論文

Electro-oxidation of Molybdenum Concentrate in Sodium Chloride Solution*

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Dissolution behavior of molybdenum concentrate by electro-oxidation has been investigated in acidic and alkaline condition at constant current density of 625 A/m² (1 A) and temperature (313 K). The experiments on electro-oxidation of molybdenum concentrate obtained from Erdenet mine from Mongolia were carried out in an laboratory scale electrolysis cell with 10 mass % NaCl electrolyte. The overall current efficiency for MoS₂ dissolution was 97 % in alkaline and 92 % in acidic solution after 6 hours electrolysis, respectively. The current efficiency decreased to 82 % when the electrodes were not separated from the slurry. It has been shown that the dissolution of MoS₂ proceeds mainly by electrochemically produced oxychlorites in the solution. The residue obtained in acidic solution consisted of Si and Al, and that in alkaline solution consisted of Si, Al, Cu and Fe. In alkaline solution, Cu and Fe, which are main impurities of the concentrate, are separated by precipitation from leaching solution.

KEY WORDS : Electro-oxidation, Leaching of MoS₂, Molybdenum, Sulfide Dissolution

1. Introduction

Molybdenum recovery from porphyry copper ores, which consist of molybdenum and copper sulfides, is based on two procedures: ore upgrading by flotation and roasting the upgraded molybdenum concentrate (MoS₂) to obtain molybdenum oxide (MoO₃). The molybdenum recovery process, which includes pyrometallurgical operations, is efficient in terms of production rate, but it requires technology to overcome problems resulting from the emission of sulfur dioxide during roasting and a major loss of molybdenum that occurs during upgrading flotation (Gupta, 1992 ; Kummer, 1979).

The hydrometallurgical leaching process of molybdenite (MoS₂) offers several advantages : high purity molybdenum compounds can be recovered directly both from low-grade concentrate and complex ores, and separation of closely related metals such as rhenium from concentrate can be accomplished, and the process has low energy consumption and is environmentally sound. For these reasons, several investigations on molybdenite (MoS₂) leaching were made to improve

molybdenum recovery directly from ores and concentrates using various leaching agents such as nitric acid (Vizsolvy and Peters, 1980 ; Parsons et al., 1987) and sodium hypochlorite (NaClO) (Warren et al., 1977 ; Warren and Mounsey, 1983). However, the high cost of reagents consumed during the dissolution process prevents extension of these processes to a commercial scale.

In the past, the electro-oxidation process to recover molybdenum and rhenium from low-grade concentrates was investigated by the U.S. Bureau of Mines (Lindstrom and Scheiner, 1973 ; Scheiner et al., 1976, 1979). In this process, the strong oxidizer hypochlorite (ClO⁻) is produced in-situ by electrolysis of NaCl solution in the bipolar cell. One of the problems encountered was the generation of chlorate (ClO₃⁻). The formation of chlorate is a loss of chlorine and then a loss in current efficiency, since chlorate has no oxidizing ability under alkaline conditions (Scheiner et al., 1976 ; Gupta, 1992). To minimize chlorate formation in leaching solution, the condition for electro-oxidation was proposed to be in the pH range 4~5 (Barr et al., 1975, 1977). This condition, however, ends up with precipitation of molybdenum compounds in the presence of copper, because copper molybdate (CuMoO₄) has a lower solubility at pH 2.5~6.5 (Warren and Mounsey, 1983).

In Table 1, previous investigations into the hypochlorite leaching of molybdenum concentrate are summarized. As shown in the table, very little is known on the electro-oxidation of molybdenum concentrate in acidic solution.

The main purpose of this study is to investigate the electro-oxidation behavior of molybdenum concentrate in

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Table 1 Summary of previous studies on molybdenum concentrate leaching using oxychlorites.

Concentrate	References	pH of slurry	Oxidizer
Low grade molybdenum concentrate	Lindstrom and Scheiner, 1973; Scheiner et al., 1976, 1979	5.5 - 8.5	Produced by electrolysis of 10 mass% NaCl
High grade molybdenum concentrate	Warren et al., 1977 Warren and Mounsey, 1983	8.5 - 9	NaClO
	Barr et al., 1975, 1977	5 - 4	Produced by electrolysis of 10 mass% NaCl
High grade molybdenum concentrate	Present study	1.4 - 2 and 10	Produced by electrolysis of 10 mass% NaCl

acidic solution. The efficiency of utilization of in-situ generated oxidizers and recovery of molybdenum are also investigated.

