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Optimization of the treatment process of zinc leaching residue by using the response surface method

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Abstract: The decrease in the zinc volatilization rate is usually due to the liquid phase, which is typically generated in the rotary kiln. The response surface model was built to analyze and explore the effects of carbon content, basicity, and holding time on the zinc volatilization rate and residue state. Moreover, the model was used to optimize the experimental conditions. The results showed that the effect of basicity on zinc volatilization rate was statistically significant, whereas the effects of carbon content and holding time were relatively small. The optimized process conditions were as follows: carbon content of 32%, basicity of 3, and holding time of 30 min. Under this condition, the zinc volatilization rate was 99.65%, and the furnace residue was sintered, which proved to be beneficial to the subsequent step of iron extraction.

Keywords: response surface model; rotary kiln; zinc leaching residue.

1 Introduction

The hydrometallurgy process serves as the major route of zinc extraction, which contributes to over 80% of the zinc production all over the world. This process, however, produces great amounts of waste, particularly leaching residues. The residues from conventional acid leaching still contain traces of valuable metals that can serve as secondary resources [1, 2]. The reduction-volatilization in the rotary kiln is typically used to treat such residues to recover zinc [3], and the kiln residues can be used to recover iron in the subsequent step [4, 5].

The reduction-volatilization in the kiln usually reacts at about 1200°C. This high temperature melts the low-melting point compositions in the residue, such as silicate, thus causing several problems. First, some of the non-reduction powder will be wrapped by the liquid phase, generating the outsourcing silicate melt shell with the powder. Meanwhile, some substances, such as zinc silicate, would also be generated in the melt. In turn, these can reduce the zinc volatilization rate in the kiln. Second, the kiln's internal diameter may be reduced because of the ring formed by the sintered melt. Hence, the kiln life and handling capacity are also reduced. Finally, some iron oxides from the leaching residue can produce iron silicate, which may be wrapped in the melt. Both iron oxides and iron silicate could not be reduced to magnetite, and the corresponding components become difficult to extract during the crushing process. These are the main reasons why it is difficult to recover iron from kiln residue, which leads to the low iron recovery rate.

Hence, it can be inferred that preventing the generation of the liquid phase is not only beneficial to the volatilization of zinc but it can also prevent furnace residue sintering. According to the ternary phase diagram [6], on the one hand, the melting point of zinc leaching residues rises when CaO content is increased within a certain range. On the other hand, the addition of CaO can reduce the Gibbs free energy of the reductive reaction.

Based on the above, the current work proposed to add the slagging agent to the zinc leaching residue, thus changing the basicity and improving the melting point, which can help avoid the abovementioned problems in the rotary kiln production process. In this paper, the Gibbs free energy of the reductive reaction was calculated, and the reduction process of changing conventional acid leaching residue's basicity was investigated by using the response surface method (RSM) [5, 7–10].

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2 Materials and methods

2.1 Materials

According to previous X-ray powder diffraction (XRD) analyses, the leach residue used in the experiments contains 18% zinc, 6.3% SiO_2, and 1.76% CaO. The zinc in the residue is mainly in the form of zinc ferrate ($ZnO \cdot Fe_2O_3$) and a little bit of zinc sulfate ($ZnSO_4$). The CaO added as a slagging agent was analytical pure. The fixed carbon content of the reduction carbon powder was 78%.

2.2 Experimental procedure

The zinc leaching residue was dried at 100°C and mixed proportionally with CaO and carbon powder. The reduction of the volatilization process of zinc was simulated in a ceramic crucible with a cover at 1200°C for a certain time; at the end of the experiment, the crucible was cooled to room temperature in the furnace. Next, the residue was taken out and weighed, after which the zinc content was analyzed by using the EDTA volumetric method (according to the China National Standard GB/T 14353.3-2010). This was done to calculate the zinc volatilization rate.

Table 1: Parameters and their levels used for the response surface design.

Parameter	Levels	
	−1	1
Carbon content (wt.%)	20	50
Basicity (CaO/SiO_2)	0.28	3
Holding time (min)	30	60

Table 2: Experimental conditions and results.

