Table 6: Analysis of variance for the regression model

Source	Sum of squares	df	Mean square	F-value	p-value prob > F	Remarks
Model	4509.18	20	225.46	114.46	<0.0001	Significant
A-time	548.49	1	548.49	278.44	<0.0001	
B-temperature	2115.72	1	2115.72	1074.06	<0.0001	
C-CEC	341.38	1	341.38	173.31	<0.0001	
D-Si/Ca	484.7	1	484.7	246.06	<0.0001	
E-particle size	104.29	1	104.29	52.94	<0.0001	
AB	77.94	1	77.94	39.57	<0.0001	
AC	5.71	1	5.71	2.9	0.0993	Not significant
AD	6.92	1	6.92	3.51	0.071	Not significant
AE	4.09	1	4.09	2.08	0.1603	Not significant
BC	4.67	1	4.67	2.37	0.1346	Not significant
BD	42.37	1	42.37	21.51	<0.0001	
BE	20.58	1	20.58	10.45	0.0031	
CD	49.6	1	49.6	25.18	<0.0001	
CE	78.75	1	78.75	39.98	<0.0001	
DE	0.17	1	0.17	0.085	0.7722	Not significant
A ²	79.01	1	79.01	40.11	<0.0001	
B ²	252.17	1	252.17	128.02	<0.0001	
C ²	12.85	1	12.85	6.52	0.0162	
D ²	88.42	1	88.42	44.88	<0.0001	
E ²	395.97	1	395.97	201.02	<0.0001	
Residual	57.13	29	1.97			
Lack-of-fit	47.38	22	2.15	1.55	0.2864	Not significant
Pure error	9.74	7	1.39			
Cor total	4566.3	49

Figure 2: Predicted and actual values of phosphorus rock reduction rate.

response values. A good fit between the predicted and the actual values proves that the good fitting model can be used to analyze and predict the optimum reduction conditions of phosphorus rock.

In order to show how any two factors affect the response, the 3D response surface plots and the contour plots are demonstrated in Figures 3 and 4, respectively.

It is important to focus on the effects of the significant terms. Therefore, the 3D response surface plots of the interactions AC, AD, AE, BC, and DE are not shown.

The 3D response surface plot in Figure 3a, which gives the reduction rate as a function of the reaction time and reaction temperature, indicates that a higher reduction rate could be achieved with reaction time and temperature. Combining that with Figure 4a, the reaction temperature is more influential than the reaction time as to the reduction rate.

Figure 3b shows the 3D response surface plot at varying reaction temperatures and molar ratios of silicon to calcium. It can be inferred that the reduction rate increases with the reaction temperature and the molar ratio of silicon to calcium. Figure 4b demonstrates that the effect of reaction temperature on the reduction rate is stronger than that of molar ratio of silicon–calcium.

In Figure 3c, the 3D response surface plot is developed for the reduction rate with varying reaction temperatures and phosphorus rock particle sizes. The figure indicates that the reduction rate increases with the reaction temperature, while it increases to a certain extent and then decreases with the decrease in the phosphorus rock particle size. Figure 4c

Figure 3: Response surface plot showing the effects on the reduction rate. (a) Fixed levels C (1.20), D (1.20), E (75–106 μm). (b) Fixed levels A (75 min), C (1.20), E (75–106 μm). (c) Fixed levels A (75 min), C (1.20), D (1.20). (d) Fixed levels A (75 min), B (1,300°C), E (75–106 μm). (e) Fixed levels A (75 min), B (1,300°C), D (1.20).

reflects that the reaction temperature affects the reduction rate stronger than the phosphorus rock particle size.

The 3D response surface plot based on the independent variables coke excess coefficient and molar ratio of silicon to

calcium is shown in Figure 3d, indicating that the reduction rate increases with increasing coke excess coefficient and molar ratio of silicon–calcium. The molar ratio of silicon to calcium is obviously a stronger factor of the reduction rate

Figure 4: Contour plot showing the effects on reduction rate. (a) Fixed levels C (1.20), D (1.20), E (75–106 μm). (b) Fixed levels A (75 min), C (1.20), E (75–106 μm). (c) Fixed levels A (75 min), C (1.20), D (1.20). (d) Fixed levels A (75 min), B (1,300°C), E (75–106 μm). (e) Fixed levels A (75 min), B (1,300°C), D (1.20).

