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Application of Response Surface Methodology to Optimize the Extracting Process of Molybdenum from Nickel Molybdenum Ore

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The extraction of molybdenum was researched in order to find the effective recovery process. Through response surface methodology, the optimum condition was determined as follows: roasting temperature, 670 ºC; roasting time, 1.70 h; NaOH concentration, 60 %; liquid solid radio, 2. The yield of molybdenum was as high as 3.82 %.

Key Words: Molybdenum, Extraction, Response surface methodology.

INTRODUCTION

Molybdenum is a valuable alloying agent, as it contributes the hardness and toughness of quenched and tempered steels. It also improves the strength of steel at high temperatures. Molybdenum is used in alloys, electrodes and catalysts. The versatility of molybdenum in enhancing a variety of alloy properties has ensured it a significant role in contemporary industrial technology, which increasingly requires materials that are serviceable under high stress, expanded temperature ranges and highly corrosive environments. Moreover, molybdenum finds significant use as a refractory metal in numerous chemical applications, including catalysts, lubricants and pigments.

Nickel molybdenum ore is metal composite ores containing a variety of metallic and nonmetallic elements in China. The content of nickel is 0.17-7.03 % and molybdenum is 0.35-8.17 %. The chief source of molybdenum now is refined by molybdenite (MoS_2), which is the most valuable by-product of nickel molybdenum mining production. Many technical efforts have been developed in order to separate both metals by efficient methods[1-3]. Normally molybdenite concentrate is obtained by a selective flotation. Some of them are related to transport mechanism and permeability equations through membrane and others are concerned on practical applications of liquid membranes in diverse potential fields such as organic acid extraction, analysis of substances, nuclear waste processing, desalination of sea water and others. Usually the processing continues by roasting the sulphide concentrate to molybdenum trioxide in a step[4-7], which is highly demanding of energy and environmentally objectionable due to the production of sulphur oxides. Then, leaching of molybdenite concentrates and recovery of dissolved metals by solvent extraction, which has become very important as a promising industrial process for the recovery of molybdenum from all kinds of molybdenum ores.

In a preliminary study, optimization could be used to maximize the extraction of molybdenum (molybdenum yield). Roasting temperature, roasting time, NaOH concentration and liquid to solid ratio were found to influence significantly the extraction of molybdenum. Response surface methodology is an effective tool for optimizing the process. Response surface methodology uses an experimental design such as the central composite design to fit a model by least squares technique. If the proposed model is adequate, as revealed by the diagnostic checking provide by an analysis of variance (ANOVA) and residual plots, contour plots can be usefully employed to study the response surface and located the optimum[8]. The purpose of current work was to optimize the yield of molybdenum in the nickel molybdenum ore by response surface methodology.

EXPERIMENTAL

The nickel molybdenum ore for this study was obtained from Luanchuan (Henan, PR China). NaOH and HNO_3 of analytical grade were used as received.

Experimental processing: Nickel molybdenum ore was crushed in a mill and separated by sieving different sizes.

Firstly, the powders were placed in muffle furnace (Shanghai Jinghong laboratory instrument Co. Ltd.) roasted at different temperature for different times. Then, the roasted products reacted with sodium hydroxide solution of different concentrations at 95 ºC for 2 h according to response surface methodology. Finally, after filtering the reaction products, the filtered solution was transferred into a volumetric flask and made up to 25 mL with 2 % HNO_3. The concentration of molybdenum was detected by an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima 2100 DV, Perkin Elmer, USA).

Response surface methodology design: One response was measured: the yield of molybdenum (Y), defined as the ratio of total molybdenum in the extract to total amount of molybdenum expressed as percentage. Each of variables to be optimized was coded at 5 levels: -2, -1, 0, 1 and 2. Table-1 shows the variables, their symbols and levels. The selection of variable levels was based on our preliminary study.

