Recovery of Molybdenum from Sulfide Concentrate by Electro-Oxidation and Precipitation*

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Leaching of molybdenum concentrate in NaCl aqueous solutions by electro-oxidation has been investigated, and the major process parameters, such as current density, temperature, and pulp density (nominal content of the concentrate in slurry) have been experimentally examined. The leaching rate of the concentrate was found to be proportional to current density, while the molybdenum concentration in the leach solution increased linearly with time. These results show that the concentrate was effectively oxidized by oxidizers produced by electrolysis of the NaCl solution, then dissolved rapidly into the solution. Increase in pulp density results in preferential oxidation of iron and copper in the concentrate, and it reduces the efficiency of molybdenum extraction. With the purpose of examining the feasibility of molybdenum recovery through solubility change, the pH dependence of molybdenum solubility in 10 mass% NaCl solution was investigated at various temperatures between 298 and 353 K. The solubility of molybdenum was found to be lower than 0.05 mol/l in the range of pH from 2 to 3, and increased with increasing temperature and pH of the solution. Precipitation experiments from leach solution were then examined by changing pH of the solution, and solid $\text{MoO}_3 \cdot (\text{H}_2\text{O})_x$ crystals, free of sulfur, were obtained from the leach solution containing large amount of SO_4^{2-} . Trace rhenium in the concentrate was found dissolve into the leach solution and co-precipitate with molybdenum during this process.

KEY WORDS : Molybdenum Sulfide, Electro-Oxidation, Leaching of MoS_2 , Separation and Recovery, Rhenium

1 . Introduction

In the previous paper (Darjaa *et al.*, 1999), the effectiveness of leaching molybdenum concentrate by electro-oxidation has been confirmed. This work includes production of oxidizers and the mechanism of leaching reaction during the process. The experimental results show that the electro-oxidation process can be explained by the 18 electron transfer reaction of molybdenite (MoS_2) with oxidizers produced from aqueous NaCl solution by electrolysis.

The electro-oxidation process is known to strongly depend upon many interconnected parameters. In the past, process parameters such as salt concentration, pH of leachante, electrolysis time and temperature on molybdenum extraction during electro-oxidation were investigated using a bipolar cell system by the researchers at the U.S. Bureau of Mines (Lindstrom and Scheiner, 1973; Scheiner *et al.*, 1976, 1979). Warren and Mounsey (1983) have described the roles of pH and carbonate ion during molybdenum extraction. Hypochlorite decomposi-

tion and chlorate formation in the leaching process were also examined, and many process parameters were investigated to minimize byproduct chlorate formation (Barr *et al.*, 1975, 1977). These electro-oxidation process studies are discussed for neutral or alkaline solution, and little is known about acidic solutions.

The purpose of this work is to describe major process parameters, such as current density, pH of slurry, leaching time, pulp density and temperature, which are examined in both alkaline and acidic solution. The feasibility of molybdenum recovery from the leach solution was tested by changing the solubility of molybdenum entities with pH. For a better understanding of molybdenum recovery experiments by precipitation, the solubilities of molybdenum in NaCl solutions are also given.

2 . Experimental

2 · 1 Electro-oxidation experiment

The molybdenum concentrate used in this study was obtained from Erdenet Mine of Mongolia, which contains 95 % of MoS_2 . Major impurities are iron and copper at the level between 1 and 2 mass%, and it contains about 40 mass ppm of rhenium. This trace rhenium is well known to be important as this is the primary resources of this rare element (Gupta, 1992). The morphology and detailed chemical composition of the concentrate is shown in the previous paper (Darjaa *et al.*, 1999).

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Fig. 1 Flow chart of the experimental procedures for dissolving concentrate by electro-oxidation.

Fig. 1 shows a flow chart of the electro-oxidation experiments. The slurry, a mixture of molybdenum concentrate and 10 mass% NaCl solution, is used for the electro-oxidation leaching. The slurry is intermittently sampled during electrolysis. It is then subjected to various chemical analyses after filtration.