Table 7: Comparison with the results of similar literature

Temperature (°C)	Time (min)	Si/Ca	CEC	Additives	Reduction rate (%)	Authors	Reference
1,350	60		0.67	Methyl cellulose	94.84	Q. Wu et al.	Mater. Res. Express 2019; 6 :075513
1,300	240	1.1	1.1	NiSO ₄	90.68	R. Cao et al.	Silicon 2019; 11 :2829–36
1,350	60		1.6		78	Y. Liu et al.	Adv. Mater. Res. 2012; 361–363 :268–74
1,400	40		1.5	Potassium feldspar and K ₂ CO ₃	96.8	Z. Chen et al.	Silicon 2020; 12 :613–20
1,300	40	0.8			90	Y. Li et al.	Phosphorus, sulfur, and silicon 2018; 193 :141–8
1,300	240	1.1	1.1	K ₂ CO ₃ –NiSO ₄	92.77	G. Zheng et al.	Silicon, 2019, DOI: 10.1007/s12633-019-00311-5
1,340	92	1.27	1.28		96.88	This study	

than the coke excess coefficient, which can be found in Figure 4d.

Figure 3e gives the 3D response surface plot at varying phosphorus rock particle sizes and coke excess coefficients. It shows that the reduction rate increases with increasing coke excess coefficient. However, the reduction rate increased to a certain level and then decreased with decreasing phosphorus rock particle size. It can be seen from Figure 4e that the influence of coke excess coefficient on the reduction rate is slightly stronger than that of phosphorus rock particle size.

3.4 Response surface optimization validation test results

Under the prediction result of the CCD model, the theoretical optimum reduction conditions and the result are as follows: reaction time 92 min, reaction temperature 1,340°C, coke excess coefficient 1.27, molar ratio of silicon–calcium 1.28, phosphorus rock particle size 75–106 μm, and the maximum reduction rate 99.40%. In order to test the accuracy of the model, the reduction rate of phosphorus rock is 96.88% under the optimum reduction conditions. The deviation from the predicted value is only 2.52%, which implies the model can predict the experimental results well. Based on the investigation of the related literature, the reduction rate is close to or higher than most of the reported values in the literature.

In order to illustrate the innovation and the significant improvement of this study, similar reports about phosphorus rock carbothermal reduction were searched. Their reaction conditions and results are listed in Table 7. It can be seen that our optimized conditions of phosphorus rock carbothermal reduction are relatively mild and the reduction rate is fairly good as compared to the other published results.

4 Conclusions

The process conditions of carbothermal reduction of medium- and low-grade phosphorus rocks were optimized by the response surface methodology. The effects of reaction time, reaction temperature, coke excess coefficient, molar ratio of silicon to calcium, and phosphorus rock particle size on the reduction rate of phosphorus rock were investigated. The optimum

conditions are as follows: reaction time 92 min, reaction temperature 1,340°C, coke excess coefficient 1.27, molar ratio of silicon–calcium 1.28, and phosphorus rock particle size 75–106 µm. Under these conditions, the reduction rate of phosphorus rock (96.88%) is close to the predicted value (99.40%). The reduction rate of phosphorus rock in this paper is close to or higher than most of the reported results in the literature, which provides the experimental basis for energy saving and consumption reduction in thermal phosphoric acid process.

