

Received January 12, 2011; reviewed; accepted March 1, 2011

Hydrometallurgical recovery of molybdenum from Egyptian Qattar molybdenite concentrate

Ashraf M. AMER

Environmental Science Dept., Faculty of Science, Alexandria Univ., Egypt, ashrafamer0408@yahoo.com

Abstract. An attempt has been made in this investigation to develop a chemical method for treating molybdenite concentrate from Qattar (Eastern Desert, Egypt). The core of the process lies in replacement of pyrometallurgical processing with a hydrometallurgical method using oxygenated nitric acid leaching under atmospheric and oxygen pressure. The effects of temperature, acid concentration, partial pressure as well as the kinetics of leaching process were studied.

keywords: hydrometallurgy, flotation, leaching, molybdenum, kinetics

1. Introduction

Molybdenite deposits in Egypt are located in four main localities in the northern part of the Eastern Desert. These localities are Gebel Qattar, Abu Marwa, Abu Harba and Umm Disi. The Qattar molybdenite deposit is considered the largest (Dardir 1968; Said, 1990). At Gebel Qattar molybdenite mineralization occurs at the intersection of 27° 05' 29" N and 33° 16' 10" E. Molybdenite occurs in quartz veins as disseminations in the host granite. Total reserve of the area was estimated to be about 4.5 gigagrams (Gg) (Burgov 1983). Hydrometallurgical processing of molybdenite has received attention recently by process which involves roasting and pressure leaching with ammonium sulphate (Janngg, 1963). Oxidation and leaching of molybdenite concentrate using sodium hypochlorite (Bhappu et al. 1965; Iordanov 1962; He et al., 2007; Peng et al., 2007), acid chlorate or sulphuric acid with added manganese dioxide were also triad (Reznikov and Necheava 1962; and Zelikman and yashine et al., 1991). The use of hypochlorite or chlorine solution for leaching was abandoned due to the corrosive effects of leachants and problems associated with using highly toxic gases. Other methods were examined using sodium chromate as a leaching agent (Barteccki and Rycerz, L. 1988; Antonigeric and pacovic 1992) and bacterial leaching (Ivanov, 1962; Yashine et al., 1991). In India chlorination is used for treatment of low-grade molybdenite concentrate in fluidized bed reactor (Evans 1988; Nair et al. 1988; Johnston and Pickles 1990). In Russia, interaction of molybdenite concentrate with

nitric acid was investigated (Bjarling, G. and Kolta, G.A. 1964; Chursanov et al., 1987; Peters, 1992; Zhang (2009); Smirnov et al., 2010).

The objective of this investigation is to study nitric acid leaching of molybdenite concentrate under atmospheric and oxygen pressure as well as the kinetics of pressure leaching process.

2. Experimental

2.1. Material and Methods

Gebel Qattar molybdenite ore occurs in two forms. The first form, crystals, are irregularly distributed in the quartz veinlets. They are well developed showing length variation between 2 to 3 cm. The second form is massive ore at wall rock confined to areas between molybdenite crystals bearing quartz veins and the granitic host rock. The chemical composition of the investigated Gebel Qattar molybdenite concentrate is given Table 1.

Table 1. Chemical analysis of the investigated Gebel Qattar molybdenite concentrate

composition	percentage (by weight)
Mo	30.2
S	24.3
Ni	0.17
Cu	0.35
Fe	1.62
Si	7.05
Total	99.5

2.2. Apparatus

The pressure leaching experiments were carried out in 2 dm³ laboratory autoclave. The autoclave had the following features: a maximum working pressure of 20.6 MPa temperatures of 300°C and stirring speed of 1600 rpm. Description of used apparatus is given elsewhere (Amer, 1996)

Details on leaching experiments in open vessel and in autoclave are given elsewhere (Amer, 1996).

2.3. Analysis

Molybdenum in solution and in solid samples was analyzed spectrophotometrically. The technique follows that of Jeffery and Justschison (1981) which was modified by the Chemistry Division of the Federal Geological Survey in Germany.