TABLE- 1
VARIABLES AND THEIR LEVELS FOR CENTRAL COMPOSITE DESIGN

Variable	Symbol	Code-variable level				
		-2	-1	0	1	2
Roasting temperature (ºC)	X_1	300	400	500	600	700
Roasting time (h)	X_2	1.5	2.5	3.5	4.5	5.5
NaOH concentration (g mL^{-1})	X_3	20	30	40	50	60
Liquid solid ratio	X_4	5:1	4:1	3:1	2:1	1:1

A central composite design, shown in Table-2, was arranged to allow for fitting of a second-order model. The central composite design combined the vertices of a hypercube whose coordinates are given by the 2^n factorial design with the star points. The star points were added to the factorial design to provide for estimation of curvature of the model. Six replicates (run 25, 26, 27, 28, 29 and 30) at the center of the design were used to allow for estimation of pure error sum of squares. Experiments were randomized in order to minimize the effects of unexplained variability in the observed response due to extraneous factors.

Statistic analysis: A software package (design expert 7.0) was used to fit the second-order models and generate response surface plots. The model proposed for the response (Y) was:

$$Y = b_0 + \sum_{n=1}^{4} b_n x_n + \sum_{n=1}^{4} b_{nn} x_n^2 + \sum_{n \neq m-1}^{4} b_{tm} x_n x_m$$

where, b_0 is the value of the fitted response at the center point of the design, which is point (0, 0, 0, 0). B_n, b_{nn} and b_{nm} are the linear, quadratic and cross-product regression terms, respectively.

RESULTS AND DISCUSSION

Diagnostic checking of the fitted model: ANOVA for the regression was performed to assess the goodness of fit. The model for Y was:

$$Y_2 = 1.67 - 0.29X_1 - 0.028X_2 + 0.009157X_3 + 0.016X_4 - 0.013X_1X_2 + 0.13X_1X_3 + 0.008155X_1X_4 - 0.051X_2X_3 + 0.008875X_2X_4 - 0.041X_3X_4 - 0.16X_1^2 - 0.030X_2^2 - 0.083X_3^2 - 0.045X_4^2$$

where, X_1 means roasting temperature, X_2 is roasting time, X_3 is NaOH concentration, X_4 is liquid-solid ratio. The coefficient of absolute value in equation reflects the size of the various factors on the extraction rate, positive and negative value of the reflection coefficient reflects the direction on the effect of extraction. It could be seen that calcination temperature, the interaction item of calcination temperature and the NaOH concentration, the square of roasting temperature were great influence the extraction of molybdenum.

TABLE- 2
CENTRAL COMPOSITE DESIGN ARRANGEMENT AND REPONSE

Run	Variable level				Response
	X_1	X_2	X_3	X_4	Y
1	400.00	2.50	30.00	2.00	0.8805
2	600.00	2.50	30.00	2.00	1.9956
3	400.00	4.50	30.00	2.00	1.302
4	600.00	4.50	30.00	2.00	3.8465
5	400.00	2.50	50.00	2.00	1.0307
6	600.00	2.50	50.00	2.00	2.9873
7	400.00	4.50	50.00	2.00	1.4346
8	600.00	4.50	50.00	2.00	2.7015
9	400.00	2.50	30.00	4.00	1.6044
10	600.00	2.50	30.00	4.00	2.7775
11	400.00	4.50	30.00	4.00	0.0865
12	600.00	4.50	30.00	4.00	3.5879
13	400.00	2.50	50.00	4.00	0.8463
14	600.00	2.50	50.00	4.00	2.8282
15	400.00	4.50	50.00	4.00	0.3816
16	600.00	4.50	50.00	4.00	2.3795
17	300.00	3.50	40.00	3.00	3.6546
18	700.00	3.50	40.00	3.00	1.7524
19	500.00	1.50	40.00	3.00	1.7524
20	500.00	5.50	40.00	3.00	1.8553
21	500.00	3.50	20.00	3.00	2.1028
22	500.00	3.50	60.00	3.00	2.0098
23	500.00	3.50	40.00	1.00	2.8649
24	500.00	3.50	40.00	5.00	2.2606
25	500.00	3.50	40.00	3.00	2.2606
26	500.00	3.50	40.00	3.00	2.4759
27	500.00	3.50	40.00	3.00	3.2207
28	500.00	3.50	40.00	3.00	3.4399
29	500.00	3.50	40.00	3.00	2.6938
30	500.00	3.50	40.00	3.00	2.8161

Yield of molybdenum: The result of ANOVA was shown in Table-3. Values of Prob > F less than 0.05 indicated model terms were significant. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 6.328 indicated an adequate signal. This model could be used to navigate the design space.

