

Leaching and Kinetic Modelling of Molybdenite Concentrate Using Hydrogen Peroxide in Sulfuric Acid Solution

Moazemi Goodarzi, Mehdi; Rezai, Bahram*⁺; Seifikhani, Anahita

Department of Mining and Metallurgical Engineering, Amirkabir University of Technology,
P.O. Box 15875-4413 Tehran, I.R. IRAN

ABSTRACT: Leaching of molybdenite concentrate with hydrogen peroxide in sulfuric acid solution was investigated to determine the effects of reaction time, reaction temperature, H_2O_2 concentration, H_2SO_4 concentration, pulp density and rotation speed on molybdenum extraction and molybdenite dissolution kinetics, using the Taguchi method. From analysis of variance (ANOVA) for molybdenum extraction, the most significant factors were H_2O_2 concentration, pulp density and reaction temperature. The optimal factor levels to maximize extraction were determined. As the leaching process does not result in an ash layer, only chemically controlled kinetic model was applied. ANOVA for the reaction rate constant showed that H_2O_2 concentration made the greatest contribution to the model, and reaction time and temperature were also statistically significant factors. The reaction rate constant increased with increasing temperature and H_2O_2 concentration. The order of reaction with respect to H_2O_2 and activation energy for the dissolution were determined to be 1.21 and 46.5 kJ/mol, respectively, and a semi-empirical rate equation was derived.

KEY WORDS: Molybdenite, Leaching, Kinetics, Hydrogen peroxide, Taguchi.

INTRODUCTION

Molybdenite (a mineral form of molybdenum (IV) sulfide, MoS_2) is a byproduct of froth flotation of porphyry copper and is the main source of molybdenum (widely used in steel alloys) and its compounds [1].

The standard process for the production of molybdenum involves roasting of molybdenite concentrate in air and subsequent reduction of the oxidized product (molybdenum(VI) oxide, MoO_3) with hydrogen. Although modifications have been employed such as oxidative roasting in the presence of sodium chloride [2], roasting with lime [3-5] and roasting with soda ash [6].

The roasting process consumes a considerable amount of energy and produces sulfur dioxide, with consequent concerns regarding atmospheric pollution. Also, partial vaporization of the MoO_3 leads to loss of molybdenum. Another problem with the current method is that impurities in the concentrate can combine with molybdenum to form stable molybdates, causing problems in the subsequent processing.

In the light of these shortcomings of the conventional process, hydrometallurgical methods appear to offer an attractive alternative. Leaching of molybdenite has been investigated, with nitric acid as both solvent and oxidant [7-9],

* To whom correspondence should be addressed.

+ E-mail: bahram.rezai1@gmail.com

1021-9986/14/2/73

13/\$/3.30

or with sodium dichromate [10], sodium chlorate [11], and hypochlorite [12] as oxidant. The main problem with the use of these oxidants is the production of salts or gases as byproducts that need to be removed to avoid polluting the environment.

Bioleaching of molybdenite has also been investigated [13, 14], but the process is too slow owing to the resistance of molybdenite to bio-oxidation and the toxicity of molybdenum to bacteria.

Hydrogen peroxide has been successfully used as an oxidizing agent for the leaching of sulfide minerals such as sphalerite and chalcopyrite [15] and it is therefore natural to consider its use for the treatment of molybdenite. The reaction of molybdenite with acidic H_2O_2 can be expressed as follows:



The dissolved molybdenum can be isolated by solvent extraction. A number of different extractants have been investigated for the extraction of molybdenum from aqueous solution, including High Molecular Weight Amines (HMWA) [16], Tri-*n*-Butyl Phosphate (TBP) [17], trioctylphosphine oxide (TOPO) [18], sulphoxides [19], di(2-ethylhexyl)phosphoric acid (D2EHPA) [20] and 2-ethylhexyl hydrogen (2-ethylhexyl)phosphonate (PC-88A) [21].

The parameters affecting the kinetics of molybdenite leaching have not been investigated in previous studies, since this would require a large number of experiments. However, a quantitative estimate of the effect of various parameters can be determined by optimization using the statistical Design Of Experiments (DOE) technique. For solid–fluid reactions, shrinking-particle or shrinking-core kinetics have frequently been assumed, with the dissolution rate of a mineral being controlled by the rate of chemical reaction or by the rate of mass transfer through the product layer.

In the work described in this paper, we have investigated the effects of operating parameters, including reaction time and temperature, H_2O_2 and H_2SO_4 concentration, pulp density, and rotation speed, on the leaching and kinetics of molybdenum extraction. In classical DOE, originally developed by Fisher, responses are measured for all combinations of the experimental factor levels. This method is complicated and not easy to use. In particular, when there are a large number of process parameters,

Table 1: XRF analysis of the molybdenite concentrate.

Component	Wt.%
Mo	57.5
MgO	0.39
Al ₂ O ₃	0.23
CaO	0.5
Fe	1.99
Cu	0.5
S	37.9

it is necessary to conduct a large number of experiments. As a way round this problem, the Taguchi method uses a special design of orthogonal arrays to study the entire parameter space with a smaller number of experiments, and this approach was therefore adopted in the present work to determine the most significant factors for the leaching process.

EXPERIMENTAL SECTION

A sample of 40 kg of molybdenite concentrate from a chalcopyrite flotation circuit from the Sarcheshmeh mine (Kerman, in the south east of Iran) was obtained. The sample was divided into 1 kg portions. X Ray Fluorescence (XRF) and X Ray Diffraction (XRD) studies were performed for characterization. The XRF results are presented in Table 1 and the X-ray diffractogram of the concentrate is shown in Fig. 1. The major phase is molybdenite.