The experimental set-up used for electro-oxidation of the concentrate is shown in Fig. 2. Oxidation leaching of molybdenum concentrate is carried out by oxidizers produced *in-situ* by electrolysis of the NaCl solution in the cell. A platinum plate (20 × 40 × 0.1 mm) denoted by A in Fig. 2 was used for the anode, and a spiral-shaped platinum wire (1 mm ϕ) described by C in Fig. 2 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 amount of concentrate particles directly oxidized electrochemically on the anode surface is found to be negligible (Darjaa *et al.*, 1999), therefore, the anode was not separated with filtering materials but was directly inserted into the slurry in this study. The catholyte with a chamber and a glass filter for liquid junction was separated from the slurry to avoid electrochemical reduction of oxidizers produced at anode.

The experimental conditions employed in this study are summarized and shown in Table 1. During the electro-oxidation experiments, either a constant 0.5 or 1 A (625 A/m² vs. anode surface) current was applied to the cell using a galvanostat (Hokuto Denko Co. Ltd., HAB151). The temperature of the cell was controlled at 313 or 353 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 10.0 by adding 1.0–5.0 M NaOH and to 1.4–2.0 by adding 6.0 M HCl solution.

In the most of experiments, 5 g of concentrate was slurried

- A - Anode
- C - Cathode
- 1. Anolyte
- 2. Sampling port
- 3. Burette for NaOH and HCl supply
- 4. ORP sensor
- 5. pH electrode
- 6. Ag/AgCl electrode
- 7. Thermometer
- 8. Catholyte
- 9. Glass filter
- 10. Agar separator
- 11. Magnetic stirrer
- 12. Temperature bath

Fig. 2 Schematic diagram of the cell for dissolving molybdenum concentrate by electro-oxidation.

Table 1 Experimental conditions for electro-oxidation of molybdenum concentrate.

Exp. #	Current, i / A	pH of slurry	Electrolysis time, t / hr.	Pulp density, C'_{MoS_2} (mass%)	Temp., T / K	Note
1	0.5	2	6	1	313	Fig. 4
2	1	2	6	1	313	
3	1	Uncontrolled (from 3-0.2)	10	1	313	Fig. 5
4	1	2	10	1	313	
5	1	10	10	1	313	
6	1	2	6	4	313	Figs. 6 & 7
7	1	2	6	16	313	
8	1	2	6	27	313	
9	1	Uncontrolled (from 3.8-0.2)	10	1	353	Fig. 8
10*	1	9	10	5	313	Tables 2&3
11*	1	9	16	5	313	

Constant parameters: 500 ml, 10 mass% NaCl solution.

* : 100 ml solution was used.

with 500 ml of 10 mass% NaCl solution, and the electrolysis was conducted for 6 to 10 hours. In some experiments, 4 to 27 times larger pulp density was employed for identifying the behavior of impurities present in the concentrate. In these experiments with high pulp density, 20, 100, and 200 g of the concentrate were mixed with 500 ml of NaCl aqueous solution. The slurry was stirred at 300 rpm during leaching for all cases, and 5 ml of the solution containing suspension was intermittently taken for analysis. Chemical analysis of the solution is carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis (Parkin Elmer, Optima 3300 SYS). The reliability of the sulfur analysis was confirmed by sulfate (SO_4^{2-}) ion concentration analysis by EDTA (ethylenediamine-tetraacetic acid) titration of Ba^{2+} after adding an excess of barium ion into the SO_4^{2-} solution (Kolthoff *et al.*, 1978).

