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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 MoS₂. TEM images showed that particle size has been reduced to nanoscale. The initial powder size was 80% between 2-44 μm 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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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 severe 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 $44\mu\text{m}$ and 10% are below $2\mu\text{m}$. The residual flotation oil in concentrate was removed by 5 times washing with acetone 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), Vizsolanyi and Peters (1980), Zhao et al. (2003). Vizsolanyi proposed the following reaction in this case, Vizsolanyi and Peters (1980):



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:

$$\text{Leaching Efficiency (\%)} = 36.2200 - 3.2800(A) - 1.2920(B) - 0.1214(C) + 0.0290(AC) + 0.0073(BC) \quad (2)$$

$$\text{Leaching Efficiency (\%)} = -19.41 + 21.7467(A) - 0.8787(B) + 0.0439(C) + 0.2659(D) - 0.0679(AC) + 0.0081(BC) \quad (3)$$

In these equations A is activation time, B is ball to powder ratio, C is rotational speed and D is alumina weight percent. The R^2 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	
A-Milling Time	63.04	1	63.04	< 0.0001	Significant	14.91
B-Ball / Powder	109.41	1	109.41	< 0.0001	Significant	25.87
C-Speed	181.17	1	181.17	< 0.0001	Significant	42.84
AB	0.048	1	0.048	0.7889	-	0.011
AC	8.41	1	8.41	0.0065	Significant	1.99
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	
A-Milling time	97.35	1	97.35	0.0165	Significant	6.23
B-Ball / Powder	528.39	1	528.39	0.0031	Significant	36.59
C-Speed	453.97	1	453.97	0.0036	Significant	30.08
D-Alumina	168.65	1	168.65	0.0096	Significant	12.06
AB	11.47	1	11.47	0.1184	-	0.75
AC	51.84	1	51.84	0.0303	Significant	3.14
AD	20.55	1	20.55	0.0715	-	1.16
BC	67.46	1	67.46	0.0235	Significant	4.53
BD	17.75	1	17.75	0.0814	-	1.25
CD	22.78	1	22.78	0.0652	-	1.30
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

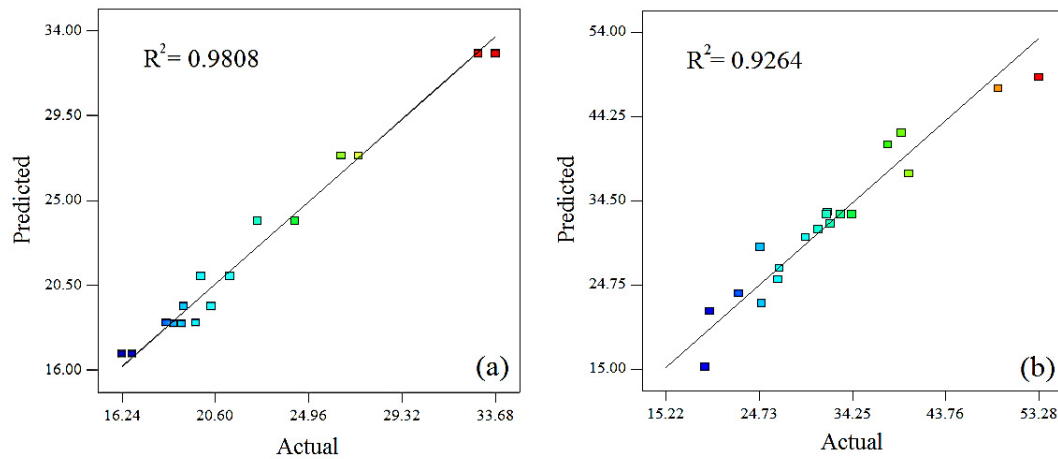


Fig. 1. The graphical plots of actual vs. predicted values for: (a) leaching efficiency of group I (MA without alumina); and (b) leaching efficiency of group II (MA with alumina).

TEM evaluations demonstrated that particle size dropped to about 140 nm and 10nm 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.