Fig. 2 shows a schematic view of the leaching apparatus. The 1-liter glass balloon reactor (1) was immersed in a water bath (2) equipped with an IKA mechanical stirrer (EUROSTAR Digital) with a digital controller (3). The water bath was heated using an IKA RCT-Basic heater-stirrer (4) with a rotating magnet (5). The reactor was fitted with standard ports for feed entrance and periodic sampling (6), temperature measurement (7), and a condenser (8) (the condenser was necessary to prevent evaporation of liquid from the reaction mixture with a consequent increase in pulp density above the desired value). The bath temperature was monitored by an IKA PT-1000 sensor (9).

After the desired temperature of the reactor contents was reached, a predetermined amount of molybdenite concentrate was added to 500 ml of leaching solution,

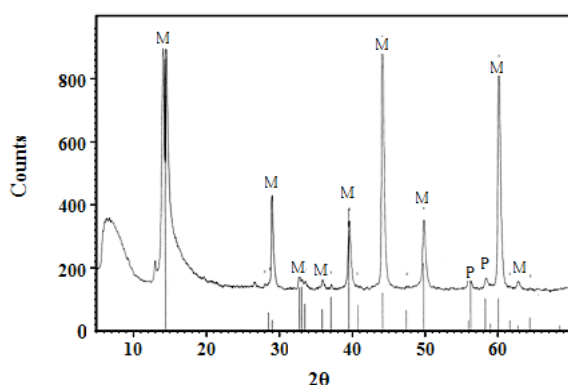


Fig. 1: X-ray diffractogram of the molybdenite concentrate.

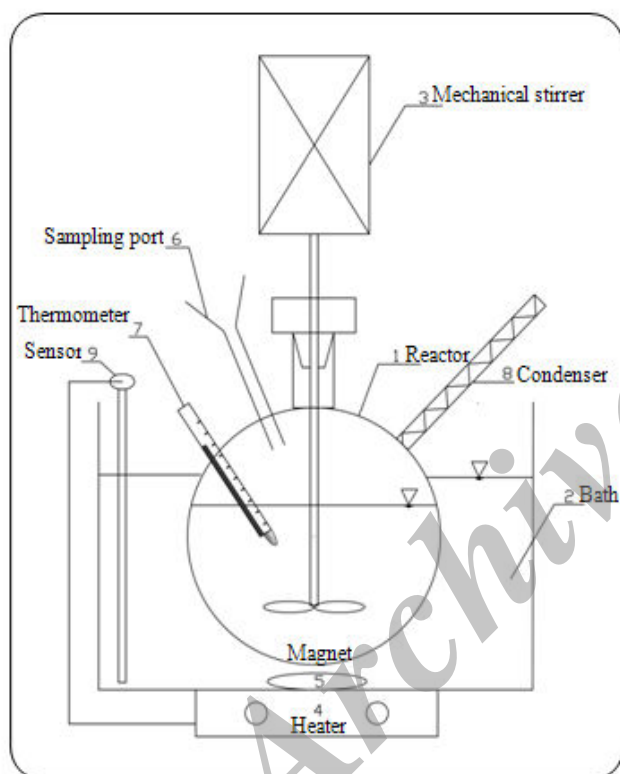


Fig. 2: Schematic view of the leaching apparatus.

based on a predetermined pulp density. The leaching was carried out using analytical grade H_2O_2 and H_2SO_4 at the required concentrations in distilled water. Samples were taken over the reaction period at pre-determined intervals, and were filtered using a syringe filter and analyzed for molybdenum using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES). To calculate the fraction of molybdenum leached, the following equation was used:

$$X_i = \frac{\left(V_0 - \sum_{i=1}^{i-1} v_i \right) C_i + \sum_{i=1}^{i-1} v_i C_i}{M \left(\frac{C_M}{100} \right)} \quad (2)$$

Where X_i is the molybdenum extraction corresponding to sample i , V_0 the initial volume of the leaching solution in the reactor (mL), v_i the volume of sample i withdrawn from the reactor (mL), C_i the molybdenum concentration in sample i (mg/L), M the initial mass of the molybdenite concentrate added to the reactor (g) and C_{M0} the percentage of molybdenum in the molybdenite concentrate.

For the Taguchi design and results analysis, Design-Expert 7 (DX7, StatEase Inc.) and Minitab-14 (Minitab Inc.) statistical software were used. The appropriate orthogonal array for the experiments using the Taguchi fractional factorial design was selected by the DX7 software. The Taguchi technique employs orthogonal arrays to reduce the number of experiments, while still giving statistically meaningful results. The selection of a suitable orthogonal array depends on the number of control factors and their levels. Six selected control factors in five levels were applied in this study, as shown in Table 2. The purpose of this investigation was estimation of effects of experimental factors on molybdenum extraction and the dissolution kinetics of molybdenite. In the classical experimental design using full factorial experimentation, the number of experiments required to study the selected process space would be $5^6=15625$. By selecting an L25 (5^6) orthogonal array, the number of experiments required can be drastically reduced to 25. The parameter combinations for each of the 25 leaching experiments are presented in Table 3.

RESULTS AND DISCUSSION

Statistical analysis of molybdenum extraction

The molybdenum extraction for the 25 leaching experiments is presented in Table 4. Analysis of variance (ANOVA) was carried out for these results to determine whether the effects of process factors are statistically significant. The contribution of each factor can also be obtained from ANOVA. The results of ANOVA for molybdenum extraction are shown in Table 5, according to which the H_2O_2 concentration is the most important factor, with a 56.24 % contribution to the statistical model. The pulp density, with a 15.63 % contribution,

Table 2: Control factors and their levels in leaching experiments.