2.2 Solubility measurement of molybdenum in 10 mass% NaCl solution

The solubility of the molybdic acid was determined at con-

stant temperatures 298, 313, 333, and 353 K in the range of pH between 0 and 6.5. Pure molybdic acid (assay 94 % MoO_3 , Wako Pure Chemical Ind. Ltd.) or sodium molybdate (99.0 %, Wako Pure Chemical Ind. Ltd.) was weighed and dissolved into 100 ml of 10 mass% NaCl solution. Temperature of the solution was controlled using a digital hot plate / stirrer. The pH of the solution was adjusted by adding 5.0 M NaOH or 6.0 M HCl solution using an automatic infusion pump (Nipro, FP-950). When temperature and pH became constant after about 15 minutes, 5 ml of solution was taken by syringe connected with a disc-capsule filter. The sampled solutions were then diluted to 100 ml, and some solutions having even higher concentration of molybdenum were further diluted by 5 or 10 times. The molybdenum concentration in the solution was determined by ICP-AES.

2 · 3 Molybdenum recovery from leach solution

Precipitation of molybdenum from leach solution after electro-oxidation at pH = 9 was investigated. Fig. 3 represents a flow chart of this procedure. The procedure for recovering molybdenum from its sulfide concentrate consists of two major steps; (1) electro-oxidation of molybdenum concentrate in alkaline medium, which is described above, and (2) pH adjustment and heating of the leach solution for precipitation of molybdenum oxide compounds. The apparatus and experimental methods for electro-oxidation of molybdenum concentrate are identical to those described in the previous section. 5 g of molybdenum concentrate is added to 10 mass% NaCl solution (100 ml) and the pH of the slurry is adjusted to about 9 with 5 M NaOH solution. The electro-oxidation experiment of molybdenum concentrate is carried out for 10 and 16 hours at constant temperature 313 K. After electro-oxidation, solid particles in the slurry are filtered and removed by vacuum suction. Precipitation of molybdenum compound oxides from the solution is conducted in a 100 ml beaker equipped with pH meter and automatic infusion pump for HCl solution. After changing pH to around 0.5, the solution is heated to 343–353 K with stirring by a glass stick. The resultant precipitate is then dried in a vacuum dryer (Vacuum Drying Oven, Iuchi DP 33) at 473 K. Chemical analysis of the leach solution before and after precipi-

Fig. 3 Flow chart of the experimental procedures for separating molybdenum from the leach solutions from electro-oxidation experiments.

itation is carried out by ICP-AES. The composition of the precipitate is analyzed both by X-ray fluorescence analysis (XRF) and ICP-AES. The solid samples are also subjected to X-ray diffraction analysis (XRD) and morphology observation by scanning electron microscopy (SEM) after drying.

3. Results and Discussion

3 · 1 Effect of major process parameters on electro-oxidation of molybdenum concentrate

Fig. 4 shows the change of molybdenum and sulfur concentration in the solution during an electro-oxidation experiment at 313 K and pH = 2. The experiments were carried out either at 0.5 or 1 A constant current (Exp. # 1 and # 2 in Table 1). The corresponding current densities are 313 and 625 A/m^2 (anode surface), respectively. When the current density doubles from 0.5 A to 1 A, the rate of molybdenum dissolution increases two times. This result shows that leaching of the concentrate is rate limited by the supply of electrochemically generated oxidizers.

The solid and broken lines shown in Fig. 4 are calculated values for molybdenum and sulfur concentration according to following equation.

In both experiments, the calculated values agree well with the changes in measured concentration of molybdenum and sulfur. During electro-oxidation, the electron in the right hand side of the Eq. (1) is consumed by reduction of anodically generated oxidizers such as ClO_3^- , and dissolution of MoS_2 proceeds rapidly. Detailed discussion for electrochemical generation of the oxidizers has already been given in the previous paper (Darjaa *et al.*, 1999).

The ORP of the slurry was almost constant throughout the electro-oxidation experiment, but the value at 1A condition was about 0.3 V higher than that at 0.5 A condition. This is probably due to differences in the accumulated amount of oxidizers present in the solution.

Fig. 4 (a) : Change of molybdenum and sulfur concentration during electro-oxidation with different current densities, (b): ORP of slurry (Exp. # 1 & 2).

