

Article

Selective Leaching of Molybdenum from Bulk Concentrate by Electro-Oxidation

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Abstract: This paper proposes selective leaching of molybdenum from Mo/Cu complex bulk concentrates in a 5 M NaCl solution using the electro-oxidation method. Here, the effects of several factors such as pH, pulp density, current density, and temperatures were investigated. A higher leaching yield of Mo increased with increasing pH from 5 to 9 and decreased with increasing pulp density from 1 to 10%. A rise in current density did not help enhance Mo, and the elevating temperature did not always result in a higher leaching yield. Application of ultrasonic led to higher leaching yield of Mo. Ninety-two percent of leaching yield was obtained upon leaching of Mo in 5 M NaCl at 25 °C, pulp density of 5%, and the current density of 0.292 A/g under ultrasonic irradiation with a power of 27 kW. The resultant residue mainly consisted of chalcopyrite.

Keywords: electro-oxidation; molybdenum; selective leaching; molybdenite; chalcopyrite



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1. Introduction

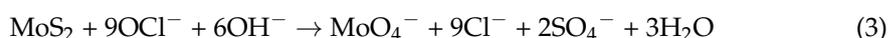
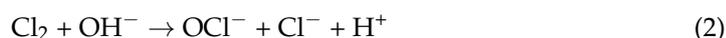
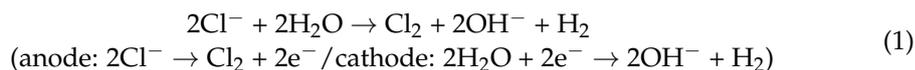
Molybdenum is mainly used as an alloying agent in the steel industry because its addition improves several properties such as strength, durability, weldability, and the corrosion resistance of steel [1–3]. With the expansion of the construction, automotive, and oil/gas industries, the consumption of Mo alloyed steel, and subsequently Mo, has increased [4]. Therefore, it has been considered a strategic metal in various industries [5]. Furthermore, usage of Mo-alloyed steel expectedly grows in the renewable power industry, wind, and solar energy industries [6].

Molybdenum is mainly generated from molybdenite (MoS₂), the most primary mineral resource of Mo, usually associated with copper minerals [7]. More than 50% of Mo marketed is produced as a by-product in the copper industry [8]. High reliance of its production on the copper industry makes Mo subject to supply fluctuations because a drop in copper production reduces molybdenum productions. The supply risk of Mo is considered high, and its stabilization is a critical issue to some countries with poor resources, but the increased consumption of molybdenum, such as Korea. Korea, the first importer of Mo ores, has several molybdenum mines, for example, the Jangsu mine with a pegmatite-style deposit, the Geumseong Mine with a skarn/porphyry-style deposit, and the Geumeum mine with a veinlet-style deposit [9–11]. The Geumeum mine was known to have a reserve of ~2,600,000 tons. In addition, ores revealed a very high grade of 0.32% MoS₂. However, the low grade of copper acts as an obstacle to the commercial development of the Geumeum mine. Therefore, a highly efficient process for the separation of Mo and Cu should be developed.

Upon recovery of Mo from Mo/Cu complex ores, their separation is traditionally conducted based on the floatation process [12–14]. However, the whole process is complex and complicated to obtain a high grade of molybdenum concentrates. Furthermore, the recovery of molybdenite is low compared to copper minerals [15]. Therefore, its application to primary Mo ores containing a little Cu is not economically efficient. Here, the leaching

method was applied to separate Mo and Cu in bulk concentrates from the Geumeum mine as an alternative method. Since the 1970s, MoS₂ could be reportedly oxidized in both acidic and alkaline solution by hypochlorite and chlorate, so their application to selective leaching of Mo from Mo/Cu complex ores has been much studied [16–21]. An electro-oxidation method has also been developed and reported to be effective in selective leaching Mo from Mo concentrates [22–25]. Some researchers performed Mo leaching using hydrogen peroxide and oxygen as oxidants [26,27]. The method based on salt roasting was suggested [28].