Control factor	Unit	Level				
		1	2	3	4	5
Reaction time(t)	min	30	60	120	180	240
Reaction temperature(T)	°C	20	30	40	45	50
H ₂ O ₂ concentration(H)	%	3	6	9	12	15
H ₂ SO ₄ concentration(A)	%	2	4	6	8	12
Pulp density(D)	g/l	5	10	15	20	25
Rotation speed(R)	rpm	400	450	500	550	600

Table 3: L25 Taguchi experimental design.

Run No.	t	T	H	A	D	R
1	1	1	1	1	1	1
2	1	2	2	2	2	2
3	1	3	3	3	3	3
4	1	4	4	4	4	4
5	1	5	5	5	5	5
6	2	1	2	3	4	5
7	2	2	3	4	5	1
8	2	3	4	5	1	2
9	2	4	5	1	2	3
10	2	5	1	2	3	4
11	3	1	3	5	2	4
12	3	2	4	1	3	5
13	3	3	5	2	4	1
14	3	4	1	3	5	2
15	3	5	2	4	1	3
16	4	1	4	2	5	3
17	4	2	5	3	1	4
18	4	3	1	4	2	5
19	4	4	2	5	3	1
20	4	5	3	1	4	2
21	5	1	5	4	3	2
22	5	2	1	5	4	3
23	5	3	2	1	5	4
24	5	4	3	2	1	5
25	5	5	4	3	2	1

Table 4: Molybdenum extraction for the 25 leaching experiments.

Run No.	Molybdenum extraction (%)
1	5.20
2	6.16
3	13.68
4	20.11
5	25.73
6	4.81
7	11.83
8	25.64
9	31.69
10	6.32
11	11.78
12	18.75
13	30.19
14	5.99
15	27.02
16	16.81
17	30.47
18	8.78
19	18.35
20	13.60
21	23.95
22	6.75
23	9.78
24	37.85
25	34.80

Table 5: Results of ANOVA for molybdenum extraction.

Source	Sum of squares	DOF	Variance	F-Value	P-Value	Contribution (%)
Model	2561	24	106.7	-	-	100.00
Reaction time	202	4	50.5	-	-	7.89
Reaction temperature	378	4	94.6	-	-	14.77
H ₂ O ₂ concentration	1441	4	360.1	-	-	56.24
H ₂ SO ₄ concentration	35	4	8.9	-	-	1.38
Pulp density	400	4	100.1	-	-	15.63
Rotation speed	105	4	26.2	-	-	4.09
Error	0	0	106.7	-	-	
Total	2561	24	50.5	-	-	

Table 6: Results of pooled ANOVA for molybdenum extraction.

Source	Sum of squares	DOF	Variance	F-Value	P-Value	Pure sum	Contribution (%)
Model	2526	20	126.3	14.258	0.0097	2182	85.20
Reaction time	202	4	50.5	5.701	0.0602	167	6.50
Reaction temperature	378	4	94.6	10.676	0.0208	343	13.38
H ₂ O ₂ Concentration	1441	4	360.1	40.657	0.0017	1405	54.86
H ₂ SO ₄ concentration	(35)	(4)	-	pooled	pooled	-	-
Pulp density	400	4	100.1	11.301	0.0188	365	14.25
Rotation speed	105	4	26.2	2.953	0.1596	69	2.70
Error	35	4	8.9				14.80

and the reaction temperature, with a 14.77 % contribution, occupy second and third places.

F-value is a parameter for comparing factor variance with error variance and can be calculated by dividing the factor (or model) variance by the error variance. If the variances are close to each other, the ratio will be close to 1. Consequently, factors with *F*-value close to 1 are not significant.

According to Table 5, the Degree Of Freedom (DOF) for error is zero, and so the error variance and thus the *F*-value could not be calculated. To eliminate the zero DOF from the error term, pooled ANOVA was used. The values of the ANOVA analysis for molybdenum extraction after pooling of the H₂SO₄ concentration from the model are given in Table 6.

The *F*-value of 14.26 in this case implies that the model is significant and there is only a 0.97% chance that the model *F*-value could be due to noise. *P*-values less than 0.05 indicate that the effects of model factors are significant within a 95% confidence interval. Therefore, in the case of molybdenum extraction, only three factors (namely, H₂O₂ concentration, pulp density and reaction temperature) are significant. The *P*-values reveal that the rotation speed and sulfuric acid concentration are not statistically significant factors. Therefore, a higher molybdenum extraction should be achievable using high H₂O₂ concentration, low pulp density and high reaction temperature. The reaction time might also be an effective factor in molybdenum extraction, but, with a *P*-value of 0.0602, its statistical significance is marginal.

Table 6 indicates that 85.20% of the total variation in the molybdenum extraction is due to the experimental variables. A plot of predicted values versus experimental values for molybdenum extraction is presented in Fig. 3.

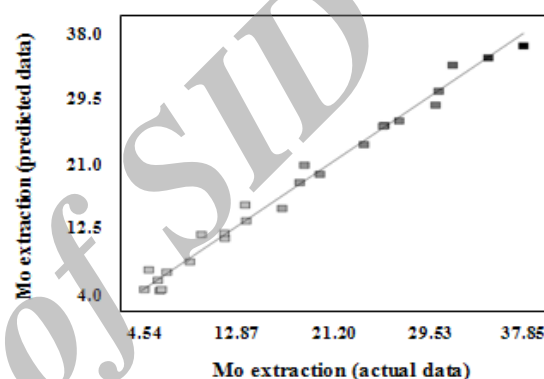


Fig. 3: Predicted versus experimental data for molybdenum extraction.

The correlation coefficient R^2 between predicted and observed data for molybdenum extraction is 0.99. The results reveal that the predicted values are close to the experimental values. Consequently, the model provides a valid relation between the leaching factors and the extraction.