Fig. 5 Change of (a) molybdenum and sulfur concentration, (b) copper and iron concentration, (c) ORP of the solution during electro-oxidation with various pH solutions. (Exp. # 3, 4, and 5). The pH change under uncontrolled condition is shown in (d).

Fig. 5 (a) shows the change of molybdenum and sulfur concentration versus time with various pH values (Exps. # 3–5 in Table 1). The electrolysis duration was extended from 6 to 10 hours using 1 mass% of molybdenum concentrate in NaCl solution. In Exp. # 4 and 5, the pH of the solution was controlled at 10.0 and 2.0, respectively, however, pH of the solution was not controlled in Exp. # 3. In all cases, molybdenum and sulfur concentration increase with time up to 6 hours electrolysis. Chained and broken lines in the figure are the calculated concentration of MoO_4^{2-} and SO_4^{2-} according to Eq. (1). These results are consistent with the previous study, in which 6 hours electro-oxidation was carried out using a separated anode cell to verify stoichiometric dissolution of MoS_2 (Darjaa *et al.*, 1999). The observed values of sulfur are slightly higher than the calculated values in all cases. This may be attributed to the leaching of other metal sulfides present in the concentrate.

It is worth noting that the molybdenum concentration in the experiment at pH = 2.0 (Exp. # 4) shown in Fig. 5 (a) started to decrease after 7 hours electrolysis, and leveled off at 0.004 mol/l. The corresponding sulfur concentration steadily increased even after 7 hours, therefore, molybdenum concentrate is considered to be dissolving in the same ratio continuously. The decrement of molybdenum concentration is probably due to precipitation of molybdenum compounds because the solubility of molybdenum is shown to be minimum at pH = 2.0 (See section 3.2 in detail).

The dissolution behavior of copper and iron at different pH levels is shown in Fig. 5 (b). In alkaline solutions (pH = 10, Exp. #5), copper and iron concentrations were about 10^{-6} to 10^{-5} mol/l for the first 3 hours, but the concentration of these elements fell below the detection limit of the analysis after 6 hours electrolysis. This result is quite reasonable because the solubility of copper and iron is very small in alkaline solutions. In the acidic or uncontrolled condition, copper concentration is found to be high from the early stages of the experiment. On the other hand, iron concentration gradually increased as electrolysis continued. These results indicate the iron is leached out by electro-oxidation, while copper dissolution occurs only by acid leaching. The dissolution behavior of iron and copper with changing pulp densities will be discussed in detail in the next section.

The ORP and pH change during the experiments are shown in Fig. 5 (c) and (d), respectively. As shown in Fig. 5 (d), the pH of the solution with uncontrolled pH (Exp. # 3) decreased from 3.1 to 0.5 at first in one hour and then gradually decreased to 0.2, and then became almost constant.

Fig. 6 shows the change of molybdenum and sulfur concentration versus time with various pulp densities at an applied current of 1 A. For identifying the behavior of iron and copper present in the concentrate at about 2 mass%, pulp density was increased to 4 to 27 times larger than the cases given in the previous sections. The leaching of molybdenum and sulfur is almost identical to the results calculated according to reaction (1) in a condition that the pulp density is low at 4 mass%. When the pulp density increases, however, the sulfur concentration increases from the beginning of experiment as shown in Fig. 6.

High sulfur content in the high pulp density solution may be caused by dissolution of other sulfide compounds such as copper and iron sulfides present initially in the concentrate. The molybdenum concentration slightly deviates towards lower value from the calculated one, especially at high pulp densities. This is probably due to consumption of the oxidizers by those

Fig. 6 Change of (a) molybdenum and sulfur concentration, (b) ORP of the solution during electro-oxidation with various pulp densities (Exp. # 6, 7, and 8).

Fig. 7 Effect of pulp density on dissolution of molybdenum, iron and copper (Exp. # 6, 7, and 8). The amounts of dissolved elements before and after electro-oxidation are shown in terms of their concentration.

sulfides which are oxidized more easily than molybdenum sulfide. The results shown in Fig. 6 imply that impurities in the concentrate affect the leaching behavior of the concentrate especially when the pulp density is high.