The electro-oxidation method is to leach Mo from MoS₂ using electrochemically generated hypochlorite ion (OCl[−]) as an oxidant as follows;



It theoretically consumes electricity and OH[−] without additional oxidants. In addition, the process can be easily controlled by control of current or voltage. Several studies reported the selective leaching of Mo from MoS₂ concentrates or CuFeS₂ concentrates [22,23,25,29,30]. However, its application to bulk concentrates comprising MoS₂ and CuFeS₂ has been little studied. Selective leaching of Mo without oxidation of CuFeS₂ from bulk concentrates leads to effective recovery of Mo as ions and Cu as concentrates in addition to the separation of Mo and Cu. Expectedly, it can simplify the flotation process for Cu/Mo complex ores and suppress the loss of Mo and Cu. Therefore, this study presents the selective leaching of Mo from bulk concentrates consisting of MoS₂ and CuFeS₂ obtained at the first stage of the flotation process, giving rise to CuFeS₂ concentrates using the electro-oxidation method. The leaching behaviors of Mo, Cu, and impurity metals at various pHs, currents, and temperatures were investigated. In addition, the effect of ultrasonic irradiation was studied.

2. Experimental Section

The bulk concentrates of Molybdenum, taken from the Geumeum mine, were supplied by Hae In Resources Corporation. Their compositions are presented in Table 1. The main phases are chalcopyrite and molybdenite, and minor sphalerite exists. All chemicals used in this study were of G. R. grades.

Table 1. The composition of ores and bulk concentrate.

Element	MoS ₂	CuFeS ₂	ZnS	Pb	Mg	Al	Ca	SiO ₂	Mean Dia. (um)
Concentrate (wt%)	10.14	62.08	1.88	1.96	0.33	1.05	1.73	5.44	52.2

The leaching of concentrates was conducted in a 1 L double-jacket glass reactor equipped with a mechanical stirrer, a thermostat, pH controller with pH electrode, NaOH input pump with NaOH inlet, and an ultrasonic generator with a probe. The cell configuration is shown in Figure 1. IrO₂ coated mesh electrode (inner diameter 130 mm × height 20 mm) and Pt mesh electrode (inner diameter 130 mm × height 20 mm) were used as an anode and cathode, respectively. First, 500 mL of 5 M NaCl was charged in a reactor, and the temperature and pH were set at desired values. Then, a certain amount of concentrates was input into the solution, and leaching was started by applying current using a potentiostat (VMP3B-20, BioLogic Science Inst., Lyon, France). During leaching, pH was controlled using a 2 M NaOH solution. For sonochemical leaching, the ultrasound irradiation was performed using an ultrasonic generator (VCX 750, Sonics & Materials, Inc., Newtown,

USA) with a probe of 25 mm in radius. Ultrasonic power was controlled by the change in amplitude.

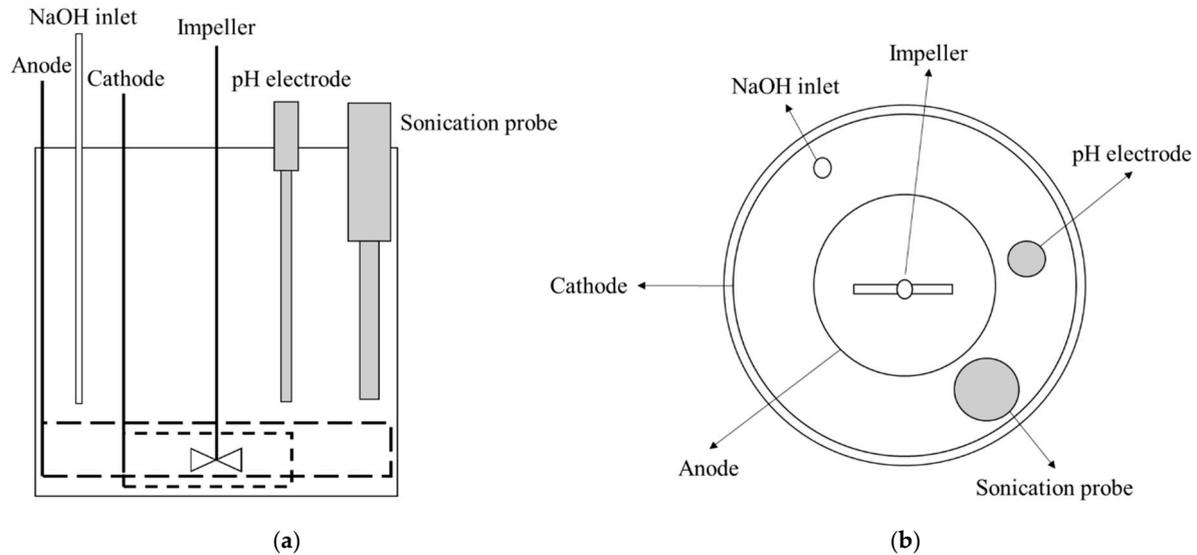
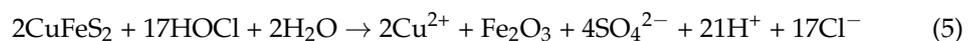
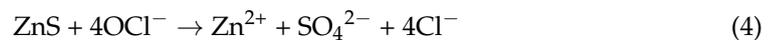


