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Statistical analysis and optimization of recovering indium from jarosite residue with vacuum carbothermic reduction by response surface methodology (RSM)

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Abstract: Vast jarosite residue was produced from traditional zinc hydrometallurgy process in China. It is necessary to recover valuable metals from the jarosite residue. Indium is the one of them. Recovering indium from jarosite residues with carbon reduction method under the condition of vacuum was investigated. The analysis of variance was used to evaluate the influence of different factors on the volatilizing rate of indium, indicating that the influence of temperature on the volatilizing rate of indium is statistically significant. Other factors have no significant influence. Response surface methodology was used to explore the best combination of four variables and to study the effects of their interactions on the indium volatilizing rate. The results showed that there was an obvious interaction between the percent content of carbon and temperature and between the percent content of carbon and hold time, and the selected optimal conditions were 30% carbon, 13% CaO, 1000°C temperature, and 60 min hold time. Under these conditions, the indium volatilization rate was up to 98.2%.

Keywords: ANOVA; indium; jarosite residue; RSM; vacuum.

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1 Introduction

A vast jarosite residue was produced from a traditional zinc hydrometallurgy process in China, and most of the residue was stored [1–3]. According to a rough calculation, no less than one million tons of this kind of residue was stored in China per year. This residue not only takes massive land but also brings forth great risk of environmental pollution as it contains significant zinc and lead as well as some arsenic and cadmium, and such toxic ingredients are dissolved in rainwater, as demonstrated. The jarosite residue mainly contains some valuable metals such as zinc, lead, iron, and indium [4–6]. Indium is a high-value metal [7]. There are two ways to extract indium from jarosite residue: leaching and reduction and volatilization. Leaching indium from the jarosite is a traditional process, and jarosite residue is dissolved using hot sulfuric acid solution. Indium is directly extracted from leach solution by an extraction agent. However, this method will produce a lot of wastewater containing metal. In reduction and volatilization, jarosite residues were reduced and volatilized in rotary kiln to fume Zn, In, and Pb in the residue. Approximately 75% Zn, 68% Pb, and 80% Ge in the residue can be recovered. However, these processes have some shortcomings, such as high fixed investment, high operation cost, and air pollution during fuming. Vacuum metallurgy has been widely used in melting nonferrous metals. However, there is no report on how this technique is used to recover indium from jarosite residues.

Response surface methodology (RSM) is often used for the development, improvement, and optimization of various processes, where certain responses are influenced by several variables [8], because it is more efficient and has easier arrangement and interpretation of experiments compared with other methods [9]. In this paper, we study the feasibility of recycling metallic indium from jarosite residues through vacuum carbon reduction at a relative low temperature. In addition, the RSM was applied to analyze experimental data and to optimize experimental conditions.

2 Materials and methods

2.1 Experimental procedure

The jarosite residue was obtained from a certain zinc smelter, and the grade of indium is 270 g/t. Jarosite residue dried at 100°C was mixed with carbon powder and calcium oxide in proportion. The mixed sample was pressed into a cylinder with a size of Φ2 cm×1 cm at 5.5 MPa. The cylinder sample was weighed and then put into crucibles. The crucible with a cover was put into a vacuum furnace. After setting the temperature, the indium volatilization experiment was conducted in a vacuum degree of 2–4 Pa. At the end of the experiment, the sample cooled with the furnace cooling. Finally, the furnace residues were weighed, and the content of indium in the obtained residues was analyzed. The indium volatilization rate was calculated by the following equation:

$$w = \frac{a-b}{a} \times 100\%, \tag{1}$$

where w (%) is the indium volatilization rate, a (g) is the indium quantity of the cylinder sample, and b (g) is the indium quantity of residue.

2.2 Experimental design

Statistical software package (JMP 10, SAS Institute Inc., Cary, NC, USA) was used in the experiment design and subsequent data analysis. A three-level four-variable response surface design (RSM) was applied to explore the better combination of variables for the recovery of indium. The range values of four independent variables are shown in Table 1. Design and experiment results are given in Table 2.

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

Parameter level	Carbon (%)	Calcium oxide (%)	Temperature (°C)	Hold time (min)
1	10	1	800	30
2	30	13	900	60
3	50	25	1000	90

3 Statistical analysis and discussion

3.1 Analysis of variance

The analysis of variance (ANOVA) was used to evaluate the influence of different factors on the volatilizing rate of indium. The results are summarized in Table 3, showing that the mean square (between groups) of temperature is six times larger than their error mean square. However, there is relatively less difference between the mean square of others and their error mean square. This indicates that the mean values at different levels of temperature are greatly different. However, as for other factors, the same conclusion cannot be reached. Furthermore, p-values <0.05 were considered to be statistically significant as the experimenter has selected $\alpha = 0.05$ [10–13]. It can be seen in Table 3 that the p-values of temperature are <0.05 whereas other the p-values are not. That is to say the influence of temperature on the volatilizing rate of indium is statistically significant. Other factors have no significant influence.

