Acidic Leaching with Chlorate as Oxidizing Agent to Extract Mo and Re from Molybdenite Flotation Concentrate in a Copper Plant

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Acidic Leaching with Chlorate as Oxidizing Agent to Extract Mo and Re from Molybdenite Flotation Concentrate in a Copper Plant

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Abstract

The technology of molybdenum extraction from molybdenite concentrate by using potassium chlorate (KClO3) or sodium chlorate (NaClO3) has been investigated. The results show that leaching time, leaching temperature, agitation speed, oxidizer type, potassium or sodium chlorate and hydrochloric acid concentration have significant effect on the molybdenum extraction efficiency. Optimum process operating parameters were established as follows: 4 hrs, hydrochloric acid concentration: 35%, solids ratio: 5%, temperature: 65-70°C, agitation speed: 600 rpm, the mass of potassium chlorate and sodium chlorate: 25 g. Under these experimental conditions, the extraction of molybdenum and rhenium were obtained about 85% and 100%, respectively.

Keywords: Hydrometallurgy; Molybdenite; Leaching; Rhenium; Oxidizing Agents
INTRODUCTION

Molybdenum is a refractory metallic element used principally as an alloying agent in cast iron, steel, and superalloys to enhance hardenability, strength, toughness, wear- and corrosion-resistance, oil and gas industry (1) and is a strategic metal in the industrial sector, medicine and a necessary element for the human body and plants (2). Molybdenite is the principal ore from which molybdenum is now extracted. Molybdenite concentrate is commonly obtained as a byproduct in the treatment of copper porphyry ores in which the molybdenite is a minor constituent. The commercial route for the extraction of molybdenum from its sulphide mineral involves roasting of the concentrate, purification of the resultant calcine, either by distillation of MoO$_3$, or by a hydrometallurgical route, and, finally, hydrogen reduction of the trioxide to the metal. During roasting, much rhenium is lost due to volatilization and the SO$_2$ generated is a source of environmental pollution. In the past years, several mineral processes have been tested for treating the ore, such as flotation separation, gravity separation combined with flotation (3). However, with the development of industry, high grade and easy-handling Mo mineral is decreasing, while the proportion of low-grade and complex ore is increasing, pressure on the traditional technology will be larger. With the increasingly stringent environmental requirements, the traditional technology gradually shows its shortcomings, hydrometallurgical processing becomes more attractive especially for low-grade and complex ores. Since the 1970s, research on Mo wet alkali and acidic leaching has attracted more attention (2, 4-10), the oxygen pressure process (6, 11), nitric acid decomposition (11), sodium hypochlorite (12), electro-oxidation and bio-leaching (13-17) method have been developed one after another. Cheap
oxidants, air or pure oxygen is consumed in oxygen pressure process and nitric acid oxidation. Not only high temperature and high pressure are needed in this process but also high demands are required for chemical reactor. The leaching process is difficult to control, and there are certain security risks in the production. So some domestic manufacturers have already discarded those technologies, which are barely applied in small and medium sized manufacturers. Compared with the above two former processes, NaClO method has moderate reacting conditions, low equipment investment, and is easy to control. But the main shortcoming lies in large reagent consumption. And it is mainly used in low-grade molybdenum, tailings leaching and molybdenum reclamation from the traditional process (18-25). The main chemical reaction can be described by the equation 1 (5):

\[
\text{MoS}_2 + 3\text{NaClO}_3 + 3\text{H}_2\text{O} = 3\text{NaCl} + \text{H}_2\text{MoO}_4 + 2\text{H}_2\text{SO}_4
\]

The purpose of the present work is to examine the dissolution rate of molybdenite concentrate using potassium or sodium chlorate as the oxidant in acidic condition. Hydrochloric acid was used with potassium or sodium chlorate as powerful oxidizer to dissolve molybdenite sample which was obtained from Sarcheshmeh copper mine, south-eastern of Iran. Several influential parameters such as leaching time, leaching temperature, agitation speed, oxidizer type, potassium or sodium chlorate and hydrochloric acid concentration were investigated.
MATERIAL AND METHODS

Concentrate preparation and characterization

A representative sample of molybdenite concentrate from the Sarcheshmeh Copper Complex of Iran with a size distribution of 90% (in weight) less than 38 μm was used for chemical leaching experiments. The d_{80} of the sample was determined 33 μm using cyclosizer equipment. Cumulative pass percent versus size of fraction graph in a semilogarithmic scale is presented in Figure 1.