Figure 1. The configuration of cell for leaching. (a) side view (b) top view.

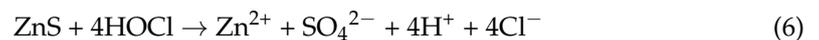
During all experiments, the reaction mixture was sampled at the desired time, filtered, and analyzed for the concentration of metal ions using the inductively coupled plasma-atomic emission spectrometer (ICP-AES, iCAP6000, Thermo Fisher, Cambridge, UK).

3. Results and Discussions

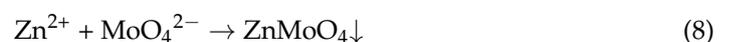
Figure 2 reveals the leaching yields of molybdenum in 5 M NaCl solution at a current density of 0.292 A/g, pulp density of 1% (*w/v*) and 50 °C as a function of pH. The current density used in this study means the ratio of applied current to concentrates mass input, and pulp density does the balance of concentrates mass to solution volume. Mo, Zn, and Cu were observed to be leached at some pH or all pHs studied in this study, while no leach was found for Fe, Pb, and Mg at all pHs. At pH 5, Zn and Cu, as well as Mo, were shown to be leached. Several studies reported that the electro-oxidation method was effective in leaching sulfide ores [31–33]. The leaching of Zn and Cu were also due to the oxidation of ZnS₂ and CuFe₂S as follows;

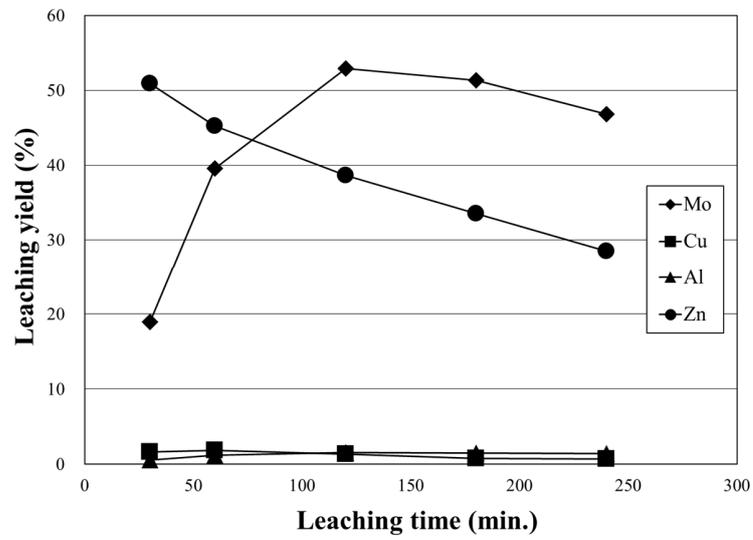


Strictly expressed, Equations (4) and (5) should be presented as Equations (6) and (7) because HOCl is much more dominant than OCl[−] [34].