2. Experimental

The molybdenum concentrate used in this study was obtained from Erdenet Mine of Mongolia. The chemical composition of the concentrate is shown in Table 2 together with the mineral phases. Figure 1 provides photos of scanning electron microscopy (SEM) photos of the molybdenum concentrate. The experimental set-up used for electro-oxidation of the concentrate is shown in Fig. 2. The catholyte was separated from the concentrate slurry by a glass filter. In some experiments anolyte was also separated from the slurry with a filter to avoid the oxidation of concentrate at the anode surface. Oxidizers formed in the anode compartments were mixed with slurry by pumping with 200 ml/min circulation. A platinum plate (20 mm × 40 mm × 0.1 mm) was used for the anode, and a spiral-shaped platinum wire (1 mm ϕ) served as the cathode counter electrode. The cell was isolated from air by an o-ring sealed gas-tight acrylic flange and rubber plugs.

The experimental conditions of this study are shown in the Table 3. During the electro-oxidation experiments, a constant 1 A current (625 A/m², anode surface) was applied to the cell using a galvanostat (Hokuto Denko Co. Ltd., HAB151). The temperature of the cell was controlled at 313 K using a digital hot plate/stirrer (Iuchi Co. Ltd., PM-730). The anode potentials (versus Ag/AgCl sat. KCl reference electrode), pH, and oxidation-reduction potential (ORP) of the anolyte solution were monitored during electrolysis. In some experiments, the pH of the anolyte was adjusted to 10 by adding 1.0~5.0 M NaOH and to 1.4~2.0 by adding 6.0 M HCl solution, respectively.

In all experiments, 500 ml of 10 mass % NaCl solution was used and the electrolysis was conducted for 6 hours. Molybdenum concentrate dispersed in the anolyte was stirred at 300 rpm. Every hour, 5 ml of suspension was taken for chemical analysis. The contents of oxidizers, as a hypochlorite (ClO⁻) and chlorate (ClO₃⁻) produced in-situ by electrolysis, were determined by thiosulfate titration after reduction of these oxidizers by an excess of iodide and bromide ion (Farkas and

Table 2 Chemical composition and mineral phases of molybdenum concentrate used in this study.

Elements		Amount of elements (mass %)
Molybdenum	Mo	49.0
Sulfur	S	44.0
Iron	Fe	1.90
Copper	Cu	1.60
Silicon	Si	1.10
Chlorine	Cl	0.58
Phosphorus	P	0.48
Aluminum	Al	0.48
Calcium	Ca	0.33
Potassium	K	0.27
Magnesium	Mg	0.22
Rhenium	Re	0.04

Minerals		Content of minerals (mass %)
Molybdenite	MoS ₂	95.0
Chalcocite	Cu ₂ S	3.0
Haycockite	Cu ₃ Fe ₂ S ₅	2.0

Fig. 1 SEM image of the molybdenum concentrate used in this study. **Fig. 2** A schematic diagram of the experimental set-up (A glass filter for anode was removed in some experiment).

Lewin, 1947; Fumina et al., 1983; Kolthoff et al., 1978). Sulfate (SO₄²⁻) ion concentration was analyzed by EDTA (ethylenediaminetetraacetic acid) titration for Ba²⁺ after adding an excess of barium ion over the amount of SO₄²⁻ in solution (Kolthoff et al., 1978). The reliability of this sulfur

analysis was confirmed by ICP-AES analysis (Parkin Elmer, Optima 3300SYS).

After electrolysis, the residue was dried and its morphology was observed by SEM. The contents of molybdenum, rhenium, copper, iron and silicon in the leach solution, cathode deposit and residue were analyzed by ICP-AES analysis.