The dissolution behavior of molybdenum, copper and iron in the concentrate before and after 6 hours electrolysis for each pulp density is summarized in terms of their concentrations in Fig. 7. In all experimental conditions, the amount of oxidizers produced during the experiments were unchanged because a constant current electro-oxidation was carried out for the same periods. The figure indicates that dissolution of molybdenum and iron is very low before electrolysis in all pulp densities. When pulp density increases, dissolved amount of iron increases after electro-oxidation, and in turn, that of molybdenum decreases. This result clearly indicates that oxidizers produced by electro-oxidation are preferentially consumed for dissolving iron sulfides. As shown in Fig. 7 (c), copper dissolution increases with increasing pulp density before electrolysis. The copper in the concentrate probably dissolved as Cu^{2+} in the solution. However, the amount of copper dissolved by electro-oxidation is found to be small in all experimental conditions.

So far it has been shown that MoS_2 can be oxidized completely at 313 K even under strong acidic conditions (uncontrolled electro-oxidation process, Exp. # 3 in Table 1). The effect of temperature on the oxidation of molybdenite was then examined under uncontrolled pH condition. Fig. 8 gives the results of Exp. # 9 carried out at temperature 353 K, together with the result of Exp. # 3 at 313 K. Electro-oxidation of the concentrate at 353 K appears to be as efficient as that at 313 K. This result is useful for practical application because the higher temperature solution is suitable for subsequent precipitation to recover molybdenum.

The concentration of copper and iron at 353 K was about 2

Fig. 8 Change of (a) molybdenum and sulfur concentration, (b) copper and iron concentration, (c) ORP of the solution during electro-oxidation at 313 and 353 K. (Exp. # 3, and 9) The pH change under uncontrolled conditions is shown in (d).

times higher on average than that at 313 K. As indicated in the previous section, iron sulfide leaching induces loss of oxidizer for molybdenum leaching, and as a result the extraction efficiency for molybdenum slightly decreases. This tendency is also observed in the results of Fig. 8.

3 · 2 Solubility measurement of molybdenum in NaCl solution

Fig. 9 shows the pH dependence of molybdic acid solubility in 10 mass% NaCl solution at various temperatures. At 298 K, the solubility of molybdenum shows a minimum at pH = 2 to 3, then radically increases when pH of the solution increases. The solubility increment below pH = 2 is probably due to polymerization of molybdic acid. Polymers of molybdic acid such as $\text{H}_3\text{Mo}_4\text{O}_{13}^+$ are reported to be stable in acidic solution, and this increases the nominal concentration of molybdenum. Although the system presently investigated contains large quantities of NaCl in the solution, the tendency of the solubility of the molybdenum is similar to the solutions without NaCl.

When the pH of the solution is higher than 4.5, the dissolved amount of molybdenum increases with increasing temperature. These results show that higher temperature is preferable for dissolving molybdenum at pH level higher than 4.5. Furthermore, it is worth noting that the solubility of molybdenum is lower than 0.05 mol / l at pH = 2, and almost indepen-

Fig. 9 pH dependence of solubility of molybdenum in 10 mass% NaCl solution at various temperatures.

dent of temperature within the present experimental range. In the pH range below 2.0 at which a minimum solubility appeared, a rise in temperature lead to reduced concentration of molybdenum entity, a reverse trend observed in high pH region. The temperature variation of molybdenum solubility is now under further investigation.

The experimental results shown in Fig. 9 suggest that the recovery of molybdenum from leach solutions by adjusting pH from alkaline ($\text{pH} > 6.5$) to acid ($\text{pH} = 1 \sim 3$) is effective over a wide temperature range, and that precipitation by changing solution temperature is found to be inefficient especially with the solution at pH around 2.