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References

- [1] Wang Z, Jiang M, Ning P. Thermodynamic modelling and gaseous pollution prediction of the yellow phosphorus production. *Ind Eng Chem Res.* 2011;50:12194–202.
- [2] Li X, Hu B, Wu Y. Reaction kinetics of phosphate ore with carbon by smelting reduction technology. *Chem Eng.* 2013;41:53–6.
- [3] Zhong B, Chen L, Li J. New progress in purification of wet-process phosphoric acid by solvent extraction. *Chem Ind Eng Prog.* 2005;24:592–602.
- [4] Wang X, Tang L, Jiang Z. Numerical simulation of Venturi ejector reactor in yellow phosphorus purification system. *Nucl Eng Des.* 2014;268:18–23.
- [5] Ma L, Ning P, Zang Y. Experimental and modeling of fixed-bed reactor for yellow phosphorous tail gas purification over impregnated activated carbon. *Chem Eng J.* 2008;137:471–9.
- [6] Tang A, Jiang D, Chen H. Numerical simulation of phosphorus furnace. *Phosphate Compound Fertilizer.* 2011;26:42–5.
- [7] Geng R, Xia J, Chen Z. Effects of potassium feldspar on slagging and fluxing in phosphorus produced via electric furnace. *Phosphorus Sulfur and Silicon Relat Elem.* 2017;192:475–80.
- [8] Xue K, Zhang R. Research progress on phosphate resource distribution and metallogenic characteristics in China. *Acta Mineral Sin.* 2019;39:7–14.
- [9] Kijkowska R, Kowalski Z, Pawlowska-Kozinska D, Wzorek Z, Gorazda K. Tripolyphosphate made from wet-process phosphoric acid with the use of a rotary kiln. *Ind Eng Chem Res.* 2008;47:6821–7.
- [10] Lv L, Liang B, Liu Q. Back adsorption process of calcium phosphate to P_2O_5 in kiln phosphoric acid. *J Chem Ind Eng.* 2016;67:4399–405.
- [11] Chen S. Summary of comprehensive utilization of phosphorus by-products from electric furnace in China. *Sulphur Phosphorus Bulk Mater Handling Relat Eng.* 2011;5:44–8.
- [12] Jiang L, Liang B. Kinetics of hot carbon reduction of fluorapatite. *J Univ Sci Techno Chengdu.* 1995;5:1–8.
- [13] Li X, Hu B, Wu Y. Process and kinetics of reduction of middle and low-grade phosphate ore by fusion method. *J Chem Eng Chin Univ.* 2014;28:905–10.
- [14] Cao R, Xia J, Li W. Effect of alkali metal carbonate on carbothermal reduction of phosphorus rock. *J Chem Eng Chin Univ.* 2018;32:568–76.
- [15] Yang J, Chen J, Liu H. Process analysis of solid phase carbothermal reduction of fluoroapatite with aluminum impurities. *J Sichuan Univ Eng Sci Ed.* 2015;47:186–91.
- [16] Li L, Yan Y, Hu Z. Investigation on reduction of low phosphorite with high calcium to silica ratio by the kiln method and the pozzolanic activity of the calcining residue. *J Wuhan Univ Technol.* 2014;36:11–6.
- [17] Li Y, Han Y, Sun Y, Gao P, Li Y, Gong G. Growth behavior and size characterization of metallic iron particles in coal-based reduction of oolitic hematite-coal composite briquettes. *Minerals.* 2018;8:177.
- [18] Li Y, Xia J, Chen Z. Feasibility study on potassium feldspar as flux to reduce phosphate ore. *Bull Chin Ceram Soc.* 2017;8:2737–42.
- [19] Long Y, Tan F, Yang K. Investigation Response surface optimization of process parameters for $LiFePO_4/C$ preparation with a low temperature carbothermal reduction method. *J Chem Eng Chin Univ.* 2013;27:125–30.
- [20] Verma P, Agrawal US, Sharma AK, Sarkar BC, Sharma HK. Optimization of process parameters for the development of a cheese analogue from pigeon pea (*Cajanus cajan*) and soymilk using response surface methodology. *Int J Dairy Technol.* 2005;58:51–8.
- [21] Luo Y, Zhang W, Li J. Optimization of uranium removal from uranium plant wastewater by response surface methodology (RSM). *Green Proc Synth.* 2019;8:808–13.
- [22] Ma H, Yan C, Wang Y, Xie H. Statistical analysis and optimization of recovering indium from jarosite residue with vacuum carbothermic reduction by response surface methodology (RSM). *Green Proc Synth.* 2017;6:211–6.
- [23] Guo R, Li X, Huo W, Feng W, Liu X, Gao W. Optimization of synthesis of bisphenol A formaldehyde phenolic resin by response surface methodology. *China Adhes.* 2019;2:1–3.