Separation of molybdenite from copper bearing minerals was carried out using a rougher and sequential seven flotation cells as cleaner in four series bank with capacity of approximately 20 tons per day (final concentrate). The schematic flotation process and sampling places in the circuit is illustrated in Figure 2.

The chemical and mineralogical analyses of the 5th, 6th and final concentrate are given in Table 1. There was 0.98% Cu in the 5th cleaner sample, the highest grade of the copper content in the three cleaners. The final concentrate was sampled from different barrels to prepare a representative sample and used for oxidative-chemical leaching experiments to extract molybdenum and rhenium. Molybdenite is the preferred host mineral for rhenium. Table 1 shows the rhenium content of molybdenite concentrates in different stages of the flotation circuit. The rhenium content of molybdenite concentrate produced by the Sarcheshmeh Copper Complex is relatively high (26-27).
The relationship between molybdenum, rhenium and copper in the different concentrate samples is demonstrated in Figure 3. The grade of molybdenum is increased from 5th stage to the 7th stage of the cleaner, and consequently by increasing the molybdenum content in the concentrate, the grade of rhenium is also increased from 550 ppm to 700 ppm in the final concentrate. In contrast, final concentrate had the lowest amount of copper (0.44 %).

Semiquantitative X-ray diffraction (SQXRD) technique was implemented to determine the major and minor minerals in the sample. X-ray powder diffraction patterns were obtained by a Siemens D-500 diffractiometer with Ni-filtered Cu–Ka radiation, and a goniometer speed of 1°2θ /min. The diffraction profiles with a 0.01 precision of d-spacing measurements were conducted from 5° to 70° 2θ. The results of the mineralogical characterization revealed molybdenite is the major phase of the Mo-bearing concentrate. Mineralogical characterization of the sample was also performed using an optical polarizing microscope (Leitz, ORTHOLUX II Pol-BK). This examination showed that molybdenite as the main mineral phase, chalcopyrite and covellite as Cu-bearing minerals, and pyrite as the minor phase (Figures 4 and 5). Chalcopyrite and pyrite could be distinguished readily in the molybdenite concentrate. These minerals liberated from the molybdenite in this size fraction but in some cases, Cu-bearing minerals and also pyrite were interlocked with molybdenite. Optical microscopy also provided information on color, morphology and crystallinity. The preparation procedure was as follows: small amounts of the sample were dispersed on a glass slide and were then mounted in embedding resin (Entellan (Merck) or Canada balsam) and overlain with a cover slip. This technique was routinely used both in the field and in the laboratory.
Polished and grain samples of the final molybdenite concentrate were gold coated, and analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray analyses (EDS) using Philips XL SEM. The samples were also analyzed with the back scattered electrons (BSE) technique. The results confirmed the mineralogical observations (Figure 6). Silicate minerals were also detected by EDS (Figure 6, point 3). The concentrate (feed) and the residues from the leaching experiments were examined under SEM. Samples were mounted on Al stubs and coated with gold. The instrument used for these studies was a CamScan MW 2300, with a field emission electron gun operating at 20 keV. The EDS data were analyzed using the CamScan MW 2300 software. The SEM technique generates X-rays with energies characteristic of the elements to a depth of approximately 5 µm. Secondary electron images revealing morphological contrasts were obtained. This technique allows resolution of surface features to a practical limit of about 1 µm, facilitating the distinction of pores, precipitates and areas of preferential reaction on the surface of particles.

It should be noted that there is no information on mineralogy of rhenium presented in the Mo-concentrate. After different characterization studies, neither SEM/EDS nor XRD could distinguish the rhenium in the concentrate. It seems that rhenium is presented or interlocked (Physical encapsulation) in the molybdenite lattice. Therefore, for extraction of rhenium in the liquid, molybdenite should be dissolved.

**Oxidative-chemical leaching tests**

The leaching experiments were carried out in a 1000 mL three neck flask (reactor). A magnetic heater-stirrer (IKA RH D-KT/C, Germany) was used as the base of the setup. The reactor was
fitted on magnetic heater-stirrer that reactor had two ports. The ports were used for temperature measurement, feed entrance and condenser. Temperature could be measured by thermometer and a condenser was needed to be reduced evaporation during experiments. The condenser ensured the pulp density remained constant. The scheme of the experimental setup is given in Figure 7.