Response surface plotting: Variables giving quadratic and interaction terms with the largest absolute coefficients in the fitted models were chosen for the axes of contour plots to account for curvature of the surfaces.

In Fig. 1, the effect of roasting temperature and NaOH concentration on the extraction of molybdenum at 3 liquid-solid ratio and 500 ºC is shown. The incease in NaOH concentration enabled higher alkalinity increase for oxidation reactions resulting in enhanced the yield of molybdenum within 2 h. Above 2 h roasting temperature and between 30 and 50 % NaOH concentration, a region of more than 1 % molybdenum yield was obtained. Maximum 3.84 % of molybdenum yield obtained at 3.5 h roasting temperature and 40 % NaOH concentration.

TABLE-3
ANOVA FOR THE FITTED MODEL

Source	Sum of squares	d_f	Mean square	F value	Prob > F
X_1	1.98	1	1.98	23.36	0.0002
X_2	0.018	1	0.018	0.22	0.6478
X_3	0.002	1	0.002	0.024	0.8795
X_4	0.006	1	0.006	0.071	0.7928
X_1X_2	0.002	1	0.002	0.033	0.8588
X_1X_3	0.25	1	0.25	2.97	0.1055
X_1X_4	0.001	1	0.001	0.013	0.9122
X_2X_3	0.042	1	0.042	0.49	0.4929
X_3X_4	0.027	1	0.027	0.32	0.5794
X_1^2	0.74	1	0.74	8.73	0.0099
X_2^2	0.024	1	0.024	0.29	0.6011
X_3^2	0.19	1	0.19	2.21	0.1578
X_4^2	0.056	1	0.056	0.67	0.4273
Residual	1.27	15	0.085		
Cor Total	4.44	29			

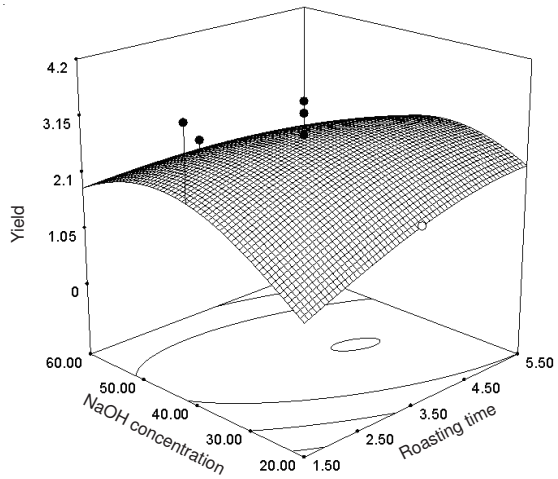

Fig. 1. Effect of NaOH concentration and roasting temperature on the yield of molybdenum (reaction temperature: 500 ºC; liquid-solid ratio: 3)

Fig. 2 shows the change of the yield of molybdenum with roasting temperature and roasting time at 3 liquid-solid ratio and 40 % NaOH concentration. The increase in roasting temperature and roasting time both increased the yield of molybdenum. Maximum 3.86 % of the yield of molybdenum was obtained at 500 ºC reaction temperature and 3.5 h. It could be seen the yield of molybdenum was almost constant with the increase in roasting temperature.

Fig. 3 shows the change of the yield of molybdenum with NaOH concentration and roasting temperature at 3 liquid-solid ratio and 3.5 h roasting time. The yield of molybdenum increased first and then decreased with the decrease in NaOH concentration and roasting temperature. A region of more than 3.83 % the yield of molybdenum was achieved below 600 ºC roasting temperature and 45 % NaOH concentration.