3.2 Mean value analysis

The mean value of the indium volatilizing rate at each level was calculated. The relationship graphs between the mean value and the different levels of each factor are shown in Figure 1, indicating that the indium volatilizing rate presents

Table 2: The experimental conditions and results of reduction distillation for jarosite.

Experiment no.	Carbon (wt.%)	Calcium oxide (wt.%)	Temperature (°C)	Hold time (min)	Volatilizing rate of indium (wt.%)
1	30	13	900	60	66.05
2	50	13	800	60	18.06
3	10	1	1000	60	45.43
4	10	13	800	90	0.00
5	30	25	800	90	0.00
6	50	1	1000	30	36.64
7	10	25	1000	30	38.11
8	50	1	900	90	62.02
9	10	1	900	30	0.00
10	50	25	900	30	0.00
11	30	1	800	60	0.00
12	10	25	900	90	30.28
13	50	25	1000	60	96.22
14	10	25	800	30	1.48
15	30	13	1000	90	85.0

Table 3: ANOVA for the influence of different factors.

Source	*df*	Sum of squares	Mean square	*F* ratio	p-Value
Carbon (wt.%)	2	1678.4800	839.24	0.7274	0.5033
Error	12	13845.864	1153.82		
Total	14	15524.344			
Calcium oxide (wt.%)	2	593.2770	296.64	0.2384	0.7915
Error	12	14931.067	1244.26		
Total	14	15524.344			
Temperature (°C)	2	7967.788	3983.89	6.3265	0.0133
Error	12	7556.555	629.71		
Total	14	15524.344			
Hold time (min)	2	2331.010	1165.50	1.0601	0.3767
Error	12	13193.334	1099.44		
Total	14	15524.344			

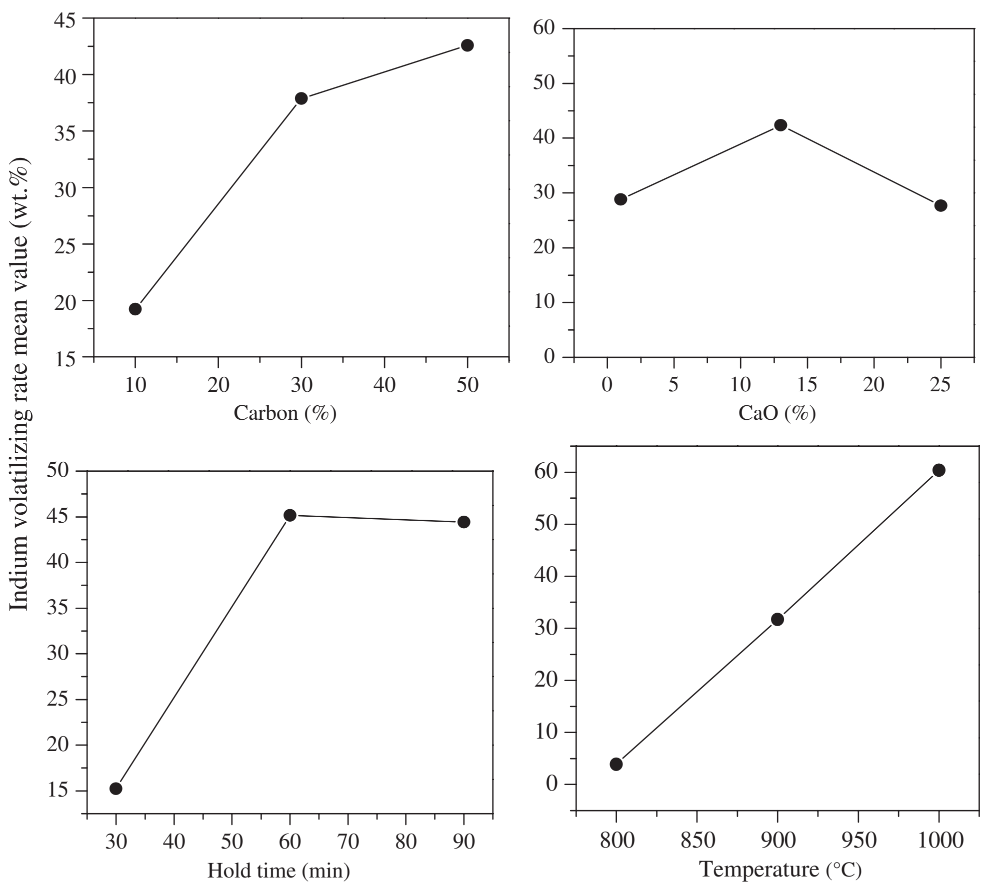

Figure 1: Effect of four variables on the volatilizing rate of indium.