No.	Carbon content (wt.%)	Basicity	Holding time (min)	Volatilization rate of zinc (%)
1	20	1.50	60	61.08
2	30	0.89	45	74.72
3	30	0.89	45	72.65
4	30	0.28	45	70.17
5	40	1.50	30	83.87
6	30	1.50	45	79.24
7	20	1.50	30	67.25
8	40	0.89	45	78.84
9	20	0.89	45	71.89
10	40	0.28	60	67.34
11	40	1.50	60	84.54
12	30	0.89	30	76.20
13	30	0.89	60	77.99
14	20	0.28	30	63.97
15	40	0.28	30	67.60
16	20	0.28	60	69.79
17	50	0.28	60	72.73
18	50	3.0	30	99.56
19	20	3.0	60	96.90
20	35	3.0	60	99.79
21	20	3.0	30	92.15
22	50	3.0	60	99.77
23	50	3.0	30	99.37
24	50	0.28	30	70.12

2.3 Experimental design and results

The response surface experiment design was carried out using the response surface design platform of JMP (USA), a data statistics software. Three parameters were considered (carbon content, basicity, and holding time) and the setting of each parameter is shown in Table 1. The variable values of nos. 1 to 16 were designed by using the central composite design (CCD) and nos. 17 to 24 belonged to the extended experiments. The experimental results are shown in Table 2.

3 Statistical analysis and discussion

3.1 Statistical analysis

The stepwise regression method was chosen to analyze the experimental data in Table 2, and the quadratic response surface model was established after eliminating the non-significant items. The model for zinc volatilization rate is calculated by the obtained quadratic regression equation given by

$$\begin{aligned}\text{Zinc volatilization rate (\%)} = {} & 82.108005 + 3.4303333X_1 \\ & +14.440229X_2 + 0.4451064X_3 \\ & -5.258419X_1^2 + 4.982143X_2^2,\end{aligned} \tag{1}$$

where X_1, X_2, and X_3 are equal to $\frac{\text{carbon content (wt.\%)} - 35}{15}$, $\frac{\text{basicity} - 1.64}{1.36}$, and $\frac{\text{holding time (min)} - 45}{15}$, respectively.

According to the analysis of variance and test for lack of fit (Table 3), this equation is suitable for expressing the model. The $R^2 = 0.91$ and the high F value (35.0302) and low p-value ($p < 0.0001$) indicate that the fitting model is reasonable. Hence, the model can be used to analyze and optimize the process of zinc leaching in the rotary kiln. The p-value ($p > 0.05$) of the test for lack of fit also shows that the fitting model does not exhibit lack of fit. Table 4 shows the significance of each coefficient in the equation, which is determined by the p-value listed. As can be

Table 3: Analysis of variance and test for lack of fit for the regression model.

Quadratic response surface model of zinc volatilization rate ($R^2=0.91$)					
Source	**Df**	**Sum of squares**	**Mean square**	**F value**	**p-value**
Analysis of variance					
Model	5	3263.6160	652.723	35.0302	<0.0001
Error	18	335.3970	18.633		
Total	23	3599.0130			
Test for lack of fit					
Lack of fit	16	333.2365	20.8273	19.2801	0.0504
Pure error	2	2.16050	1.0803		
Total	18	335.39698			

Table 4: Significance test for the regression coefficients.

Source	Df	Sum of squares	F value	p-value
X_1	1	129.6178	6.9563	0.0167
X_2	1	2628.0798	641.0431	<0.0001
X_3	1	3.4802	0.1868	0.6707
X_1^2	1	101.3841	5.4411	0.0315
X_2^2	1	82.2455	4.4139	0.0500

seen, the effects of the first term X_1, X_2 and the quadratic term X_1^2, X_2^2 on the response of zinc volatilization rate are significant. This means that the carbon content and the basicity are the main parameters affecting the rate of zinc volatilization, and do not indicate a simple linear relationship.