The effect of the factors on the mean response is shown in Fig. 4, from which it can be seen that the molybdenum extraction increases with increasing leaching time, leaching temperature and H₂O₂ concentration. By increasing leaching time and temperature more molybdenum is dissolved and extraction increased. In addition, molybdenum extraction increases from 6.60 % to 28.40 % with increasing H₂O₂ concentration. The main reason for this is the increasing concentration of reactants.

Fig 4 indicates that with increasing pulp density from 5 to 25 g/L molybdenum extraction decreases from 25.23 % to 14.02 %. By increasing pulp density the amount of molybdenite in reactor increases as a result available oxidant per mole of molybdenite decreases and finally

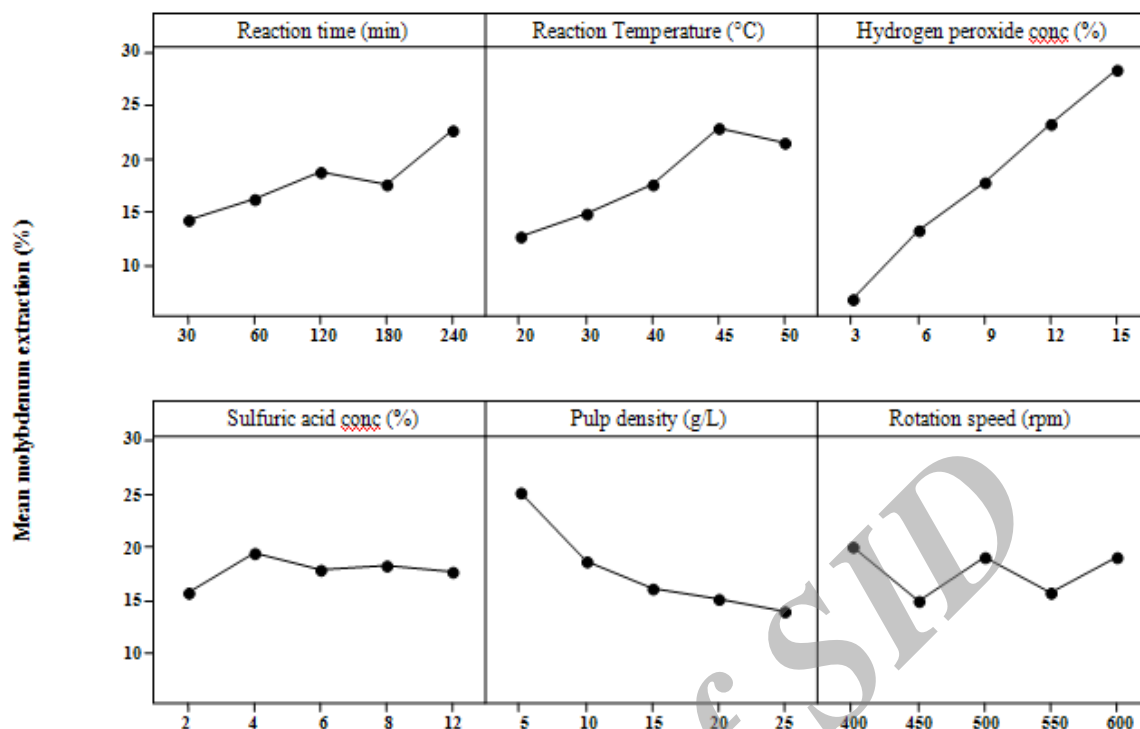


Fig. 4: Effect of leaching factors on the mean molybdenum extraction.

leaching process has less progress and total extraction decreased. The optimal level of each factor is the level with the highest mean. For maximizing molybdenum extraction, a reaction time of 240 minutes (level 5), reaction temperature of 45°C (level 4), H₂O₂ concentration of 15% (level 5), H₂SO₄ concentration of 4% (level 2), pulp density of 5 g/l (level 1) and rotation speed of 400 rpm (level 1) were selected.

A leaching experiment to confirm these results, carried out at the optimal levels, yielded a molybdenum extraction of over 79.8%. This considerable increase of molybdenum extraction in comparison with Taguchi experiments could be due to positive interaction between parameters e.g. reaction temperature and H₂O₂ concentration. This difference might be as result of Taguchi method which do not consider the effects of interactions between parameters within statistical model. It is also concluded that the statistical method applied is suitable for rejection of non-effective parameters on the other hand, it can be used as screening step of process.

Fig. 5 shows the effect of pulp density and reaction temperature on molybdenum extraction. It can be seen that the highest extraction can be achieved in the

temperature range 45 - 50 °C (between levels 4 and 5). It can also be seen that extraction decreases with increasing pulp density.

Kinetic modelling

Reaction model

The shrinking-core model assumes that the leaching process is controlled by diffusion of reactant through the solution boundary, through an ash layer, or by the surface chemical reaction rate.

Practical observations have shown that the leaching process does not result in an ash layer and that the reacting particle shrinks and finally disappears, as illustrated schematically in Fig. 6.

Under these conditions, the leaching rate is chemically controlled and diffusion models are not applicable. In this case, the following expression can be used to describe the process [22]:

$$1 - (1 - X)^3 = \frac{k_C M_B C_A}{\rho_B a r_0} = kt \quad (3)$$

where X is the fraction reacted, k_C the kinetic constant, M_B the molecular weight of the solid, C_A the

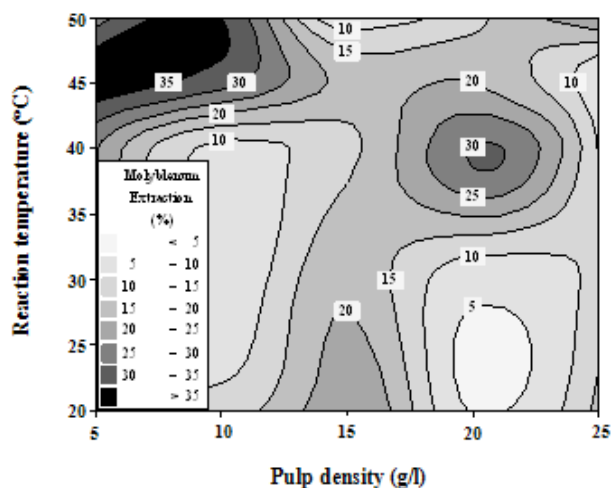


Fig. 5: Contour plot of molybdenum extraction versus pulp density and reaction temperature.