a straight climb tendency with the increase in final temperature. From the point of view of thermodynamics, the increase in temperature provided a good thermodynamics condition and promoted the reduction and volatilization of indium. As far as dynamics is concerned, higher temperature could enhance the reaction speed and reduce the reaction time. This could give a reasonable explanation why the indium volatilizing rate presents a tendency of straight climb with the increase in final temperature. For the increase in carbon content, the indium volatilizing rate greatly increases and slows down subsequently. As for the reducing agent of the reaction process, the increasing content of carbon made the reduction reaction more thoroughly. However, when the reducing reaction reaches a certain extent, the influence of carbon content becomes relatively less. In calcium oxide, the indium volatilizing rate first increases and then decreases. Calcium oxide was used as a sulfur-fixing agent in the reaction process, which can decrease the partial pressure of sulfur trioxide and furthermore promote the transformation of $In_2(SO_4)_3$ into In_2O_3 or $In_2O_3 \cdot \alpha$-Fe_2O_3 [14]. It can also prevent burden from sintering, which was favorable to the volatilization of indium. However, the overabundance of CaO could decrease the grade of indium in furnace charge and reduce the indium volatilizing rate. In terms of hold time, the indium volatilizing rate first increases and then keeps invariant. Hold time is related to the degree of reaction. Long holding time means the interaction between furnace charges will go thoroughly. However, with the holding time extension, the indium volatilizing rate maintained a stable value when the reaction went to the greatest extent.

3.3 Parameter optimization by RSM

The response surface quadratic model was applied to explore the best combination of four variables and to study the effects of their interactions on the indium volatilizing rate. The values of regression coefficients were calculated, and the response variable and the test variables are related by the following second-order polynomial equation:

$$\begin{aligned} y(\%) = {} & 65.344615 + 6.8196172X_1 + 4.683507X_2 \\ & +34.016317X_3 + 15.306681X_4 \\ & -6.756347X_1X_2 + 12.457266X_1X_3 \\ & +14.239093X_1X_4 - 0.376619X_2X_4 + \\ & 3.4965737X_3X_4 + 0.2736029X_1^2 \\ & -15.68763X_2^2 - 7.5603164X_3^2 - 26.80915X_4^2, \end{aligned} \quad (2)$$

where X_1, X_2, X_3, and X_4 are equal to $\frac{\text{carbon(wt.\%)} - 30}{20}$, $\frac{\text{CaO(wt.\%)} - 13}{12}$, $\frac{\text{temperature(°C)} - 900}{100}$, and $\frac{\text{hold time(min)} - 60}{30}$, respectively. Table 4 gives the statistics or the model summery, and Table 5 gives the ANOVA for response surface quadratic model. The R^2 value of 0.9997 (Table 4) and $p < 0.05$ (Table 5) indicate that the quadratic model was adequate for prediction within the range of experimental variables. The 3-D response surface plot was used to study the effects of four variable interactions on the indium volatilizing rate. The results are shown in Figure 2.

Table 4: Model summery statistics.

R^2	Adjusted R^2	RMSE
0.9997	0.9961	2.0763

Table 5: ANOVA for response surface quadratic model.

Source	*df*	Sum of squares	Mean square	*F* ratio	p-Value
Model	13	15520.033	1193.85	276.9226	0.0470
Error	1	4.311	4.31		
Total	14	15524.344			

The 3-D response surface plot in Figure 2A, which gives the indium volatilizing rate as a function of the percent content of carbon and calcium oxide at fixed temperature (900°C) and hold tine (60 min), indicates that a higher indium volatilization rate could be achieved when the percent content of carbon and the percent content of calcium oxide were at the level of 30% ($X_1 = 0$) and 13% ($X_2 = 0$).

Figure 2B shows the 3-D response surface plot at varying percent content of carbon and temperature at fixed calcium oxide (13%) and hold time (60 min). It can be seen that the indium volatilization rate decreases with the increase in the percent content of carbon at a temperature of 800°C ($X_3 = -1$), but when the temperature is higher than 800°C, it increases with the increase in the percent content of carbon. At a temperature of 1000°C ($X_3 = 1$), even 30% of the carbon can make the indium volatilization rate close to 100%.

In Figure 2C, the 3-D response surface plots were developed for the indium volatilization rate with varying percent content of carbon and hold time at fixed calcium oxide (13%) and temperature (900°C). It indicates that the indium volatilization rate decreases with the increase in the percent content of carbon when the hold time is <60 min ($X_4 = 0$), but when the holding time is between 60 and 90 min ($X_4 = 1$), it increases with the increase in the percent content of carbon.

