5th International Biennial Conference on Ultrafine Grained and Nanostructured Materials, UFGNSM15

Investigating the Effect of Mechanical Activation Parameters on Structural Changes and Leaching Rate of Molybdenite Concentrate

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Abstract

In this research, mechanical activation (MA) was employed for leaching rate improvement of molybdenite concentrate in nitric acid media. These experiments were performed in two groups: with and without aluminum oxide (alumina). A full factorial design was used for each group of experiments. Leaching rate increment up to 5 times was observed only in 2 hours activation procedure. XRD analysis demonstrated structural disordering in activated MoS\textsubscript{2}. TEM images showed that particle size has been reduced to nanoscale. The initial powder size was 80\% between 2-44 \textmu m and dropped to about 10nm and 140nm in MA experiments with and without alumina, respectively. This size reduction would be the main reason of leaching rate enhancement which is more achievable in MA in presence of alumina. The results demonstrate that alumina has a motivating effect in activation procedure to achieve a nanostructure molybdenite. Analysis of variance revealed milling speed is the main parameter in MA without alumina, while, ball to powder ratio is the most important factor in MA procedure in presence of alumina on leaching rate.

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Keywords: Mechanical activation; Leaching rate; Nanostructure molybdenite; Analysis of variance.

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Peer-review under responsibility of the organizing committee of UFGNSM15
doi:10.1016/j.mspro.2015.11.074
1. Introduction

Molybdenite (MoS$_2$) is the main raw material in molybdenum metallurgy. Hydrometallurgical processes could be a suitable method for molybdenum extraction, but high chemical stability of sulfide ores makes the processes technically and economically difficult. Thus, either sever leaching conditions have to be applied or the chemical stability of sulfide has to be decreased by a suitable preleaching treatment. The mechanical activation (MA) of the ore by intensive grinding is one option, Hu et al. (2002).

The MA of MoS$_2$ is carried out by several researches, previously and it is concluded that molybdenite is relatively inert to the mechanical action in grinding process, Hu et al. (2004), Hu et al. (2007), Simeonov et al. (2014), Zhao et al. (2003). The specific layered structure of MoS$_2$ is the reason in this case. In hexagonal MoS$_2$ each Mo layer is sandwiched between two sulfur layers. Molybdenum and sulfur atoms have covalent bonds in each layer, while S-S connections are Vander Waals forces, Takagi et al. (1999). The mechanical actions induced by balls in grinding process causes sulfur-sulfur inter layer slippage. So MoS$_2$ acts as a solid lubricant during milling, Hu et al. (2004).

The lubrication behavior of molybdenite makes it relatively inert during MA. So, in this research effect of a brittle additive as a slip prohibiting agent in MA procedure of molybdenite is investigated. This effect was evaluated by structural changes and reactivity of MoS$_2$ in leaching process. Two groups of experiments were designed for this purpose. The first group of experiments was carried out without any additive, while in the second one aluminum oxide (alumina) added as a brittle material. In this way, comparison of two groups revealed the effect of alumina in molybdenite MA procedure.

2. Experimental details

In this research, the molybdenite concentrate was supplied by Sarcheshmeh Copper Complex in Iran. Wet chemical analysis of concentrate obtained as follows: 55.51%Mo, 1.14%Cu, 1.45%Fe, 38.76%S and 3.12%insoluble. Particle size analysis showed that 90% of particles are below 44µm and 10% are below 2µm. The residual flotation oil in concentrate was removed by 5 times washing with aceton and distilled water followed by drying at 150°C. The MA procedure was carried out in a 2 cups planetary ball milling machine. Leaching Experiments of mechanically activated molybdenite were carried out in nitric acid solution. Nitric acid as a relatively strong oxidizing agent is used in molybdenite leaching, frequently, Khoshnevisan et al. (2012), Vizsolyi and Peters (1980), Zhao et al. (2003). Vizsolyi proposed the following reaction in this case, Vizsolyi and Peters (1980):

$$\text{MoS}_2 + 6\text{HNO}_3 \rightarrow \text{H}_2\text{MoO}_4 + 2\text{H}_2\text{SO}_4 + 6\text{NO}$$

Leaching conditions were constant in all experiments and set based on some preliminary tests. In these experiments 1.25 g mechanically activated molybdenite concentrate was leached in 250 ml of 0.6 molar nitric acid solutions for 45 minutes at 50°C controlled temperature. After each leaching test, the leaching liquor was filtered, the solid residue remained on the paper was fully dried and leaching efficiency of concentrate was measured by gravimetric method.

In the present work, a full factorial design was used for each group of experiments: A $2^3$ factorial design for MA without additive and a $2^4$ factorial design for MA of concentrate in presence of alumina. In order to calculate the error in experiments, which is necessary for analysis of variance (ANOVA), each run was repeated in the first group. Four center point run were considered in the second group, instead of repetition of all runs to reduce the number of experiments (Table 1).