Fig. 4 shows the change of the yield of molybdenum with liquid-solid ratio and NaOH concentration at 500 ºC roasting temperature and 3.5 h roasting time. The increase in liquid-solid ratio and NaOH concentration both increased the yield of molybdenum. Maximum 3.28 % of the yield of molybdenum was obtained at 3 liquid-solid ratio and 40 % NaOH concentration. It could be seen the yield of molybdenum was almost constant with the increase in liquid-solid ratio.

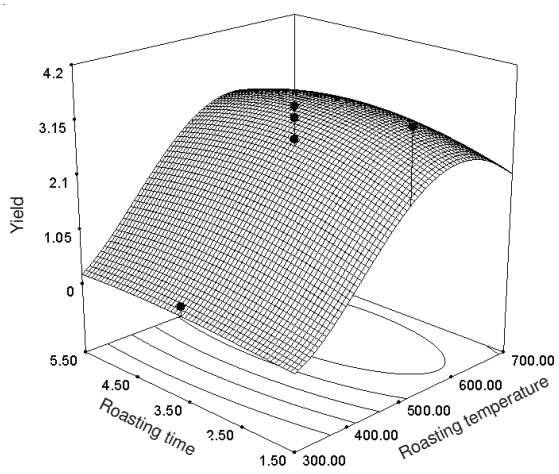

Fig. 2. Effect of roasting time and roasting temperature on the yield of molybdenum (NaOH concentration: 40 %; liquid-solid ratio: 3)

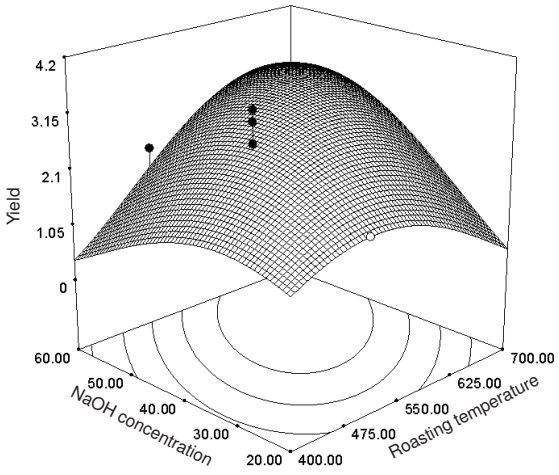

Fig. 3. Effect of NaOH concentration and roasting temperature on the yield of molybdenum (roasting time : 3.5 h; liquid-solid ratio: 3)

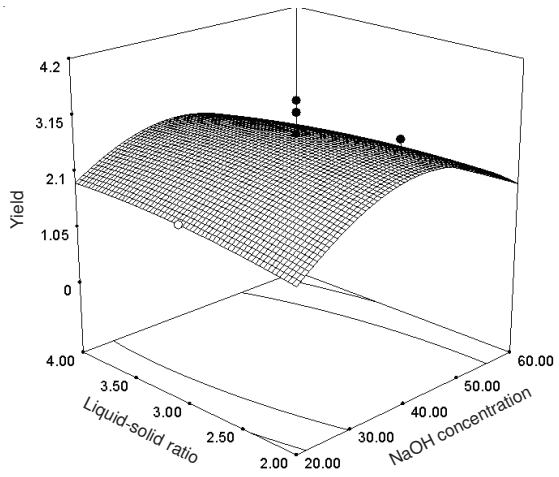

Fig. 4. Effect of liquid-solid ratio and NaOH concentration on the yield of molybdenum (roasting time : 3.5 h; reaction temperature: 500 ºC)

Optimization: The model is useful in indicating the direction in which to change variables in order to maximize the yield of molybdenum (Y). By using Design Expert 7.0 software, the point at roasting temperature 670 ºC, roasting time 1.70 h, NaOH concentration 60 % and 2 liquid-solid ratio could be recommended as a practical optimum. The estimated

values for Y were 3.82 %. A verification experiment at the optimum condition, consisting of 3 runs, was performed and the practical Y was 3.82 %.

Conclusion

Optimum extraction of molybdenum from nickel molybdenum ore with 60 % NaOH extraction and 1.7 h roasting time at 2 liquid-solid ratio and 670 ºC roasting temperature. Such conditions resulted in extraction of 3.82 % molybdenum from nickel molybdenum ore.

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