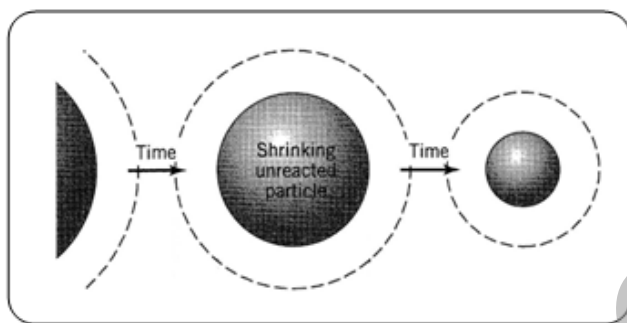


Fig. 6: Schematic representation of a shrinking core particle in a reaction without the formation of an ash layer.

concentration of dissolved lixiviant, A the bulk of solution, ρ_B the density of molybdenite, a the stoichiometric coefficient of the reagent in the leaching reaction, r_0 the initial radius of the solid particle, t the reaction time and k the rate constant.

The values of the apparent rate constant k obtained from the 25 leaching experiments are given in Table 7, together with the correlation coefficients R^2 for a fit of the experimental data to equation (3). It can be seen that there is a good correlation between the chemically controlled model and the experimental results (average $R^2 = 0.87$).

Statistical effect of control factors on reaction rate

For statistical analysis of the kinetic results, it is necessary to apply a suitable mathematical transform so that they satisfy the conditions for validity of the ANOVA method. In this case, a logarithmic function was considered to be the most appropriate transform for

the apparent rate constant, and the corresponding ANOVA results are given in Tables 8 and 9.

The model F-value 19.67 shows that the model is significant and that there is only a 0.52 % chance that this F-value could have occurred because of noise. It can be seen that H_2O_2 concentration (49.53% contribution) is the most significant parameter affecting the reaction rate. According to the P-values, H_2O_2 concentration, reaction time and reaction temperature are the factors with statistically significant effects on reaction rate. According to Table 9 It can also be seen that 93.96% of the total variation in the reaction rate constant is due to the experimental variables.

The predicted values for the reaction rate constant are plotted versus experimental data in Fig. 7.

The correlation coefficient $R^2 = 0.99$ between the predicted and observed values shows that the model provides a valid relationship between the molybdenite leaching factors and the reaction rate constant.

The effect of the leaching factors on the mean reaction rate constant is shown in Fig. 8, the rate of molybdenum extraction increases significantly as function of temperature in range of 20 -50 °C. Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy and as a result, reaction rate increases. Fig 8 shows an increase in the concentration of H_2O_2 will result in the corresponding increase in the reaction rate, while a decrease in the concentrations will have a reverse effect. This could be due to collisions of reactant. The frequency with which the molecules or ions collide depends upon H_2O_2 concentration. The more crowded the molecules are, the more likely they are to collide and react. Also according to Fig. 8, reaction kinetics are fast in the first hour of reaction time, but slowing in the remaining period. It can be concluded here that as soon as the solid particles are contacted in the leach solution, reaction products are immediately released.

The results obtained from mean reaction rate constant indicate that the rate of molybdenite dissolution is independent of rotation speed which shows that the reaction is chemically controlled.

Determination of order of reaction

The order of reaction with respect to H_2O_2 concentration can be determined from the logarithmic

Table 7: Dissolution rate constant k for the 25 leaching experiments and correlation coefficient R^2 for a fit to Eq. (3).

Run No.	$k \times 10^3$	R^2
1	0.4626	0.9809
2	0.4809	0.8612
3	1.5669	0.9189
4	1.8901	0.8935
5	3.6444	0.9991
6	0.2759	0.9618
7	0.7251	0.9509
8	1.2899	0.917
9	3.7276	0.9985
10	0.3757	0.8684
11	0.3682	0.932
12	0.5189	0.885
13	0.8260	0.7338
14	0.1396	0.6557
15	0.6721	0.8669
16	0.3149	0.8688
17	0.6513	0.9643
18	0.1440	0.8119
19	0.3227	0.8163
20	0.7433	0.5552
21	0.4506	0.9761
22	0.0807	0.8799
23	0.1097	0.6561
24	0.5277	0.9131
25	0.5582	0.7914

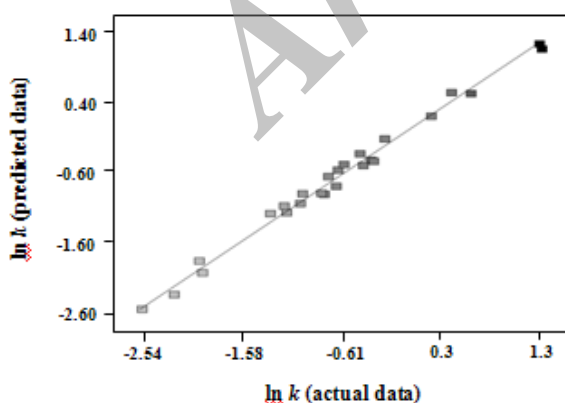


Fig. 7: Predicted values versus experimental data for the logarithm of the reaction rate constant.

plot of rate constant versus H_2O_2 concentration shown in Fig. 9. It can be seen from the slope of the line that the order of reaction is 1.21. The orders of reaction with respect to this and other parameters are presented in Table 10, together with the corresponding correlation coefficients.