3. Results and discussion

The leaching data obtained from the MA of molybdenite concentrate were analyzed using Design-Expert Version 7.0.0 software. ANOVA was employed to determine the statistical significance of main variable effects as well as the interaction effects. The significance level employed in the analysis evaluated by p-values is less than 0.05 (Table 2 and Table 3).
Based on ANOVA calculations two polynomial equations for the first and second group of experiments were proposed as follows, respectively:

Leaching Efficiency (%) = 36.2200 – 3.2800(A) – 1.2920(B) – 0.1214(C) + 0.0290(AC) + 0.0073(BC) \hspace{1cm} (2)

Leaching Efficiency (%) = -19.41 + 21.7467(A) – 0.8787(B) + 0.0439(C) + 0.2659(D) – 0.0679(AC) + 0.0081(BC) \hspace{1cm} (3)

In these equations A is activation time, B is ball to powder ratio, C is rotational speed and D is alumina weight percent. The R² for the first and second group are 0.9808 and 0.9264, respectively.

These values indicate a reasonable agreement between actual and predicted values (Fig. 1).

The most significant factor effects are rotational speed, ball/powder ratio, activation time and interaction of rotational speed and ball to powder ratio for the activation experiments without any additive. This sequence has changed in MA tests in presence of alumina: ball/powder ratio, rotational speed, alumina wt% and activation time.

In comparison with leaching efficiency of un-affected molybdenite concentrate which obtained 10.5% in a separate test with the same conditions, MA has improved leaching efficiency 3 times more (up to 32%) and MA in presence of alumina improved it 5 times (up to 53%).

Table 1. Experimental design of two groups of experiments with leaching efficiency values.

| Run number | Group I (MA without Alumina) | Group II (MA with Alumina) |
|------------|-----------------------------|---------------------------|
|            | Activation Time (hour) | Ball to Powder ratio | Rotational Speed (rpm) | Leaching Efficiency (%) | Activation Time (hour) | Ball to Powder ratio | Rotational Speed (rpm) | Alumina (Wt%) | Leaching Efficiency (%) |
| 1          | 1 | 15 | 200 | 16.72 | 1 | 15 | 200 | 25 | 19.2 |
| 2          | 1 | 15 | 200 | 16.24 | 2 | 15 | 200 | 25 | 22.61 |
| 3          | 2 | 15 | 200 | 20.4 | 1 | 25 | 200 | 25 | 24.96 |
| 4          | 2 | 15 | 200 | 19.12 | 2 | 25 | 200 | 25 | 30.72 |
| 5          | 1 | 25 | 200 | 19.04 | 1 | 15 | 300 | 25 | 26.67 |
| 6          | 1 | 25 | 200 | 18.64 | 2 | 15 | 300 | 25 | 26.77 |
| 7          | 2 | 25 | 200 | 19.92 | 1 | 25 | 300 | 25 | 37.87 |
| 8          | 2 | 25 | 200 | 21.28 | 2 | 25 | 300 | 25 | 39.47 |
| 9          | 1 | 15 | 300 | 18.32 | 1 | 15 | 200 | 50 | 20.16 |
| 10         | 1 | 15 | 300 | 19.68 | 2 | 15 | 200 | 50 | 29.44 |
| 11         | 2 | 15 | 300 | 22.56 | 1 | 25 | 200 | 50 | 25.76 |
| 12         | 2 | 15 | 300 | 24.32 | 2 | 25 | 200 | 50 | 40 |
| 13         | 1 | 25 | 300 | 26.48 | 1 | 15 | 300 | 50 | 32 |
| 14         | 1 | 25 | 300 | 27.28 | 2 | 15 | 300 | 50 | 31.68 |
| 15         | 2 | 25 | 300 | 33.68 | 1 | 25 | 300 | 50 | 49.12 |
| 16         | 2 | 25 | 300 | 32.88 | 2 | 25 | 300 | 50 | 53.28 |
| 17         | - | - | - | - | 1.5 | 20 | 250 | 37.5 | 34.18 |
| 18         | - | - | - | - | 1.5 | 20 | 250 | 37.5 | 31.62 |
| 19         | - | - | - | - | 1.5 | 20 | 250 | 37.5 | 28.03 |
| 20         | - | - | - | - | 1.5 | 20 | 250 | 37.5 | 33.02 |
Table 2. Analysis of variance for group I leaching efficiency data (MA without Alumina).