3. Results and Discussion

3.1 Electro-oxidation of molybdenum concentrate in acidic and alkaline solution

The typical SEM images of the residue and the corresponding elemental mapping of Si, Fe, Cu, Al, Mo or S are shown in Figs. 3 and 4. The residues shown in Figs. 3 and 4 are respectively obtained under acidic and alkaline conditions that corresponds to Exp. # 1 and # 2 in Table 3. Because of the small energy difference in the characteristic X-rays for Mo and S (~ 2.28 keV), these elements could not be mapped separately, and are given in the same image.

No significant difference in morphology of solid particles was observed before and after the experiments, when comparing Figs. 1, 3 and 4, although the mass of the sample was reduced to 75 % both in acidic and alkaline solution after the experiment. Figures 3 and 4 indicated that the residue particles consist of Si and Al components, and that those obtained from alkaline solutions contain also Fe and Cu. A summary of the mass balance after 6 hours electrolysis is presented in Table 4. The dissolved amount of molybdenum, sulfur and rhenium was almost same both in acidic and alkaline condition. A large amount of Cu and Fe entered the residue in the alkaline medium. They were distributed randomly in the resi-

due particles. These results suggest that dissolution rate of the concentrate both in acidic and alkaline solution is almost

Table 3 Experimental conditions for electro-oxidation of molybdenum concentrate. ($I = 1$ A, $T = 313$ K, $t = 6$ hrs., 500 ml, 10 mass % of NaCl solution).

Exp. #	Weight of concentrate, ω_{MoS_2} / g	pH of slurry	Cell configuration	Note: Corresponding Figs. and Tables
1	2	2	Cathode separated	Fig. 3 and Table 4
2	2	10	Cathode separated	Fig. 4 and Table 4
3	5	2	Both anode and cathode separated	Fig. 5
4	5	2	Cathode separated	
5	5	10	Cathode separated	Fig. 7
6	5	Uncontrolled, (from 3.4 to 1.4)	Cathode separated	Fig. 8
7	5	10	Without separation of anode and cathode	Table 5

Table 4 Elemental distribution of molybdenum concentrate after 6 hours electro-oxidation with concentrations ($\omega_{\text{MoS}_2} = 2$ g).

Exp. #	Location	Elemental distribution (mass %)						pH
		Mo	S	Re	Cu	Fe	Si	
1.	Solution	79.4	70.0	65.3	69.1	62.9	18.7	2
	Catholyte	0.3	0.3	0.1	0	0	0	
	Cathode	0	0	0.3	1.0	0	0	
	Residue	20.3	29.7	34.3	29.9	37.1	81.3	
2.	Solution	75.1	68.9	46.3	1.2	0.2	33.1	10
	Catholyte	0.9	0.7	0.4	0	0	0	
	Cathode	0	0	0	0.3	0.3	0	
	Residue	24.0	30.4	53.3	98.5	99.5	66.9

Fig. 3 SEM image and corresponding elemental mapping of Si, Fe, Cu, Al, Mo or S in the residue at acidic condition (Exp. # 1).

Fig. 4 SEM image and corresponding elemental mapping of Si, Fe, Cu, Al, Mo or S in the residue at alkaline condition (Exp. # 2).

Fig. 5 Electro-oxidation of Mo-concentrate when use separated and unseparated anode at pH = 2. (a): Mo and S concentration, (b): ORP of slurry. (Exp. # 3 and # 4).

identical, and Cu and Fe were precipitated out from alkaline solution after dissolution.

3 · 2 Anode separation to clarify of oxidation process of molybdenum concentrate

During the electro-oxidation process, molybdenite particles can be oxidized on the anode surface when the anode is not separated from the slurry. To clarify the contribution of this direct oxidation on the anode, preliminary experiment were carried out using separated and unseparated anode cells.