It can be seen from Table 10 that the correlation coefficient is greatest for the order of reaction with respect to H_2O_2 . This order of reaction, 1.21, can then be employed in the following equation:

$$k = k_0 (C_{H_2O_2})^a e^{\frac{E_a}{RT}} \quad (4)$$

where k_0 is the frequency factor, E_a is the activation energy and R is the universal gas constant. The activation

Table 8: Results of ANOVA for reaction rate constant.

Source	Sum of squares	DOF	Variance	F-Value	P-Value	Contribution (%)
Model	22.366	24	0.932			100.00
Reaction time	7.608	4	1.902			34.02
Reaction temperature	2.517	4	0.629			11.26
H ₂ O ₂ concentration	11.078	4	2.769			49.53
H ₂ SO ₄ concentration	0.225	4	0.056			1.01
Pulp density	0.624	4	0.156			2.79
Rotation speed	0.313	4	0.078			1.40
Error	0.000	0				0.00
Total	22.366	24				100.00

Table 9: Results of pooled ANOVA for reaction rate constant.

Source	Sum of squares	DOF	Variance	F-Value	P-Value	Pure sum	Contribution (%)
Model	22.141	20	1.107	19.67	0.0052	21.015	93.96
Reaction time	7.608	4	1.902	33.79	0.0024	7.383	33.01
Reaction temperature	2.517	4	0.629	11.18	0.0191	2.292	10.25
H ₂ O ₂ concentration	11.078	4	2.769	49.21	0.0012	10.853	48.52
H ₂ SO ₄ concentration							
Pulp density	0.624	4	0.156	2.77	0.1736	0.399	1.78
Rotation speed	0.313	4	0.078	1.39	0.3782	0.088	0.39
Error	0.225	4	0.056				6.04
Total	22.366	24					

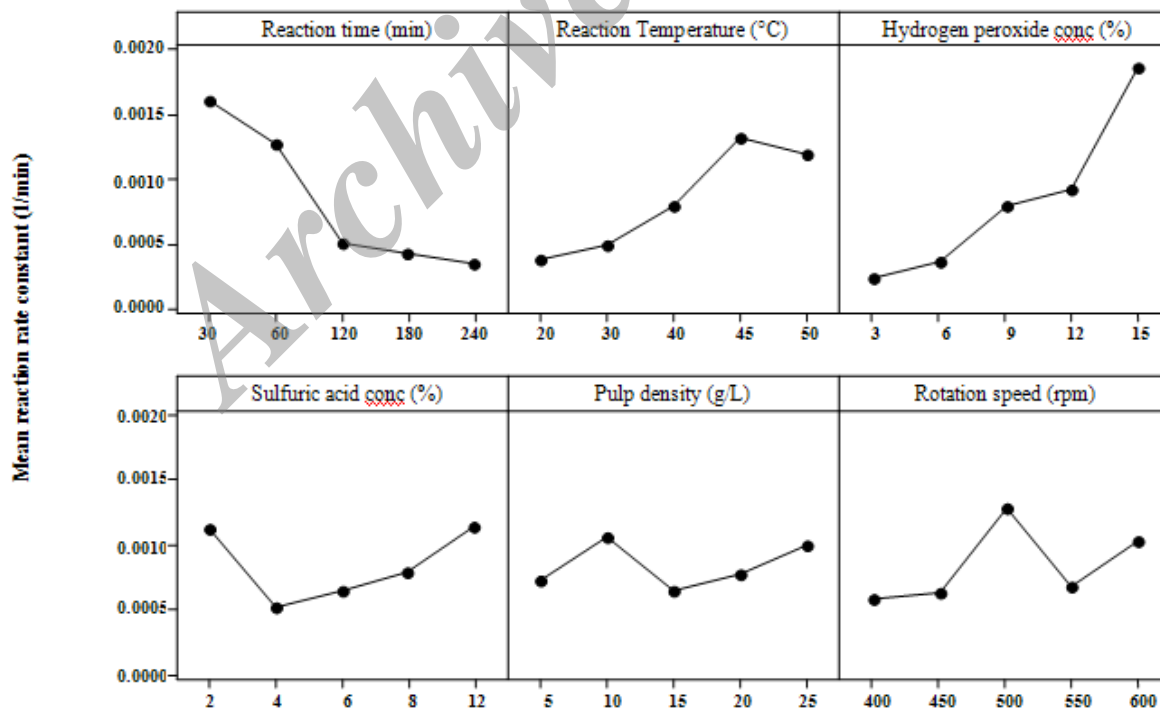
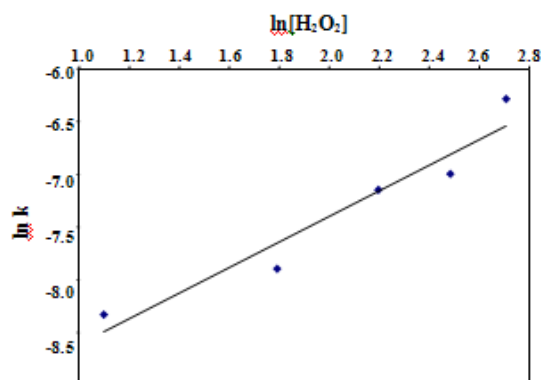


Fig .8: Effect of leaching factors on the mean reaction rate constant.

Table 10: Order of reaction and correlation coefficient R^2 for control factors.