| Source | sum of squares | df  | Mean square | p-value    | Significance | Contribution (%) |
|--------|----------------|-----|-------------|------------|--------------|------------------|
| Model  | 417.82         | 7   | 59.69       | < 0.0001   | Significant  | 14.91            |
| A-Milling Time | 63.04         | 1   | 63.04       | < 0.0001   | Significant  | 25.87            |
| B-Ball / Powder | 109.41       | 1   | 109.41      | < 0.0001   | Significant  | 42.84            |
| C-Speed | 181.17        | 1   | 181.17      | < 0.0001   | Significant  | 1.99             |
| AB     | 0.048          | 1   | 0.048       | 0.7889     | -            | 0.011            |
| AC     | 8.41           | 1   | 8.41        | 0.0065     | Significant  | 1.19             |
| BC     | 52.71          | 1   | 52.71       | < 0.0001   | Significant  | 12.46            |
| ABC    | 3.03           | 1   | 3.03        | 0.0600     | -            | 0.72             |
| Pure Error | 5.05          | 8   | 0.63        | 1.19       | -            |                  |

Table 3. Analysis of variance for group II leaching efficiency data (MA with Alumina).

| Source | sum of squares | df  | Mean square | p-value    | Significance | Contribution (%) |
|--------|----------------|-----|-------------|------------|--------------|------------------|
| Model  | 1465.18        | 15  | 97.68       | 0.0167     | Significant  | 6.23             |
| A-Milling time | 97.35        | 1   | 97.35       | 0.0165     | Significant  | 36.59            |
| B-Ball / Powder | 528.39       | 1   | 528.39      | 0.0031     | Significant  | 30.08            |
| C-Speed | 453.97        | 1   | 453.97      | 0.0036     | Significant  | 12.06            |
| D-Alumina | 168.65        | 1   | 168.65      | 0.0096     | Significant  | 0.75             |
| AB     | 11.47          | 1   | 11.47       | 0.1184     | -            | 3.14             |
| AC     | 51.84          | 1   | 51.84       | 0.0303     | Significant  | 1.16             |
| AD     | 20.55          | 1   | 20.55       | 0.0715     | -            | 4.53             |
| BC     | 67.46          | 1   | 67.46       | 0.0235     | Significant  | 1.25             |
| BD     | 17.75          | 1   | 17.75       | 0.0814     | -            | 1.30             |
| CD     | 22.78          | 1   | 22.78       | 0.0652     | -            | 1.07             |
| ABC    | 0.26           | 1   | 0.26        | 0.7309     | -            | 0.00758           |
| ABD    | 2.48           | 1   | 2.48        | 0.3446     | -            | 0.13             |
| ACD    | 11.29          | 1   | 11.29       | 0.1200     | -            | 0.64             |
| BCD    | 10.93          | 1   | 10.93       | 0.1232     | -            | 0.67             |
| ABCD   | 7.111E-004     | 1   | 7.111E-004  | 0.9853     | -            | 0.00059           |
| Pure Error | 3.29          | 2   | 1.64        | 1.46       | -            |                  |
TEM evaluations demonstrated that particle size dropped to about 140 nm and 10 nm in the first and second group, respectively. Fig. 2 shows TEM images of activated MoS$_2$ particles in each group of experiments. As it can be seen, there are agglomerates of ultrafine particles in activation with alumina which reveals a change in grinding mechanism in activation process.

Figure 3 shows X-ray patterns of unaffected molybdenite and final powder of run 16 in two groups of experiments. As it can be seen, MA has reduced peak intensity and resulting peak broadening which is realizable from FWHM values of the main peak. These two trends are consequence of crystallite size reduction that could results to an amorphous structure, finally.

Pick shift is another result of MA that would be seen in these patterns. The change in peak position reveals structural changes, especially distance of crystal planes and lattice strain, which have induced by MA. These results demonstrate that presence of alumina in MA has a great effect in activation process due to generation of more structural changes and lattice imperfections in the mineral structure. This outcome has been reported previously by Hoseinpur et al., Hoseinpur et al. (2014). It seems alumina acts as a slip prohibiting agent and improves grinding.
efficiency of molybdenite which in turn resulting in more structural changes and more particle size reduction. These two phenomena increase energy level of mineral. Subsequently less activation energy is needed when taking part in chemical reactions and more leaching rates are achievable (Tromans and Meech, 2001, Zhao et al., 2003).

Fig. 3. X-ray patterns of un-affected molybdenite (without activation), 2hours activated molybdenite without alumina and 2hours activated molybdenite in presence of 50% alumina.

4. Conclusion

In this research, mechanical activation of molybdenite concentrate in two groups of experiment was carried out. ANOVA revealed that without any additive, the most significant factor is rotational speed, while in presence of alumina as a brittle additive, ball to powder ratio is the most important factor.

Leaching efficiency was improved up to 3 times (32%) and up to 5 times (53%) in the first group and second group of experiments, respectively.

TEM and XRD analysis showed a more trend to amorphisation and particle size reduction in the second group of experiments, based on reduction in peak intensity and shift in peak position that is a consequence of lattice deformation.

The results demonstrated alumina has changed mechanism of MA and consequently it has improved molybdenite leaching rate more than a simple MA without any additive.

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