Figure 5 shows a representative result of electro-oxidation of molybdenum concentrate when using separated and unseparated anode cell at slurry pH 2.0 (cf. Exp. # 3 and # 4 in Table 3). In both cases, the concentration of molybdenum, C_{Mo} , and that of SO_4^{2-} , $C_{SO_4^{2-}}$, in the solution increased linearly with time. The leaching rate with unseparated anolyte was slightly higher than that with separated anolyte condition. This result clearly shows that the main oxidation process of molybdenite occurred in the bulk of solution, not on the electrode surface. The sulfate ion concentration determined by EDTA titration method was identical with the results of total sulfur analysis by ICP-AES. The sulfur in the concentrate is, therefore, oxidized to sulfate. This result is reasonable considering the high ORP of the slurry, which probably corresponds to Cl^-/ClO^- equilibrium, as shown in Fig. 5 (b), monitored during the course of the experiments. Under this condition, molybdenum in the solution is expected to exist in the highest oxidation state such as $HMoO_4^-$ (Brookins, 1988). The concentration of sulfur was 2.2 times larger on average than the molybdenum concentration in the slurry. This result corresponds well with the stoichiometry of MoS_2 , and the value slightly higher than 2 may be attributed to the dissolution of other metal sulfides in the concentrate.

Assuming SO_4^{2-} and $HMoO_4^-$ formation during dissolution, the oxidation reaction of MoS_2 may be associated with an 18-electron transfer per mole of MoS_2 , as expressed by the equation :

Fig. 6 Production of oxychlorites during electrolysis of 10 mass% NaCl solution (a) : In alkaline solution (pH = 10) (b) : In acidic solution (pH = 2) (c) : ORP of the solutions (T = 313 K, I = 1 A).

The dash and chain lines in Fig. 5 (a) are calculated concentration of Mo and SO_4^{2-} , respectively, using electric charge (Q) applied to electrolysis and Eq. (1) when current efficiency, ϵ , is unity. The calculated values agree well with the experimental results of molybdenum and SO_4^{2-} concentration, which implies that a current efficiency for dissolution of the concentrate is close to 100 % ($\epsilon = 1$) in the present condition. It is considered that sufficiently strong oxidizers are generated electrochemically in acidic solution to decompose molybdenite concentrate at high efficiency.

3 · 3 Electrochemical production of oxidizers

Figure 6 illustrates the change in the concentration of oxychlorites as a function of time during electrolysis of NaCl solution in the absence of molybdenum concentrate. Due to the difference in the oxidation state of oxychlorites, the oxychlorite concentrations were normalized by equivalent-electron transfer number ($n = 2$ for ClO^- , $n = 6$ for ClO_3^-), and expressed as equivalent concentration, N_{ox} ($N_{ox} = n C_{ox}$). The corresponding scales for mole concentrations of ClO^- and ClO_3^- , respectively, are given on separate axes on the right side of the figure.

As shown in Fig. 6 (a), when the anolyte pH is controlled at 10.0, ClO^- production increases with time at the beginning of the electrolysis but the production rate decreases substantially after two hours of electrolysis. When the concentration of ClO^- in solution reaches about 0.05 mol/l, the ClO_3^- generation appears to start. The broken line in Fig. 6 (a) presents the calculated concentration of oxidizer, N_{ox} , directly from following equation ;

$$N_{\text{ox.}} = \varepsilon \cdot Q / F = \varepsilon / F \int_0^t i dt \quad (2)$$

where Q is charge passed through the electrodes (C), i : applied current (A, C/s), t : time (s); ε : current efficiency for oxidizer production, F : Faraday's constant (96500 C/mol).

The total concentrations of oxidizer at pH=10.0 are indicated by the filled triangles. These values are turned be close to the calculated values. When the anolyte pH is kept at 2.0, the oxychlorite concentration does not increase significantly, and is lower than 0.01 mol/l. The initially transparent and colorless electrolyte solution turned pale green during electrolysis. This indicates the formation of hypochloric acid in acidic solution.

As shown in Fig. 6 (b), the ORP of the anolyte solutions increases sharply at the beginning of the electrolysis, and becomes almost constant at 1.07 and 1.39 V at pH 2.0 and 10.0, respectively. This result shows that both solutions have a very high oxidizing potential, and that solutions are thermodynamically suitable for dissolution of MoS_2 by oxidation.