Factor	Order of reaction	R^2
H ₂ O ₂ concentration	1.21	0.9275
Rotation speed	1.24	0.3366
Pulp density	0.07	0.0447
H ₂ SO ₄ concentration	0.03	0.0037

Fig. 9: Determination of order of reaction with respect to H₂O₂ concentration.

energy and frequency factor can be determined from the Arrhenius equation.

Effect of temperature

The effect of temperature on molybdenum extraction from the molybdenite concentrate in acidic H₂O₂ solution is shown in Fig. 10. The results of an application of equation (3) to the values from Fig. 10 are shown in Fig. 11, where $1 - (1 - X)^{1/3}$ is plotted versus time for different temperatures. The rate constant k for each temperature is found as the slope of the corresponding straight-line plot through the data points. The correlation coefficient R^2 is also presented in Fig. 11 for each temperature.

The Arrhenius plot of $\ln k$ versus T^{-1} is shown in Fig. 12. From this plot, an activation energy of 46.5 kJ/mol can be estimated for the leaching,

This estimated activation energy suggests that the leaching of molybdenum from molybdenite is controlled by chemical reaction [23]. From equations (3) and (4), the following kinetic expression can then be used to describe the dissolution process of the molybdenite concentrate in acidic H₂O₂ solution:

$$1 - (1 - X)^{\frac{1}{3}} = 6.24 \times 10^4 (C_{\text{H}_2\text{O}_2})^{1.21} e^{\frac{46500}{RT}} t \quad (5)$$

CONCLUSIONS

Leaching of molybdenite concentrate was carried out under a wide range of conditions. The effect of process factors including: reaction time, reaction temperature, H₂O₂ concentration, H₂SO₄ concentration, pulp density and rotation speed (each parameter at five levels) were studied. Leaching experiments were designed and analyzed with the Taguchi method using an L25 (5⁶) orthogonal array. The purpose of this investigation was to estimate the effects of experimental factors on molybdenum extraction and dissolution kinetics of the molybdenite. According to experimental results and their analysis the following conclusions can be drawn:

- The most significant leaching factors affecting molybdenum extraction are H₂O₂ concentration (56.24%), pulp density (15.63%) and reaction temperature (14.77%). Reaction time might also be an effective parameter but with marginal significance. Rotation speed and H₂SO₄ concentration are not statistically significant factors.
- Based on the effect of leaching factors on the mean responses, in order to maximize molybdenum extraction, a reaction time of 240 minutes, reaction temperature of 45 °C, H₂O₂ concentration of 15%, H₂SO₄ concentration of 4%, pulp density of 5 g/L and rotation speed of 400 rpm should be selected.
- An experiment to confirm that these values gave maximum molybdenum extraction resulted in 79.8% extraction.
- As the process does not result in an ash layer, the leaching kinetics are chemically controlled and diffusion models are not applicable.
- According to the percentage contribution of leaching factors, H₂O₂ concentration (with a 49.53% contribution) is the most significant effective parameter for the reaction rate.

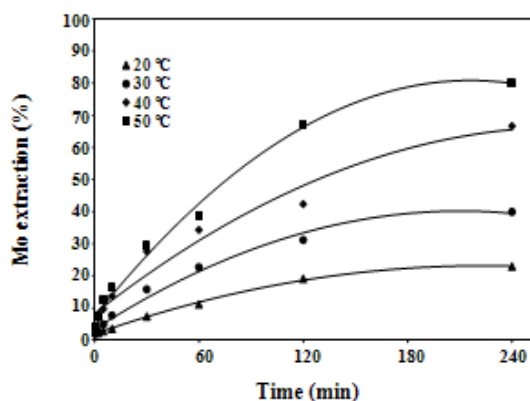


Fig. 10: Effect of temperature on molybdenum extraction, (H_2SO_4 concentration 10%, H_2O_2 concentration 15%, pulp density 5 g/l and rotation speed 600 rpm).

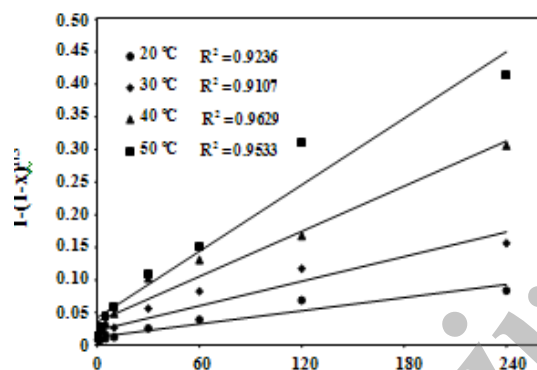


Fig. 11: Plot of $1 - (1 - X)^{1/3}$ versus time for different reaction temperatures.

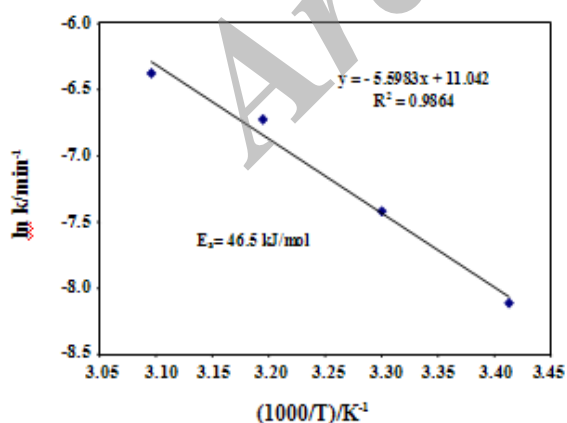


Fig. 12: Arrhenius plot for molybdenite leaching with hydrogen peroxide.

• According to the P -values H_2O_2 concentration, reaction time and reaction temperature are statistically significant factors affecting the reaction rate.