3. Results and discussion

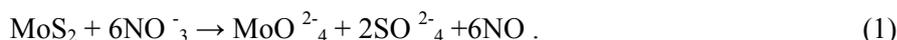
3.1. Mineralogical study

X-ray examination along with microscopic investigation of representative molybdenite sample revealed that molybdenite mineral content is about 1%. Quartz seems to be the main gangue mineral, present mainly as coarse anhedral crystals with smooth interlocking borders, constitutes about 70 % of the sample. Feldspars follows quartz in abundance. Oligoclase and orthoclase occur as fine to coarse anhedral grains, occasionally interstitial, or being enclosed in quartz. They form about 17% of the volume in the studied sample. Some micaceous minerals are present as muscovite and biotite (about 7%). Molybdenite is represented by globular forms having well developed concentric texture. Molybdenite grains show wide size variation.

3.2. Hydrometallurgical processing of molybdenite concentrate

3.2.1. Atmospheric leaching

The purpose of atmospheric acid leaching of molybdenite is to produce a very pure molybdenite oxide as the ordinary roasting process does not involve any purification and provide volatilization losses. Leaching of molybdenite with aqueous nitric acid is carried out according to the following reaction:



Factors which influence the leaching rate of molybdenite are temperature, leaching time and nitric acid concentration. Results showing the effect of these factors on the leaching of molybdenite are illustrated in Figs 1 and 2. Molybdenum extraction has been found to increase with the increase of temperature and leaching time. Maximum molybdenum leaching recovery (96%) was reached at temperature of 100°C after 225 min of leaching a time. The effect of nitric acid concentration on molybdenum extraction is shown in Fig. 2. Generally as nitric acid concentration increases from 5 to 10 %, the molybdenum recovery increases at different leaching times. Practically, an increase of the acid concentration more than 10%, especially at long leaching time of 180-225 min had no effect on the molybdenum leaching recovery. It could be concluded that under atmospheric leaching conditions the maximum molybdenum extraction of 96% is reached under the following conditions:

temperature : 100°C
 leaching time : 225 min
 nitric acid concentration : 10%
 pulp density : 10%.

From these conditions, it appears that the process of molybdenite leaching is slow under atmospheric conditions. For that, a series of experiments were carried out using autoclave to accelerate the rate of molybdenum recovery and to increase Mo recovery.

The temperature effect on the molybdenum leaching recovery has been studied over a temperature range from 120° to 200°C and the results are given in Fig. 3.