3 · 4 Electro-oxidation reactions of molybdenum concentrate in acidic and alkaline solution

Figure 7 shows the result of electro-oxidation of molybdenum concentrate when the anolyte pH is controlled at 10.0 (Exp. # 5). In this case, the anode was not physically separated from the slurry with the purpose to increase the leaching efficiency. In addition to their concentration changes determined by chemical analysis, the amount of MoO_4^{2-} and SO_4^{2-} calculated from the charge (Q) using Eqs. (1) and (2) are shown by the dash and chain lines, respectively, in Fig. 7

Fig. 7 Result of electro-oxidation of molybdenum concentrate in alkaline solution.

(a): Mo, S, and hypochlorite (ClO^-) concentration,
(b): ORP of slurry,
(c): consumption of OH^- ion for pH adjustment. (Exp. # 5).

(a). An excellent agreement of the calculated values with the observed concentrations of both Mo and SO_4^{2-} indicates that MoS_2 is leached at a sufficiently high potential to form SO_4^{2-} with a very high current efficiency.

It was reported that ClO_3^- is stable and has a limited oxidizing potential in alkaline solution, and therefore, the main leaching reaction of MoS_2 can be expressed by the following reaction with ClO^- as an oxidizer (Warren and Mounsey, 1983; Barr et al., 1975, 1977).

The amount of OH^- added during the experiment to keep the pH at 10.0 is shown in Fig. 7 (c). The broken line in Fig. 7 (c) denotes the calculated amount of OH^- consumed according to the reaction of Eq. (3) and Q assuming an 18-electron transfer (Eq.(1)). After 2 hours of leaching, the variation of OH^- consumption with time becomes parallel to the calculated line. The difference between the observed and calculated values is probably attributable to the amount of OH^- necessary for the adjustment of the pH of the solution containing the oxidizers.

An n_{OH} value of the intercept of an interpolated straight line obtained by least squares fitting of the last 5 points in Fig. 7 (c) is 0.035 mol OH^- . As is well known (Takahashi and Masuko, 1979; Novak, 1982), the Cl_2 gas generated by electrolysis of NaCl-solution dissolves into alkaline solution according to the following reactions;

According to Eq. (5), 2 moles of OH^- are consumed for

Fig. 8 Result of electro-oxidation of molybdenum concentrate in acidic solution.

(a): Mo, S, and hypochlorite (ClO^-) concentration,
(b): ORP of slurry,
(c): Changes of pH (Exp. # 6).

each mole of ClO^- formed by dissolving Cl_2 gas in the slurry. The observed concentration of ClO^- in the solution throughout the experiments (Fig. 7 (a)) was found to be about 0.002 mol/l. This also may suggest the rapid consumption of hypochlorite by reaction with the concentrate.

Figure 8 shows representative results of the electro-oxidation of the molybdenum concentrate in acidic solution (Exp. # 6). As shown in Fig. 8 (a), the sulfate and molybdenum contents in the solution increased linearly with time of current passage. The concentrations of Mo and SO_4^{2-} calculated by Eq. (2), on the basis of an 18-electron exchange, are also shown in Fig. 8 (a) as dash and chain lines, respectively. Similarly to leaching in alkaline solution, the expected values for concentration of Mo and SO_4^{2-} are in good agreement with the observed values. This indicates that the electrochemically produced oxidizer effectively reacts with the concentrate to convert sulfide sulfur into sulfate ion. The low concentration of the oxidizer in the solution (less than 0.002 mol ClO^- /l), suggests that the generated oxidizer is rapidly consumed for the oxidative leaching of MoS_2 also in acidic solution. Figure 8 (c) shows the variation of pH as a function of time. In the first one hour of electrolysis, the pH value of the solution decreased from 3.4 to 1.7. It then gradually approached pH 1.4.

The variation of Mo and SO_4^{2-} concentration with time indicates that the reaction described by Eq. (1) is an oxidation reaction also in acidic solution. The oxidizers taking part in the leaching are represented to be HClO , and ClO_3^- according to the reactions (7) and (8).

The leaching reaction for MoS_2 can be given by Eq. (9) and (10).

From the present results alone, it is difficult to identify which reaction is predominant because the electrochemically produced oxidizers are consumed rapidly with high efficiency.