3.2 Reduction mechanism

Although the zinc ferrite in the zinc leaching slag cannot easily undergo thermal decomposition, they tend to be easily decomposed when added carbon or under the conditions of carbon monoxide atmosphere [11–13]. This can be explained by the following reactions expressed by Equations (2) and (3). Another zinc–bearing phase in the slag can also be reduced by carbon as shown in Equations (4) and (5).

$$3ZnO\cdot Fe_2O_3 + C = 3ZnO + 2Fe_3O_4(s) + CO(g) \tag{2}$$

$$3ZnO\cdot Fe_2O_3 + CO(g) = 3ZnO + 2Fe_3O_4 + CO_2(g) \tag{3}$$

$$ZnO(s) + C(s) = Zn(g) + CO(g) \tag{4}$$

$$2ZnO(s) + C(s) = Zn(g) + CO_2(g). \tag{5}$$

The values of the Gibbs free energies in Equations (2) to (5) can be respectively estimated by using Equations (6) to (9). The values at the temperature over 1060.85°C are less than zero, indicating that the reduction reaction with carbon can be carried out spontaneously with a temperature higher than 1060.85°C. Thus, the effect of carbon will not be significantly larger when the temperature reaches this condition.

$$\Delta G_1^{\ominus} = 133888 - 224.28T \tag{6}$$

$$\Delta G_2^{\ominus} = -28869.6 - 56.50T \tag{7}$$

$$\Delta G_3^{\ominus} = 344552.4 - 281.17T \tag{8}$$

$$\Delta G_4^{\ominus} = 526347.2 - 394.55T \tag{9}$$

3.3 Optimization

The above response surface quadratic model was applied to explore the best combination of the three variables. The changes of zinc volatilization rate with different selection of variables are shown in the prediction profiler (Figure 1).

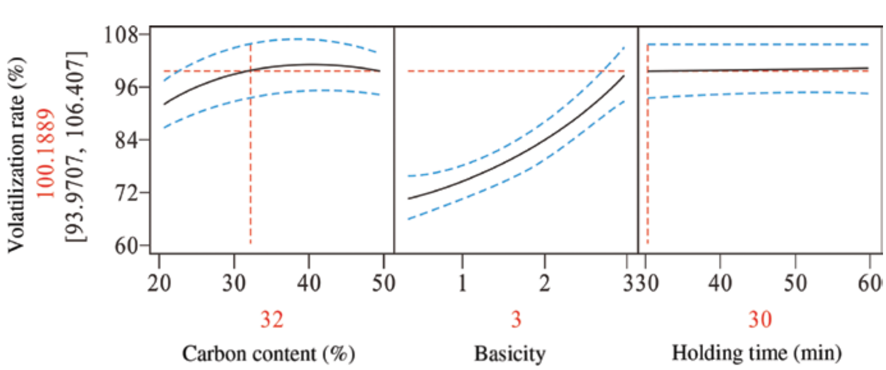

Figure 1: Prediction profiler for the zinc volatilization rate.

As can be seen, the rate tends to be high with the increase of content of carbon. Until the content of carbon reaches 32%, the rate change is very small. While basicity has a more significant effect on the zinc volatilization rate, there exists a nearly linear relationship between them when basicity is higher than 1.5. Moreover, the holding time had little effect on zinc volatilization. Thus, it can be concluded that the zinc volatilization rate could achieve almost 100% with carbon content of 32% carbon, basicity of 3, and holding time of 30 min.

4 Verification

The selected optimal conditions of 32% carbon, basicity of 3, and holding time of 30 min for the optimum response values were tested. The experimental results indicated that the zinc volatilization rate reached 99.65% and obtained a powdery residue under the optimal conditions.

5 Conclusions

Adding CaO into zinc leaching residue is technically feasible in optimizing the process of reduction volatilization in e rotary kiln. Adding CaO can effectively prevent the sintering of the charge, thereby reducing the kiln ring. This result is beneficial to the next iron extraction step and can ultimately help improve the service life of the kiln.

Under the optimized conditions, the volatility of zinc can reach 99.65%. Compared with the current rotary kiln zinc volatilization rate, it increased by 5%–6% to improve the metal recovery rate, thus effectively preventing the generation of residues in the volatile liquid phase.

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