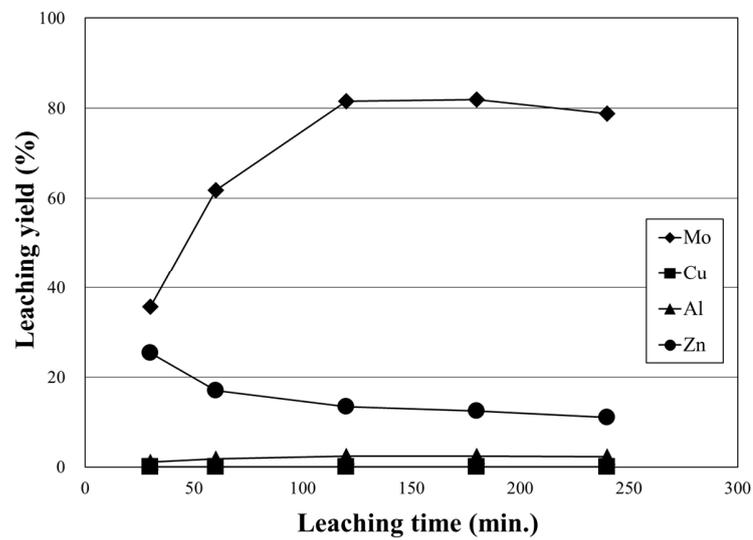


Notably, the leaching yield of Zn reduced with time. Interestingly, Mo also showed decreasing leaching yield with time passing over the maximum value at 120 min. In other words, Mo and Zn ions dissolved initially simultaneously disappeared with a prolongation in time. The reason may be the precipitation of zinc molybdate (ZnMoO₄) as follows:

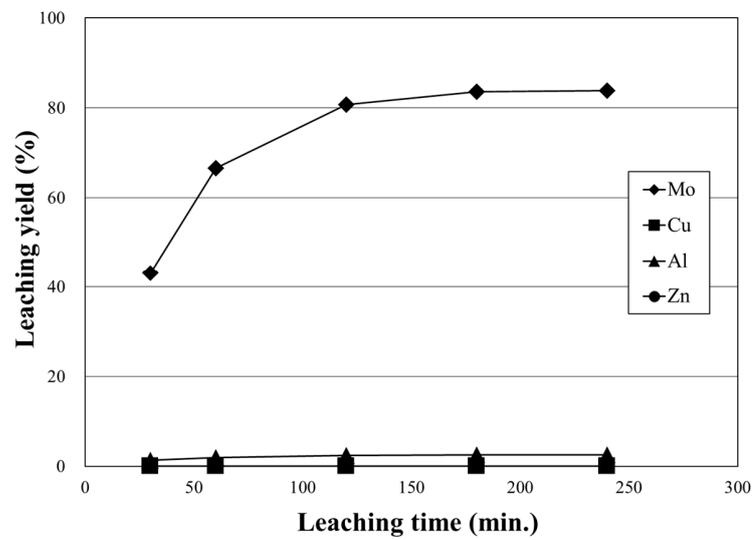




(a)



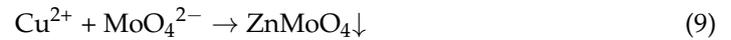
(b)



(c)

Figure 2. Leaching yields of metal ions with time at various pHs. (a) pH5 (b) pH7 (c) pH9.

At pH higher than 5 and oxidative condition, Mo is stable as MoO_4^{2-} , and upon meeting with divalent transition metal ions, metal molybdates are well precipitates [35,36]. Cu leaching revealed similar behavior to Mo leaching, indicating that Cu^{2+} reacted with MoO_4^{2-} , too.



It can be understood that the leaching of divalent cations should be hindered for the high leaching yield of Mo.

