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Development of a Kinetic Model for Predicting the Dissolution Behavior of Activated Molybdenite by Mechanical Activation

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1. Introduction

Shrinking core model (SCM) is used frequently in investigation of the rate of the dissolution reactions of minerals. In kinetic studies the SCM fits well for spherical particles, but it has some limitations. For instance, the concentration of acid during the dissolution process is considered to be fixed in this model, while it is in contrary with the practical results. On the other hand, physical properties and mineralogical factors may result in some complications and affecting the reaction rate. Such limitations show the importance of a deeper study on the dissolution reactions mechanism of molybdenite particles with unusual shape and geometry. As a result, this work tries to investigate a suitable model to forecast the dissolution behavior of milled molybdenite. Accordingly, achieving to variable activation energy model from shrinking core model is explained step by step.

2. Materials and Method

Molybdenite concentrate used in this research was prepared from Sarcheshme Copper Mine. Chemical analysis of this concentrate shows that the weight percent of molybdenum is more than 55%. Mechanical activation experiments were carried out in a planetary ball-milling machine with steel cups and balls, in the presence and absence of alumina as an additive. The milling conditions are given in Table 1.

Table 1. Milling conditions of mechanical activation tests

No.	Time (hour)	Ball/Powder	Speed (rpm)	Aluminum (Wt.%)
1	4	40	300	0
2	24	40	300	0
3	2	40	300	50
4	12	40	300	50

The dissolution experiments of the activated samples was performed under different conditions. In these experiments, nitric acid was used to dissolve molybdenite (Equation 1):

$$MoS_2 + 6HNO_3 \rightarrow MoO_3.nH_2O + 2H_2SO_4 + 6NO + (1\text{-}n)\ H_2O \qquad (1)$$

The central composite design method (CCD) was used to design the space for dissolution experiments (Table 2). The pulp density was kept constant at 1.3 g / l and the stirring rate was fixed at 500 rpm in all tests. Finally, the prepared solution was centrifuged at 4000 rpm. The molybdenum concentration and the dissolution efficiency were determined by ICP and mass balance, respectively.

3. Result and Discussion

In order to develop a suitable model and obtain a rate equation, different situations can be assumed as follows:

- The rate equation is only affected by temperature and acid concentration.
- The rate equation is only affected by the temperature and the fraction of the reaction.
- The relationship of the rate is affected by the temperature, acid concentration, and fraction of the reaction.
- In addition to the effect of the temperature, acid concentration, and fraction of the reaction, the rate equation is also affected by the above-mentioned complications (mechanical activation effects).

In order to investigate the effect of acid concentration on the reaction rate of the dissolution, the following equation can be used:

$$r = \frac{dX}{dt} = k \cdot C^m \qquad (2)$$

In which k is the rate constant that according to the Arrhenius equation is a function of temperature, C is the momentary concentration of acid, and finally m is the reaction order with respect to the acid concentration. The momentary concentration of acid can be calculated from the difference between the initial and final amount of acid used:

$$C = C_0 - XC_S \qquad (3)$$

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Table 2. Levels of temperature and acid concentration in design of experiments

Variables	Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
Temperature (°C)	22	30	50	70	78
Acid Concentration	1.17* (0.057**)	2 (0.098)	4 (0.196)	6 (0.294)	6.83 (0.335)

*Acid value is reported as multiply stoichiometry values.

**Acid value is reported as Molar.

Where C_0 is the initial acid concentration of the solution, C_S is the stoichiometric concentration according to (1) and X is the fraction of the progress of reaction.

In this research, Runge-Kutta 4th order method was used for fitting the models to the experimental data using the least squares method and for plotting curve *X* vs. t. The results showed that acceptable fit was not achieved in the previous assumed model. In the study of the rate reaction affected only by the temperature and the fraction of the reaction, instead of the acid concentration, the fraction of the reacted molybdenite is introduced into the rate equation. The use of the fraction of the reaction in the rate equation is somewhat equivalent to the effect of the surface effects on the rate equation. By reducing the amount of molybdenite in the reaction chamber, the total surface area is reduced and, as a result, the dissolution rate decreases.

If X considered as the fraction of the reaction, the remained amount of molybdenite in solution will be proportional to (1-X). So, it can be written:

$$r = \frac{dX}{dt} = k \cdot (1 - X)^n \qquad (4)$$

There n is reaction order with respect to the residual of the molybdenite content. In this case, acceptable fit was not achieved. In the next step, the simultaneous effect of the concentration of acid and the fraction of the reaction are considered in the equation rate. Accordingly, the final relation being as follows:

$$r = \frac{dX}{dt} = k \cdot C^m \cdot (1 - X)^n \qquad (5)$$

Investigations showed that in this case, better fitting than the previous ones is achieved. But in order to introduce the effect of the complexity of the mechanical activation process of particles, the concept of variable activation energy was employed. According to which the activation energy is considered to be a linear function of the fraction of the reaction (equation 6), and it is increased with the advancement of the reaction.

$$E = E^0\big(1 - \alpha(1 - X)\big) \qquad (6)$$

By putting this relation in *k* (Arrhenius's relation), finally, the relation between the rate of the previous state (5) is written as follows:

$$\frac{dX}{dt} = \exp\left(\frac{b_1(1-X)-b_2}{T} + b_3\right)(1 - X)^n(C_0 - XC_s)^m \qquad (7)$$

The results of the fitting of the above model to the empirical dissolution data in four modes of mechanical activation experiments are shown in Figure 1, which indicates acceptable fitting.

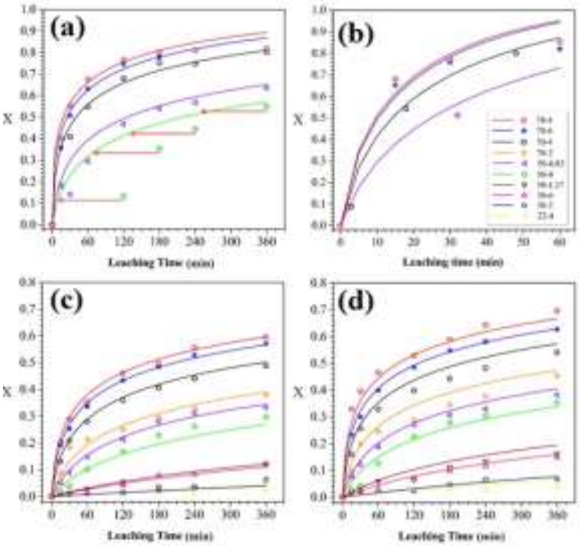

Figure 1. Fitting results of the final developed model of variable activation energy on the leaching data in nitric acid media for mechanically activated molybdenite: (a) 4hr of activation, (b) 24hr of activation, (c) 2hr of activation in the presence of alumina, (d) 12hr of activation in the presence of alumina.

4. Conclusion

In this research, it was tried to make some changes in the shrinking core model to develop a kinetic model for predicting the dissolution behavior of mechanically activated molybdenite under different conditions. Considering the effect of acid concentration, the fraction of the reaction and the complexities related to the activation of particles, finally a suitable model with an acceptable fitting on the empirical data of molybdenite dissolution in nitric acid was obtained.