For the leaching experiments, the solution was prepared using distilled water, pure HCl (Normally, concentrated HCl comes as about 36% HCl in water), and potassium chlorate or sodium chlorate from Merck Chemicals Co. and Panreac Co. After the desired temperature of the reactor content was reached, the predetermined amount of molybdenite concentrate was added to 100 ml leaching solution based on the required pulp density. The representative sample with weight of 5 g was used in all experiment. The particle size of the sample was $-37 \ \mu m$, ground using wet ball milling method and solids ratio of the pulp was approximately 5%. The solid material ($NaClO_3$ and $MoS_2$) were added into leaching solution (0.1 L of HCl with different concentration) in the round bottom flask after the temperature achieved at required level. The slurry was agitated (by a variable speed motor according to the pre-designed test). The temperature and agitation speed were read-out through controllers. Samples were taken at intervals and filtered before analysis of dissolved Mo and Re, using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The technology of molybdenum extraction from molybdenite concentrate by using sodium- or potassium chlorate has been investigated. For these experiments, six parameters (rotation speed, leaching time, temperature, type and concentration of oxidizer and acid concentration) were evaluated. The solid concentration was fixed at 5% in all tests. The parameters and their values are presented in Table 2.
For calculation of the fraction of Mo or Re leached, the following equation was applied (28):

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

[2]

where \( X_i \) is the Mo or Re extraction corresponding to sample \( i \), \( V_0 \) is the initial volume of the leaching solution in the reactor (mL), \( V_i \) is the volume of sample \( i \) withdrawn from the reactor (mL), \( C_i \) is the Mo or Re concentration in sample \( i \) (mg/L), \( M \) is the initial mass of the molybdenite concentrate in grams added into the reactor and \( C_M \) is the Mo or Re percentage in the molybdenite concentrate.

**RESULTS AND DISCUSSION**

The purpose of the present work is to examine the dissolution rate of molybdenite concentrate using potassium or sodium chlorate as the oxidant in acidic condition. Hydrochloric acid was used with K- and Na chlorate as powerful oxidizer to dissolve molybdenite to extract molybdenum and rhenium. Several influential parameters such as leaching time, leaching temperature, agitation speed, oxidizer type, potassium or sodium chlorate and hydrochloric acid concentration were investigated. In the leaching experiments, the solid concentration was constant at 5%, because of limitation in lab scale equipment.
Effect of time

The effect of leaching time on the molybdenum extraction was studied using a solid concentration 5% (MoS$_2$, 5 g), temperature 40°C, agitation speed 500 rpm, initial hydrochloric acid concentration 20% (diluted with water for five-fold) and sodium- or potassium chlorate 20 g (added separately). The results presented in Figure 8 show fast leaching of molybdenum with 40% and 18.1% molybdenum extraction within 3 hrs and ~44% and 20% after 4 hrs for (potassium or sodium) chlorate, respectively. Beyond 4 hrs, there is no significant increase in molybdenum extraction, so all further experiments were carried out for 4 hrs. The results showed that k-chlorate is more effective than sodium species for extraction of Mo-concentrate because of higher reactivity.

Effect of temperature

The extraction of molybdenum is also affected by leaching temperature. High molybdenum extraction may not be achieved in a short time at low temperatures whilst high temperatures have disadvantages such as higher energy. So, in the present study, a medium temperature range from 40 to 80°C was selected and its effect on molybdenum extraction was studied. Figure 9 shows the effect of temperature under the same conditions as before. Molybdenum extraction was increased from ~44% to ~60% for potassium chlorate and 20% to 44.5% for sodium chlorate when the temperature was increased from 40 to 80°C. There was no possibility to increase temperature to more than 80°C in these tests. MoS$_2$ leaching is a kind of chemical control reaction, in low temperature; the leaching rate is relatively low. With the increase of temperature,
the leaching reaction is increasingly accelerated (5). Therefore the appropriate temperature appears to be 65-70°C and all further experiments were carried out at this temperature range. The liquid temperature was fluctuated around 68°C.

**Effect of hydrochloric acid concentration**

Also, the extraction of molybdenum is also affected by acid addition. In our present study, a medium hydrochloric acid concentration ranges from 20% to 50% (diluted with distilled water, e.g. 50% means diluted for one-fold and 20% means diluted for five-fold) was selected and its effect on the molybdenum extraction was studied. Figure 10 shows the effect of hydrochloric acid concentration under the same conditions as before. Molybdenum extraction was increased from ~44% to ~75% for potassium chlorate and ~20% to ~73% for sodium chlorate when the hydrochloric acid concentration was increased from 20% to 50%. Therefore the appropriate hydrochloric acid concentration appears to be 35% and all further experiments were carried out at this hydrochloric acid concentration.