Table 5 Elemental distribution of molybdenum concentrate after 6 hours electro-oxidation ($\omega_{\text{MoS}_2} = 5 \text{ g}$).

Exp. #	Location	Elemental distribution (mass %)				Current efficiency (%)	pH	Note
		Mo	S	Re	Cu			
5	Solution	47.0	39.5	44.5	-	96.5	10.0	Cathode separated
	Cathode	-	-	0.2	1.0			
	Residue	52.7	60.1	55.3	99.0			
6	Solution	45.1	39.5	42.2	47.9	92.4	Uncontr. (3.4-1.4)	Cathode separated
	Cathode	-	-	0.3	1.2			
	Residue	53.9	60.0	57.5	50.9			
7	Solution	39.9	36.2	28.3	19.5	82.0	10.0	Without separation of cathode and anode
	Cathode	-	-	0.9	1.5			
	Residue	60.1	63.8	70.8	79.0			

* In all experiments catholyte solution was not analysed.

Nevertheless, equations (9) to (10) correspond well not only to the concentrations of molybdenum and sulfate ions but also to the fall of pH with time.

The distribution of Mo, Re, Cu and S after 6 hours of electrolysis is summarized in Table 5. As shown in this table, the fractions of copper and rhenium deposited on the cathode are very small. Current efficiencies calculated from the molybdenum amount in the solution using Eqs. (1) and (2) are also listed in the 7th column of Table 5. Data for Exp. # 5 and # 6 in Table 5 correspond to the results shown in Figs. 7 and 8 respectively. Exp. # 7 in Table 5 was conducted without any separation of cathode and anode, with the pH controlled at 10. The current efficiency for the unseparated cell was 82 % for MoS_2 dissolution, somewhat lower than for the other experiments with separated anode and cathode chambers. This is probably due to loss of oxidizers which can be electrochemically reduced on the cathode surface. It can be seen from the table that molybdenum and rhenium are leached to almost the same extent in both acidic and alkaline solution, whereas copper enters in the residue, especially in the case of a high pH value.

4. Conclusions

Molybdenum concentrate suspended in 10 mass % NaCl solution was dissolved by electrochemically produced strong oxidizers. The production efficiency of oxychlorites in acidic solution was found to be lower than that in alkaline solution, but current efficiency for dissolution of MoS_2 was at a high level, more than 92 % for the both cases. The dissolution behavior of MoS_2 during electro-oxidation was explained well with the analytical results and ORP of the solution, alkaline or acid consumption during the experiments, and with the SEM image of concentrate and residue. After electrolysis, the solid particle of residue obtained in acidic solution consists of Si and Al components while that obtained in alkaline solution consists of Si, Al, Cu and Fe components. In alkaline solution, Cu and Fe remained in residue due to low solubility of their hydroxide compounds. The capability of the electro-oxidation leaching process for molybdenum concentrate even in acidic sodium chloride solution has been confirmed, and this method using acidic medium could be utilized for molybdenum recovery from concentrate.

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塩化ナトリウム水溶液中におけるモリブデン精鉱の電解酸化

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酸性もしくはアルカリ性の塩化ナトリウム水溶液中におけるモリブデン硫化物精鉱の溶解メカニズムに関する研究を行った。溶解実験は、モンゴル国・エルデネット鉱山産のモリブデン硫化物精鉱粉末を 10 mass % の塩化ナトリウム水溶液と混合し、このスラリーを 313 K の電解セル内で 1 A の定電流で電解し、 MoS_2 の溶解反応を解析した。6 時間の溶解実験後、 MoS_2 の溶解の電流効率は、アルカリ性の浴の場合 97 %、酸性浴では 92 % であった。また、電解セルの電極をスラリーと分離せずに電解を行った場合の電解効率は 82 % であった。電解酸化プロセスにおけるモ

リブデン硫化物の溶解は、主として電気化学的に生成したオキシクロライドによることを反応浴の化学分析により示した。酸性浴中での溶解後の残査は Si と Al を含んでいたが、アルカリ浴の残査は精鉱中の主たる不純物である Si, Al, Cu および Fe を含んでいた。この結果より、溶液からこれらの不純物を析出除去できることが明らかとなった。

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