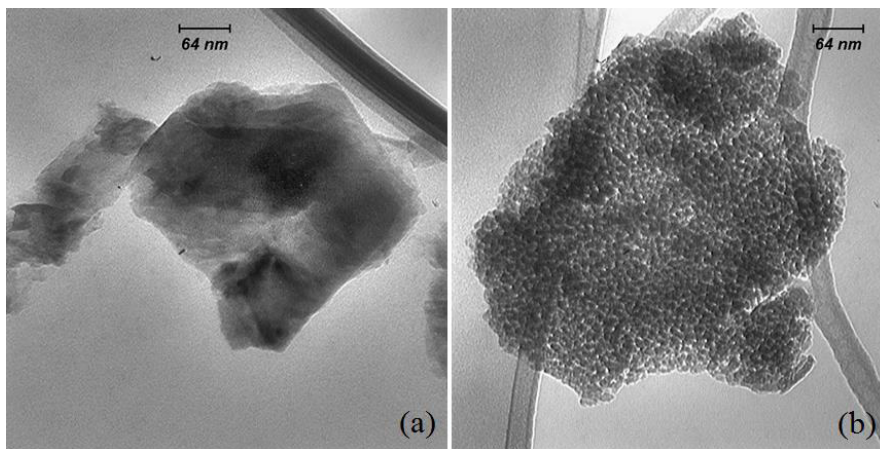


Fig. 2. TEM images of: (a) 2hours activated molybdenite without alumina; and (b) 2hours activated molybdenite in presence of 50% alumina (rotational speed of 300rpm, ball to powder ratio of 25).

Figure 3 shows X-ray patterns of un-affected molybdenite and final powder of run 16 in two groups of experiments. As it can be seen, MA has reduced pick intensity and resulting pick broadening which is realizable from FWHM values of the main pick. 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 pick 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).

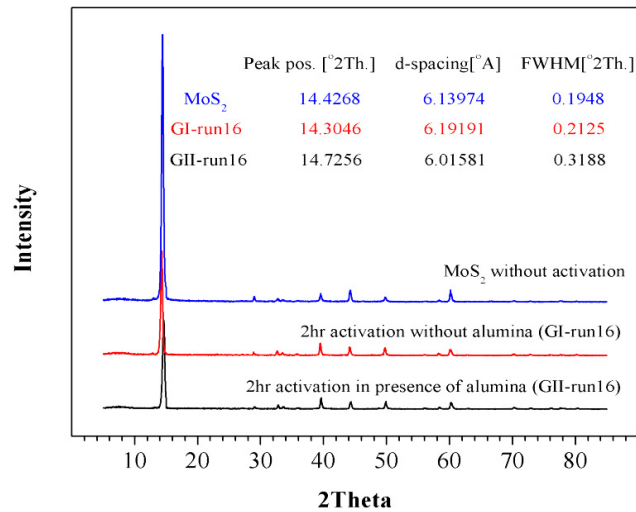


Fig. 3. X-ray patterns of un-affected molybdenite (without activation), 2hours activated molybdenite without alumina and 2hours activated molybdenite in presence of 50% alumina.

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.

References

- Hoseinpur, A., Bezanaj, M. M., Khaki, J. V., 2014. The Effect Of Al₂O₃ And Cao Presence On The Kinetics Of Mechanochemical Reduction Of Mo₂S₃ By Zn. *Journal Of Alloys And Compounds* 587, 646-651.
- Hu, H.-P., Chen, Q.-Y., Yin, Z.-L., He, Y.-H., Huang, B.-Y., 2007. Mechanism Of Mechanical Activation For Sulfide Ores. *Transactions Of Nonferrous Metals Society Of China* 17, 205-213.
- Hu, H., Chen, Q., Yin, Z., Zhang, P., Guo, G., Gottstein, G. 2004. Structural Change Of Mechanically Activated Molybdenite And The Effect Of Mechanical Activation On Molybdenite. *Metallurgical And Materials Transactions B* 35, 1203-1207.
- Hu, H., Chen, Q., Yin, Z., Zhang, P., Tang, A. 2002. Oxidation Behavior Of Mechanically Activated Galena In Thermogravimetry (Tg). *Thermochimica Acta* 395, 139-144.
- Khoshnevisan, A., Yoozbashizadeh, H., Mozammel, M., Sadmezhaad, S. K., 2012. Kinetics Of Pressure Oxidative Leaching Of Molybdenite Concentrate By Nitric Acid. *Hydrometallurgy* 111, 52-57.
- Simeonov, K., Kim, J. H., Ferrari, D., Huelsman, D., Budroni, G., Corthals, S., Pagán-Torres, Y. J., 2014. Comos/K Catalysts For Higher Alcohol Synthesis From Syngas Prepared By Mechano-Chemical Activation Of Molybdenite. *Catalysis Science & Technology* 4, 922-924.

- Takagi, S., Murakami, K., Gotoh, T., 1999. Observation Of Molybdenite Surface Using Scanning Auger Microscope. *Applied Surface Science* 144, 278-282.
- Tromans, D., Meech, J., 2001. Enhanced Dissolution Of Minerals: Stored Energy, Amorphism And Mechanical Activation. *Minerals Engineering* 14, 1359-1377.
- Vizsolyi, A., Peters, E., 1980. Nitric Acid Leaching Of Molybdenite Concentrates. *Hydrometallurgy* 6, 103-119.
- Zhao, Z.-W., Li, H.-G., Sun, P.-M., Li, Y.-J., Huo, G.-S., 2003. Influence Of Crystal Structure On Mechanical Activation Effect. *Transactions Of The Nonferrous Metals Society Of China(China)* 13, 188-194.