3 · 3 Molybdenum recovery from leach solution

The precipitation of molybdenum compounds was tested by pH adjustment for the solutions obtained in the Exps. # 10 and 11 shown in Table 1. The leaching was similar to Exp. #5 described in section 3.1.2 except for the volume of NaCl *aq.*, which was decreased to 100 ml for 5 g of concentrate with the purpose of increasing molybdenum concentration. The distribution of some major elements in the concentrate after electro-oxidation is given in Table 2. During 10 and 16 hours electro-oxidation experiments at $\text{pH} = 9.0$, about 90 % of the molybdenum and 80 % of the sulfur and rhenium were found to be leached. The copper and iron contents in the leach solution are negligibly small. These elements remained in the residue.

After filtration of the slurry, the pH of the filtrate was changed to 0.5 ~ 1 by adding conc. HCl solution. When the solution was heated to about 353 K to promote precipitation, a

Table 2 Experimental distribution of slurry after electro-oxidation of molybdenum concentrate.

Exp. #	Location	Elemental distribution (mass %)					Leaching time, t' / hr.
		Mo	S	Re	Cu	Fe	
10.	Solution	89.6	79.8	80.0	0	0	10
	Cathode	0.8	0		1.3	1.4	
	Residue	9.6	20.2	20.0	98.7	98.6	
11.	Solution	96.2	92.2	82.5	0	0	16
	Cathode	0.5	0	0	3.6	9.3	
	Residue	3.3	7.8	17.5	96.4	90.7	

Table 3 Change of amount of elements in leach solution before and after precipitation of molybdenum.

Exp. #	Elements	Amount of elements in leach solution, w_i / g		
		Before precipitation	After precipitation	Reduced amount (g) or (%)
10.	Mo	1.64	0.69	0.95 (57.9)
	S	1.07	1.04	0.03 (2.8)
	Re	$1.2 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	$0.7 \cdot 10^{-3}$ (58.3)
11.	Mo	2.36	1.07	1.29 (54.7)
	S	2.00	2.00	0 0
	Re	$1.6 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	$0.6 \cdot 10^{-3}$ (37.5)

white and pale yellow precipitate was formed from the leach solution of Exp. # 10 and # 11, respectively. After vacuum drying, the color of these precipitates changed to blue. The results of chemical analysis for leach solution before and after precipitation are summarized and listed in Table 3. These results indicate that more than 50 % of the molybdenum in solution can be precipitated. Although the sulfur concentration in the solution remains unchanged in this operation, the rhenium concentration in the solutions also decreased almost in the same ratio as molybdenum. It is concluded, therefore, that molybdenum and rhenium co-precipitate under these experimental conditions.

Fig. 10 shows an SEM image of the precipitates obtained in Exp. # 10 and 11 after vacuum drying. The X-ray diffraction patterns of the crystals precipitated from the solutions coming from Exps. #10 and # 11 are shown in Fig. 11 (a) and (b), respectively. The crystals are found to be mixture of MoO_3 and $\text{MoO}_3 \cdot (\text{H}_2\text{O})_x$ in both cases. Trace NaCl and Na_2SO_4 phases are also identified in the sample obtained in the leachate from Exp. # 10. XRD patterns shown of Fig. 11 (c) and (d) are the products obtained by precipitation either from sodium molybdate solution or molybdic acid solution prepared from chemical reagents. They are found to be identical to the crystals obtained from the leach solution.

Fig. 10 Scanning electron micrographs of precipitated crystals obtained by changing the pH of the leach solution. (a) : Sample obtained from Exp. # 10 after 10 hours electro-oxidation, (b) : from Exp. # 11 after 16 hours electro-oxidation.

Fig. 11 X-ray diffraction patterns of molybdenum precipitate obtained by changing the pH of the solutions. (a): precipitated from leach solution after 10 hrs. electro-oxidation (Exp. # 10), (b): from leach solution after 16 hrs. electro-oxidation (Exp. # 11), (c): from sodium molybdate test solution, (d): from molybdic acid test solution.