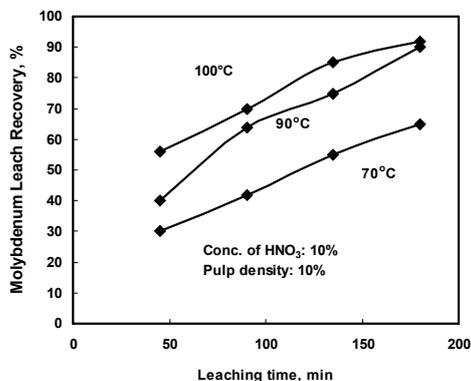


Fig. 1. Effect of leaching temperature on molybdenum extraction

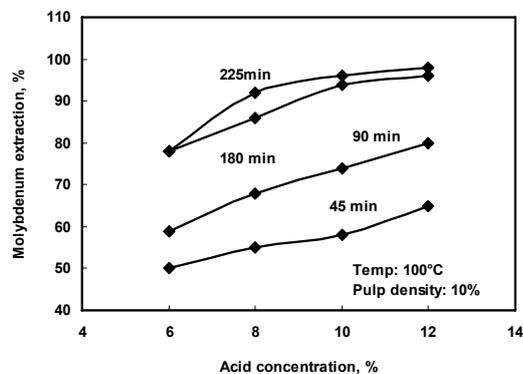


Fig. 2. Effect of acid concentration on molybdenum extraction

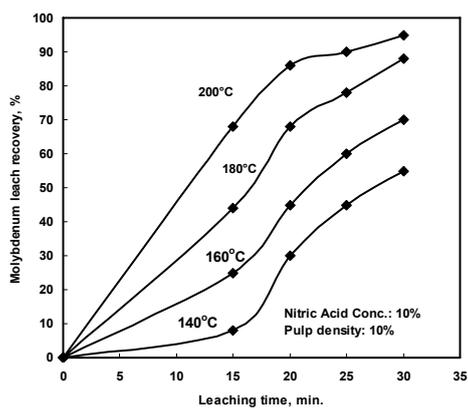


Fig. 3. Effect of leaching temperature on molybdenum extraction

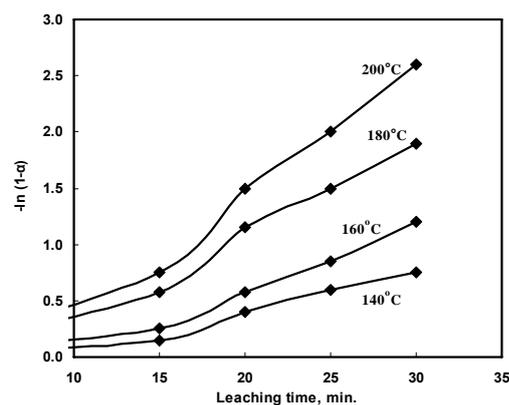


Fig. 4. Relation between $\ln(1-\alpha)$ and time

It is obvious that the reaction rate increases with increasing temperature and reaches its maximum value at 200°C ($2.9 \times 10^3 \text{ sec}^{-1}$). As illustrated in Fig. 4 the plot of $\ln(1-\alpha)$ versus t over the studied temperature range consists of a series of straight lines indicating that leaching of molybdenite fits a first order reaction, where slopes of these lines gives the rate of reaction (K).

An Arrhenius plot is constructed and shown in Fig. 5. The calculated apparent activation energy is 49 kJ/mol. This value is in a good agreement with the values reported by Kanome et al. (1987) for copper sulfide and nickel sulfide, respectively. The obtained value of activation energy (49 kJ/mol) is too high for the reaction to be controlled by mass transfer through the boundary layer but is possible for chemically controlled reactions (Wadsworth, 1972).

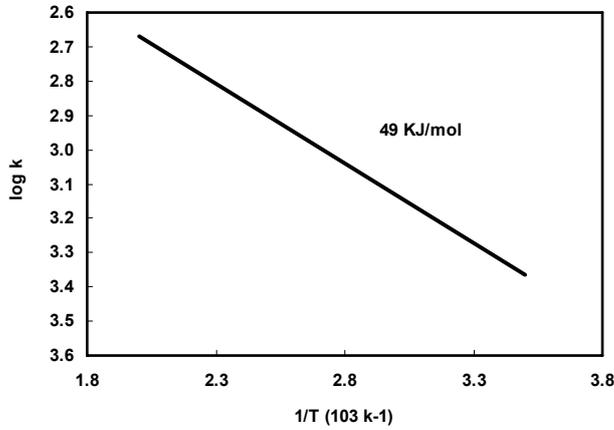


Fig. 5. The Arrhenius plot for determination of activation energy

The effect of oxygen partial pressure on molybdenum extraction is shown in Fig. 6. It is obvious that, at different leaching times of 15, 20 and 30 min, an increase of oxygen partial pressure from 0.5 up to 1.5 MPa leads to a remarkable increase in the molybdenum recovery while an increase of oxygen partial pressure to more than 1.5 MPa has practically no effect on improving molybdenum recovery.

Ninety six percent leaching recovery of molybdenum by nitric acid pressure leaching of the molybdenite concentrate seems to be an alternative applicable method of molybdenite processing.

The effect of acid concentration on the leaching recovery of molybdenum is shown in Fig. 7.

Ninety six percent leaching recovery of molybdenum is reached after 30 min of leaching time compared with 225 min in case of atmospheric leaching. A technological flow sheet of enrichment and processing of Qattar molybdenite deposits is given in Fig. 8.