It was reported that ZnS oxidation was faster than CuFeS_2 , and their oxidation rate reduced with increasing pH [25,31,37]. Here, similar behavior was observed. Zn revealed a much higher leaching yield and Cu. In addition, their leaching was more retarded at higher pH. Significantly, Zn and Cu were not leached at pH 9. However, the oxidation behavior of ZnS and CuFeS_2 was much different. XRD analysis of the residues obtained at pH 9 showed that ZnS was disappeared, as shown in Figure 3. Zn(OH)_2 is stable at a high potential region (Figure 4a). Hence, conversion of ZnS to Zn(OH)_2 might take place upon leaching at pH 9 as presented in Equation (10)

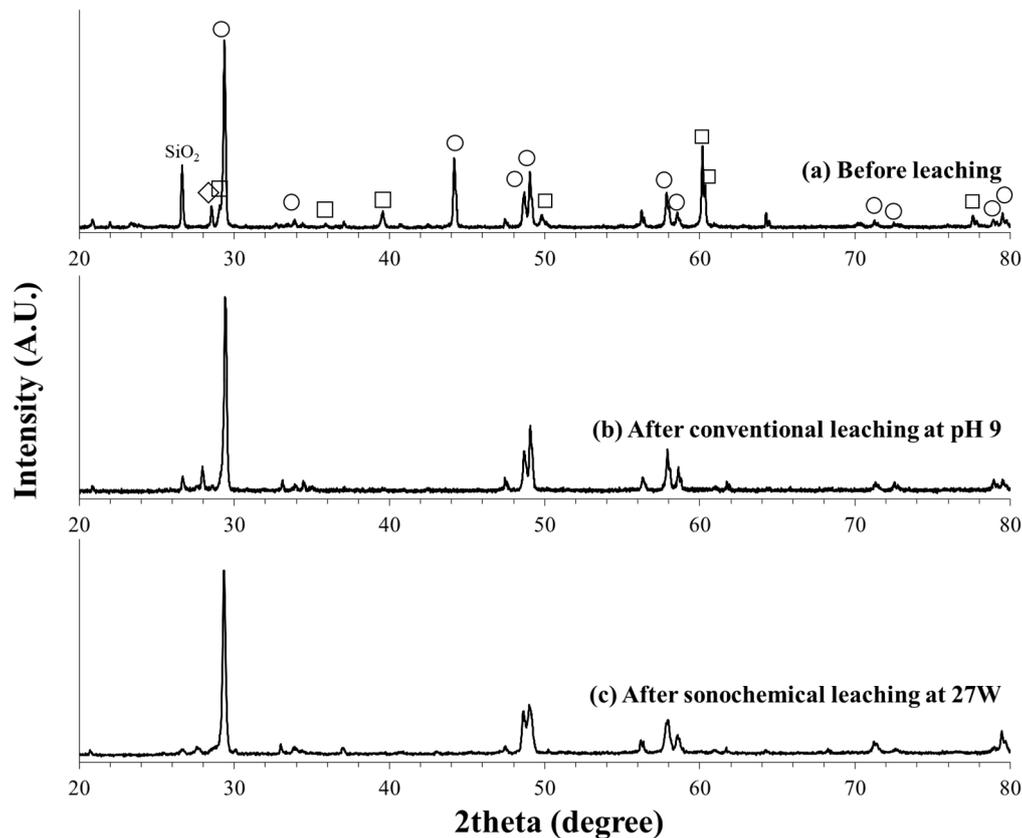
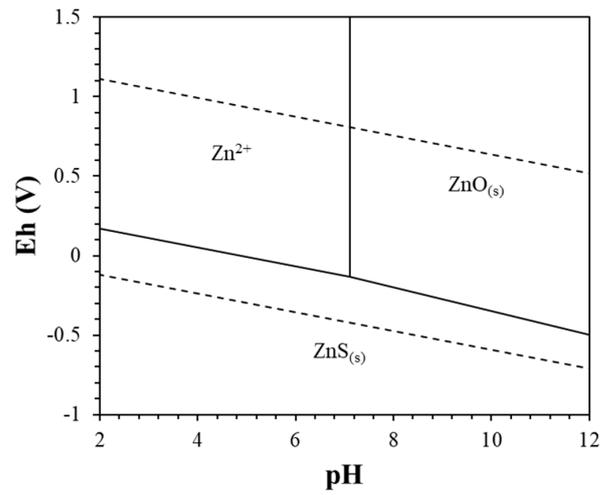