The chemical composition of the obtained precipitate is given in Table 4. The molybdenum content in the precipitate was more than 50 mass%, while the sulfur content in the sample obtained in Exp # 10 was below the detection limit of analysis although the mother solution contained a large amount of sulfate ion. The phases identified by XRD are consistent with the chemical analysis.

In the case of recovering trace rhenium from the concentrate, rhenium extraction directly from leach solution prior to precipitation process has to be considered. Otherwise, the precipitated crystal has to be subjected to recovery process for rhenium present at extremely low concentration in the precipitated molybdenum hydro-oxide.

4. Conclusions

Leaching of molybdenum concentrate in NaCl aqueous solution by electro-oxidation has been investigated, and some process parameters, such as current density, temperature, and pulp density has been experimentally examined using an unseparated anode compartment. The leaching rate of the concentrate is found to be proportional to applied current density, while the molybdenum concentration of the solution increased linearly with time in both acidic and alkaline solutions. This result demonstrates that molybdenite is instantaneously oxidized by oxidizers which are anodically produced. Increase in pulp density caused an increase in oxidant consumption due to preferential oxidation of iron and copper minerals present in the concentrate. As a result, this reduced the efficiency of molybdenum

Table 4 Analytical result of crystal precipitated by changing pH of the leach solution obtained by electro-oxidation.

Elements	Amount of elements, $C'_{\text{precip.}}$ (mass%)	
	Exp. # 10	Exp. # 11
Mo	50.3	67.2
S	5.5	0
Na	23.0*	2.5*
K	0.5*	0.6*
Cl	15.0*	0.9*
Re	0.04	0.03

* : Analyzed by XRF and shown for reference. Reminder determined by ICP.

extraction into the leach solution. The rate of leaching was found out to be high in efficiency even at higher temperatures (353 K).

Feasibility of the separating molybdenum from leach solutions by pH control was examined. Prior to the precipitation experiments, the pH variation of molybdenum solubility in 10 mass% NaCl solution was investigated at various temperatures between 298 and 353 K. In the range of pH from 2 to 3, the solubility of molybdenum species was found to be lower than 0.05 mol/l, and was almost independent of temperature. At pH more than 3, solubility of molybdenum increased with increasing temperature and pH of the solution. These results shows molybdenum can be recovered by changing the pH of the solution from alkaline to acid. Precipitation experiments from leach solution were then examined, and solid $\text{MoO}_3 \cdot (\text{H}_2\text{O})_x$ crystals, free of sulfur, were obtained even from the leach solution containing large amount of SO_4^{2-} . Rhenium in the leach solution was found to co-precipitate with the molybdenum.

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電解酸化と析出法を利用した硫化物精鉱からの モリブデンの回収

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電解酸化によるモリブデン精鉱の浸出実験を行い、電流密度、温度、パルプ密度（スラリー中の精鉱の見かけ濃度）などの主要なプロセスパラメータの影響について検討した。NaCl 水溶液の電解によって生成する酸化剤により速やかにモリブデン精鉱粉末は酸化され効率良く浸出液中に溶解したため、電流密度の増大とともに溶解速度は増加し、また電解時間に比例して浸出液中のモリブデン濃度は増加した。パルプ密度を増加した場合、精鉱中の不純物の鉄および銅が優先的に溶解し、モリブデンの浸出効率は低下した。また、溶解度の変化を利用してモリブデン化合物を析出・分離回収する手法を検討するため、298～353 K の一定温度における 10 mass% NaCl 水溶液中のモリブデンの溶解度の pH 依存性について調査した。pH が 2～3 の間ではモリブデンの溶

解度は 0.05 mol/l 以下となるが、溶液の温度と pH の増大とともにモリブデンの溶解度は急激に増加することがわかった。浸出液の pH を変化させることにより、濃厚な SO_4^{2-} を含む溶液からでもイオウの濃度が非常に低い固体の $\text{MoO}_3 \cdot (\text{H}_2\text{O})_x$ 結晶が回収できた。モリブデン中の微量元素のレニウムはモリブデンとともに溶出し、また共析することも明らかとなった。

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