**Effect of agitation speed**

Agitation plays an important role in the leaching processes. The results of agitation are shown in Figure 11. Under the optimum leach conditions, molybdenum extraction was increased from ~72% to ~87% for potassium chlorate and ~70% to ~80% for sodium chlorate as the agitation speed was increased from 500 to 700 rpm; respectively. A further increase in agitation speed up to 700 rpm had no significant effect on the molybdenum extraction, so the agitation speed was
maintained at 600 rpm, which was enough to suspend the molybdenite particles during leaching tests.

**Effect of potassium or sodium chlorate concentration**

In our present study, the effect of the potassium chlorate and sodium chlorate mass ranging from 10 to 30 g on the molybdenum extraction was studied under optimum leach conditions. Figure 12 shows that molybdenum extraction was increased from ~48% to ~87% for potassium chlorate and 30% to 88% for sodium chlorate when oxidizer mass were increased from 10 to 30 g; respectively. The appropriate mass of oxidizer appears to be 25 g (5 g oxidizer/g conc.).

After dissolution of molybdenite to extract molybdenum, separation and purification approaches should be applied to produce molybdenum metal. Several methods have been extensively reviewed for molybdenum separation and purification from solution, which are potentially applicable to leach solutions of molybdenum ores and raw materials. The main methods include solvent extraction, ion exchange, membrane based separation, and precipitation. Solvent extraction is highly selective for recovery of molybdenum and the most promising method recommended for future research and development. Membrane based separation is next for selective extraction of molybdenum, purification of molybdenum solutions or co-recovery of other valuable metals. Ion exchange offers useful means for purification and/or co-recovery of other base metal impurities, although the scale of application of ion exchange in industry is limited.
Rhenium extraction

According to the results, rhenium extraction is directly correlated to the molybdenum dissolution. The relationship between rhenium and molybdenum extraction is presented in the following graph. By increasing molybdenum dissolution, rhenium extraction increases, but the rate of its dissolution is 4.5217 times that of molybdenum dissolution. If molybdenum extraction reach 9%, nearly 40% of rhenium dissolves. The results obtained from different leaching and bio-leaching tests are presented in Figure 13. Some tests showed that by extracting about 30% of molybdenum, all rhenium content of concentrate was extracted to the solution. According to the results, rhenium might be interlocked in the molybdenite lattice. In addition, many parameters influence the difference in leaching efficiencies between metals such as selectivity of leaching agent, concentration of metals in the leach solution, leaching conditions and reactivity of minerals or metals to lixiviant.

CONCLUSIONS

These experiments proved that use of potassium or sodium chlorate is an effective technique for extraction of molybdenum from the molybdenite concentrate. The experimental results showed that leaching time, solid concentration, leaching temperature, agitation speed, potassium or sodium chlorate and hydrochloric acid concentration have significant effect on the extraction rate. Advisable process operating parameters were established as follows: time: 4 hrs, hydrochloric acid concentration: 35%, solids ratio: 5%, temperature: 65-70°C, agitation speed: 600 rpm, the mass of potassium chlorate and sodium chlorate: 25 g (5 g oxidizer/g conc.). Under
these experimental conditions, the extraction of molybdenum is greater than 85%. In addition, dissolution of rhenium is directly related to the molybdenum extraction. Thus, in this condition, 100% of the rhenium dissolved and extracted from the molybdenite concentrate (data not shown). It is recommended that detailed mineralogical studies of rhenium in molybdenite concentrate will be useful for fully interpretation of some phenomena happen in the leaching mechanisms.

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REFERENCES


Table 1. Mineralogical and chemical analyses of the molybdenite concentrate in three cleaners.

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<th>Mineralogical</th>
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<th>6th Cleaner</th>
<th>Final Conc.</th>
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<td>CuFeS₂ (chalcopyrite)</td>
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<td>Re (ppm)</td>
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Table 2. The parameters of performed experiments.

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<tr>
<td>Oxidizer mass (gr)</td>
<td>10, 20, 25, 30</td>
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Figure 1. Particle size distribution of molybdenite determined with cyclosizer.
Figure 2. The schematic flotation process and sampling places in the circuit.
Figure 3. Relation of concentration of molybdenum, rhenium and copper in different samples.
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Figure 13. The relationship between rhenium and molybdenum extraction.