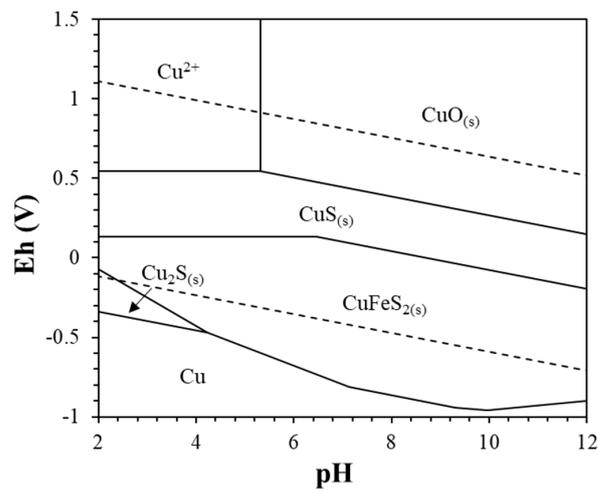
Figure 3. XRD patterns of bulk concentrates before and after leaching (current density: 0.292 A/g, pulp density: 5%, temperature: 25 °C, pH 9, ultrasonic power: 27 W).

E-pH diagram revealed in Figure 4b shows that CuFeS_2 was oxidatively transformed to CuO at high potential region. The oxidation of CuFeS_2 to CuO can be presented in Equation (11)

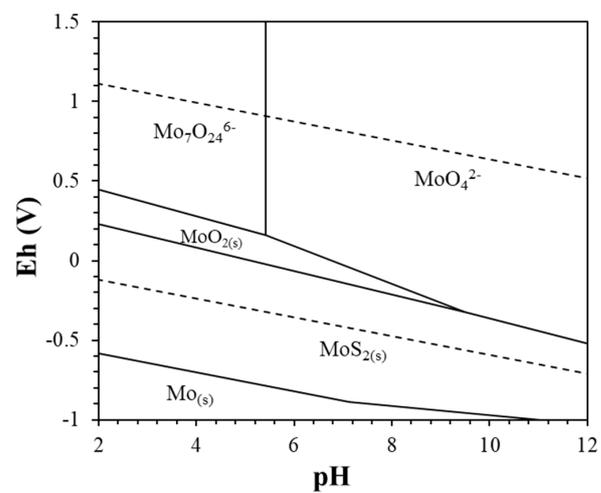




(a)



(b)



(c)

Figure 4. Eh-pH diagram for (a) Zn-S-H₂O; (b) Cu-S-H₂O, and (c) Mo-S-H₂O at 298K [Zn], [Cu], [Mo] = 0.001 mole, [S] = 0.001 mole (Zn) and 0.002 mole (Cu/Mo)) (HSC Chemistry 5.11 version. OutokumpuResearch Oy, Pori, Finland).

In addition, M.-S. Kim reported that CuFeS_2 is converted to CuO by OCl^- in 0.2 M NaOH at 60°C when the generation rate of OCl^- is high [34]. In the present study, CuFeS_2 was not oxidized and still existed as a primary phase even after leaching at pH 9, as shown in Figure 4. The main difference between the two studies is the sample; MoS_2 and CuFeS_2 mixed bulk and CuFeS_2 , but CuFeS_2 concentrates for the reported studies. A high leaching yield of Mo means that a high amount of OCl^- was consumed preferably for the oxidation of MoS_2 . The rest amount might be insufficient for the fast oxidation of CuFeS_2 . In addition, the larger size of bulk concentrates than CuFeS_2 concentrates by 1.5 times may be another reason for no or minor oxidation of CuFeS_2 , considering that its oxidation rate was determined by the diffusion of two layers with a layer of solid sulfur produced during leaching and an ash layer remaining after leaching [38]. To summarize, CuFeS_2 was unreacted, unlike MoS_2 and ZnS , which indicated that CuFeS_2 concentrates are possibly obtained by the electro-oxidation leaching of Mo from Mo/Cu mixed sulfides.