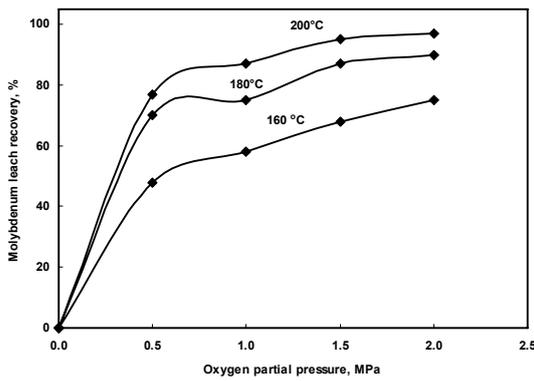


Fig. 6. Effect of oxygen partial reasure on molybdenum extraction

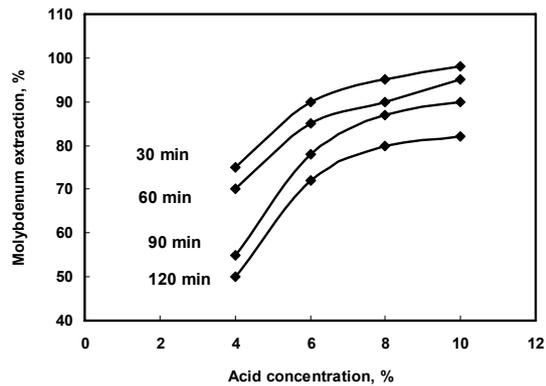


Fig. 7. Effect of acid concentration on molybdenum extraction

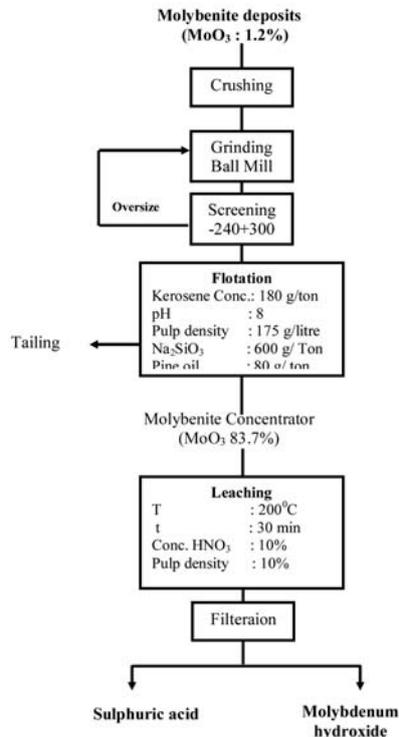


Fig. 8. Flowsheet of enrichment and processing of Qattar molybdenite deposits

4. Conclusions

Pressure leaching of molybdenite concentrates with nitric acid represents a new possible method for processing of molybdenite. The most favorable conditions for the 96% leaching recovery of molybdenum under atmospheric conditions are: temperature of 100⁰ C, 225 min of leaching and nitric acid concentration equal to 10%. The most favorable conditions for pressure leaching of molybdenite to get 96% recovery are: 200°C, 30 min of leaching, nitric acid concentration equal to 10% and oxygen partial pressure 1.5 MPa.

References

- Ang, M.; Wang, X and Liu, W. (2009): A novel technology of molybdenum extraction from low Ni-Mo ore, *Hydrometallurgy*, Vol. 97, Issues 1-2, PP. 126-130.
- Amer, A.M. (1996): leaching of a low grade Egyptian chramite ore *Hydrometallurgy*, 43, 307-16.
- Arbiter, N.; Fujii, Y.; Hansen, B. and Raja, A. (1975): Surface properties of hydrophobic solids. *ALCHE Symposium series*, 71 (150), 176-82.