The 3-D response surface plot based on independent variables calcium oxide and temperature is shown in Figure 2D, whereas the other two independent variables carbon and hold time are kept at 30% and 60 min, respectively, indicating that the maximum indium volatilization rate can be achieved when the percent content of calcium oxide and temperature were at the level of 13% and 1000°C, respectively.

Figure 2E gives the 3-D response surface plot at varying calcium oxide and hold time with fixed carbon (30%) and temperature (900°C). It shows that when the percent content of calcium oxide and hold time were 13%

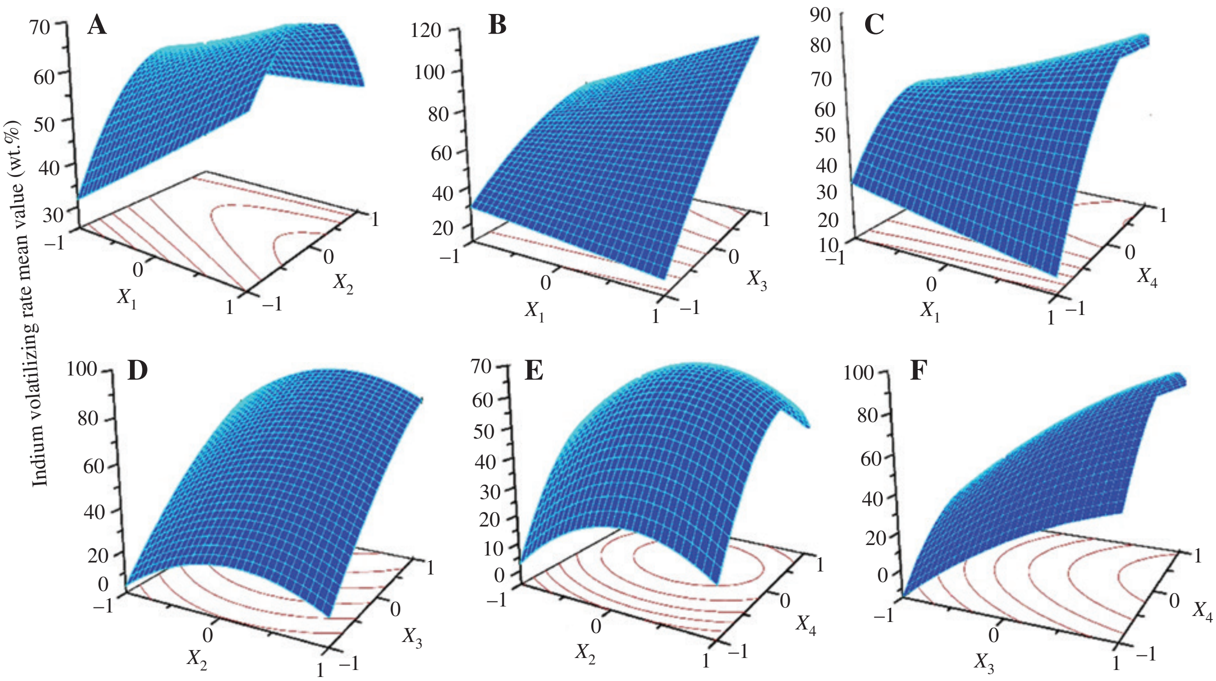

Figure 2: Response surface plot (3-D) of the interactions of four variables. (A) Fixed levels $X_3 = 0$, $X_4 = 0$. (B) Fixed levels $X_2 = 0$, $X_4 = 0$. (C) Fixed levels $X_2 = 0$, $X_3 = 0$. (D) Fixed levels $X_1 = 0$, $X_4 = 0$. (E) Fixed levels $X_1 = 0$, $X_3 = 0$. (F) Fixed levels $X_1 = 0$, $X_2 = 0$.

and 60 min, respectively, the indium volatilization rate could reach a maximum.

In Figure 2F, the 3-D response surface plot is developed for the indium volatilization rate with varying temperature and hold time, whereas the other two independent carbon and calcium oxide are 30% and 13%, respectively. It can be concluded that the maximum indium volatilization rate could be achieved when the temperature and hold time are 1000°C and 60 min, respectively.

3.4 Verification of optimal conditions

The selected optimal conditions of 30% carbon, 13% Ca, 1000°C temperature, and 60 min hold time for the optimum response values were tested. The experimental results indicated that the indium volatilization rate is up to 98.2% under the optimal conditions.

4 Conclusions

1. The ANOVA was used to evaluate the influence of different factors on the volatilizing rate of indium, showing that the influence of temperature on the volatilizing rate of indium is statistically significant. Other factors have no significant influence.
2. There is obvious interaction between the percent content of carbon and temperature and between the percent content of carbon and hold time.
3. RSM was used to optimize the experimental variables. Under the optimal conditions of 30% carbon, 13% CaO, 1000°C temperature, and 60 min hold time, the indium volatilization rate was up to 98.2%.

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Bionotes

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