• The reaction rate constant increases with increasing leaching temperature and H_2O_2 concentration.

• The reaction rate constant is a function of time, decreasing with increasing leaching time.

• The order of reaction with respect to H_2O_2 concentration was determined to be 1.21.

• An activation energy of 46.5 kJ/mol was calculated for molybdenite dissolution in acidic H_2O_2 .

Received : Mar. 11, 2013 ; Accepted : Mar. 10, 2014

REFERENCES

- [1] Kholmogorov A.G., Kononova O.N., *Processing Mineral Raw Material in Siberia: Ores of Molybdenum, Tungsten, Lead and Gold, Hydrometallurgy*, **76**: 37- 54 (2004).
- [2] Nair K.U., Sathiyamoorthy D., Bose D.K., Gupta C.K., *Processing of Low-Grade Indian Molybdenite Concentrate by Chlorination in a Fluidised-Bed Reactor, International Journal of Mineral Processing*, **23**: 171-180 (1988).
- [3] Singh S., Chetty M.K., Juneja J.M., Sehra J.C., Gupta C.K., *Studies on the Processing of a Low Grade Molybdenite Concentrate by Lime Roasting, Minerals Engineering*, **1**: 337-342 (1988).
- [4] Prasad P.M., Mankhand T.R., Rao P.S., *Lime-Scavenged Reduction of Molybdenite, Minerals Engineering*, **6**: 857-871 (1993).
- [5] Rao P.S., Prasad P.M., *Direct Synthesis of Molybdenite-Carbon Monoxide Reaction in the Presence of Lime, Materials Transactions JIM*, **34**: 1229-1233 (1993).
- [6] Shah V.D., Rakhasia R.H, Sehra J.C., *Recovery of Molybdenum as Molybdic Oxide from Rakha Molybdenite, India, by Soda-Ash Roasting, Mineral Processing and Extractive Metallurgy*, **105**: 199-203 (1996).
- [7] Vizsolyi A., Peters E., *Nitric Acid Leaching of Molybdenite Concentrates, Hydrometallurgy*, **6**: 103-119 (1980).
- [8] Parsons G.J., Brimacombe J.K., Peters E., *Computer Simulation of a Molybdenite Leaching Process Using Dilute Nitric Acid, Hydrometallurgy*, **17**: 133-154 (1987).

- [9] Khoshnevisan A., Yoozbashizadeh H., Mozammel M., Sadrnezhad S.K., [Kinetics of Pressure Oxidative Leaching of Molybdenite Concentrate by Nitric Acid](#), *Hydrometallurgy*, **111**: 52-57 (2012).
- [10] Antonijević M.M., Pacović N.V., [Investigation of Molybdenite Oxidation by Sodium Dichromate](#), *Minerals Engineering*, **5**: 223-233 (1992).
- [11] Cao Z.F., Zhong H., Qiu Z.H., Liu G.Y., Zhang W.X., [A Novel Technology for Molybdenum Extraction from Molybdenite Concentrate](#), *Hydrometallurgy*, **99**: 2-6 (2009).
- [12] Bhappu R.R., Reynolds E.H., Stahmen W.S., [“Studies on Hypochlorite Leaching of Molybdenite”](#), State Bureau of Mines & Mineral Resources, New Mexico Institute of Mining & Technology, (1963).
- [13] Pistaccio L., Curutchet G., Donati E., Tedesco P., [Analysis of Molybdenite Bioleaching by Thiobacillus-Ferroxidans in the Absence of Iron\(II\)](#), *Biotechnology Letters*, **16**: 189-194 (1994).
- [14] Olson G.J., Clark T. R., [Bioleaching of Molybdenite](#), *Hydrometallurgy*, **93**: 10-15 (2008).
- [15] Pecina T., Franco T., Castillo P., Orrantia E., [Leaching of Zinc Concentrate in H₂SO₄ Solutions Containing H₂O₂ and Complexing Agents](#), *Minerals Engineering*, **21**: 23-30 (2008).
- [16] Khan K., Ali T., [The Impact of Solvent Extraction on the Recovery of Molybdenum from Molybdenite Ore](#), *Journal of the Chemical Society of Pakistan*, **12**: 316-321(1990).
- [17] Cruywagen J.J., McKay H.A.C., [The Extraction of Molybdenum \(VI\) by Tri-n-butyl Phosphate](#), *Journal of Inorganic and Nuclear Chemistry*, **32**: 255-265 (1970).
- [18] Sato T., Watanabe H., Suzuki H., [Liquid-Liquid Extraction of Molybdenum \(VI\) from Aqueous Acid Solutions by TBP and TOPO](#), *Hydrometallurgy*, **23**: 297-308 (1990).
- [19] Dai G.S., Xuan B.Y., Su Y.F., [Separation of Tungsten and Molybdenum in Dilute Hydrochloric Acid Solution by Extraction with Sulfoxides](#), *Hydrometallurgy*, **13**: 137-153 (1984).
- [20] Des N.R., Naudi B., Bhattacharya S.N., [Solvent Extraction Separation of Molybdenum and Tungsten Using Di\(Zethyl hexyl\) Phosphonic Acid \(HDEHP\) as an Extractant](#), “Proceeding of International Solvent Extraction Conference”, (1983).
- [21] Valenzuela F. R., Andrade J.P., Sapag J., Tapia C., Basualto C., [The Solvent Extraction Separation of Molybdenum and Copper from Acid Leach Residual Solution of Chilean Molybdenite Concentrate](#), *Minerals Engineering*, **8**: 893-904 (1995).
- [22] Levenspiel O., “Chemical Reaction Engineering”, 2nd edition, John Wiley, New York (1999).
- [23] Havlik T., “Hydrometallurgy”, 1st edition, Woodhead Publishing, Cambridge (2009).