- Antonigevic, M.M. and Pacovic, N.V. (1992): Investigation of molybdenite oxidation by sodium dichromate. *Miner. Eng.* 5 (2), 223-33.
- Bartecki, A. and Rycerz, L. (1988): Kinetics and mechanism of dissolution of synthetic molybdenum disulfide MoS₂ in bromate solutions. Part I, *hydrometallurgy*, 20 (2), 235-48.
- Burgov, V. (1983): Technical report on follow-up geochemical operations in the period 1968-1968-1972. Aswan mineral survey project, Geol. Surv. Egypt.
- Bhappu, R.B.; Reynolds, D.H. and Roman, R.J. (1965): molybdenite recovery from sulfide and oxide ores. *J. Metals*, 17, 1199-1205.
- Bjarling, G. and Kolta, G.A. (1964): Oxidizing leach of sulfide concentrates and other materials catalyzed by nitric acid. *Int. Min. process. Cong. VII.*
- Chander, S.; Wie, J.M. and Fuerstenau, D.W. (1975): On the native floatability and surface properties of naturally hydrophobic solids. *ALCHE symp. Series*, 71 (150), 183-8.
- Chursanov, Yu. V.; Potashnikov, Yn. M. and Rummyantsev, V.K. (1987): Interaction of molybdenum disulfide with nitric acid. *Isvetn. Met.* (9), 56-7.
- Dardir, A.A.; and Gadalla, S.H.A. (1968): Report on expedition 7168, Eastern Desert. *Geol. Surv. Egypt.*
- Dardir, A.A.; Abu Zeid, K.M. and Gadalla, S.H.A. (1983): molybdenite deposits of Gebel Qattar area. *Annals. Geol. Surv. Egypt.* XIII, 23-37.
- Evans, D.F. (1980): Principles of extractive metallurgy, Gordon and Breach, New York, Vol. 2.
- He, D-S.; Feng, Q.M, Zhang. L-M. and Lu, Y.P. (2007): An environmentally – friendly technology of vanadium extraction from stone coal. *Miner. Eng.* 20, PP. 1184-1186 .
- Ivanov, V.I. (1962): Role of sulfur bacteria in the leaching of sulfide ores. *Dobl. Akad. Nauk SSR*, 146, 447-9.
- Iodavov, K. and Zelikman, A.N. (1962): Kinetics of oxidation of molybdenite in a solution of NaOCl, *Khim. Ind. (Sofia)* 56, 109-26.
- Jangg, G. (1963): Alkalische drucklaugung sulfidischer erze, *Z. Erzbergbau metallhutenw.* 16, 508-14.
- Johnston, C. and Pickles, C.A. (1990): Study of the reaction of molybdenum disulfide with lime and carbon at plasma temperature, *Trans. Inst. Min. Metall.*, 100-4.
- Jeffery, P.G. and Hutchinson, D. (1981): chemical methods of rock analysis. 3rd ed. Oxford: pergmon Press, 379 P.
- Kanome, O., Abe, H.; Okuwaki, A. and Okabe, T. (1987): Sulfuric acid Oxygen-pressure leaching of Ni₃S₂ prepared by a wet Process. *Hydrometallurgy*, 19, 1-9.
- Leja, J. (1982): Surface chemistry of frith floatation. Plenum Press, New York, 488P.,
- Nair, K.U.; Sathiyamoorthy, D.; Bose, D.K. and Gupta, C.K. (1988): Processing of low grade Indian molybdenite concentrate by chlorination in fluidized bed reactor. *Int. J. Miner Process.* 23 (3-4), 171-80.
- Peng, J.R.; Yang, D.J.; Chen, J.X. and Yan, J.F. (2007): Experimental study on alkaline leaching of crude molybdenite under pressure of Oxygen.

- Peters, E. (1992); Hydrometallurgical process innovation. *Hydrometallurgy*, Vol.29, Issue 1-3, pp. 43-55.
- Papangelakis, V.G. and Demopoulos, G.P. (1991): Acid pressure oxidation of pyrite: reaction Kinetics, *Hydrometallurgy*, 26, 309-25.
- Pesic, B. (1984): Dissolution of bornite in sulfuric acid using oxygen oxidant. *Hydrometallurgy*, 12, 195-215.
- Reznikov, A.A and Necheava, A.A. (1962): Oxidation of molybdenite, *Inform. Sb. Vses. Nauchn. Issled. Geol. Inst.*, 56, 109-26.
- Said, R. (1990): *The geology of Egypt*. Balkema: Rotterdam, 525-29.
- Somasundaran, P. and Anantapadmanabhan, K.P. (1979): Physico-Chemical aspects of floatation. *Trans. Indian Inst. Met.*, 32, 177-97.
- Smirnov, K.M.; Raspopov, N.A. Shneerson, Y.M., Lapin, A.Y.; Bitkov, G.A.; Menshikov, Y. A., Pashin, P.N. and Kinechenko, v.p. (2011) Autoclave leaching of Molybdenite concentrates with catalytic additives of nitric acid. *Russian Metallurgy (Metally)*. Vol. 20, Issue 7, pp.58-95.
- Wakamatsu, T. and Numate, Y. (1991): Floatation of graphite, *Min. Eng.* (4), 975-82.
- Wadsworth, M.E. (1972): Rate processes in hydrometallurgy, *Second Tutorial Symp. On extractive metallurgy*, AIME, Salt Lake City, Utah.
- Yashina, G.M.; Kostareva, M.A. and Nesterova, S.V. (1991): Leaching of Copper – molybdenum ores by chemical and biochemical methods. *Fiz. Tekh. Probl. Razrab. Polezn. Iskop.* (6), 93-7.
- Yashina, G.M.; Kostareva, M.A. and Kameav, V.D. (1991): Prospects for leaching of molybdenum – containing ores. *Tsv. Met.* (16), 13-5.
- Zhan. Fang Cao; Hang Zhang; Zhao-hui Oui, Guang – y Liu and Wen-xian Zhang (2009); A novel technology for Molybdenum extraction from Molybdenite concentrate. *Hydrometallurgy* , Vol.99, issues 1-2, pages 2-6.