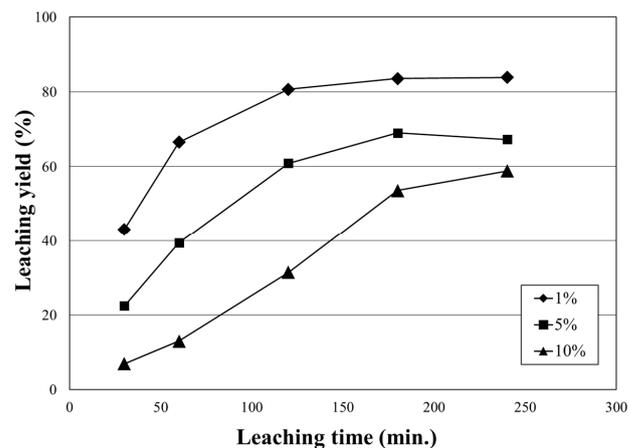
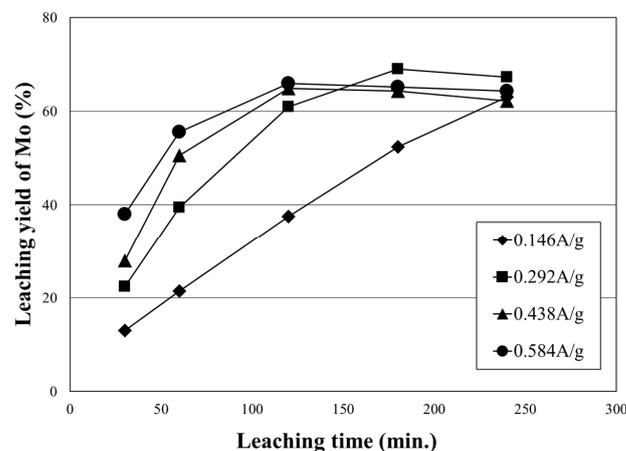
Mo is stable as soluble species as $\text{Mo}_7\text{O}_{24}^{2-}$ and MoO_4^{2-} under oxidative conditions in pH regions of this study (Figure 4c). Mo leaching was improved with rising pH. One of the reasons for this is that less divalent metal ions leached out with increasing pH, which resulted in a lower reduction of dissolved Mo ions by precipitation of metal molybdates such as ZnMoO_4 and CuMoO_4 . The higher stability of OCl^- at pH 9 was a possible reason. OCl^- was reported to decompose with time, giving rise to chlorite ion (OCl_2^-) and chlorate ion (OCl_3^-). Those two ions show much lower redox potentials of $0.681V_{\text{SHE}}$ and $0.295V_{\text{SHE}}$ compared with $0.890V_{\text{SHE}}$ of OCl^- in alkaline solution with OH^- of 1 mole/Kg [39]. Lower redox potential means lower oxidation power in the electrochemical view. According to L.C. Adam, the decomposition rate of OCl^- to OCl_2^- in 0.5 M borate buffer much reduced with increasing pH up to nine and again increased with increasing pH over 10 going through minimum near pH 9 [40]. The less decomposition of OCl^- may enhance the leaching of molybdenum at higher pH. At pH 9, a leaching yield of 83.9% was observed for Mo with a bit of aluminum leached, while other impurities, including copper, were observed. It indicates that the separation of molybdenum with copper is possible by selective leaching of molybdenum, yielding CuFeS_2 concentrates. Therefore, pH was set at nine for all sequential leaching tests.

Figure 5 shows the leaching behavior of molybdenum in 5 M NaCl solution of 500 mL at a current density of 0.292 A/g, at pH 9 and 50°C as a function of pulp density. At higher pulp density, a lower leaching yield of Mo is found at any leaching time. Generally, a rise in pulp density leads to a drop in leaching yield because the ratio of leaching agent to feed input reduces with increasing pulp density. However, the amount ratio of oxidant, OCl^- , and MoS_2 maintained constant in this study irrespective of pulp density on the assumption that current efficiency to produce OCl^- is not affected by the pulp density because the same current density was applied at any pulp density. In addition, applied current density was theoretically large enough for the entire leaching of MoS_2 input, as shown in Table 2. According to Equations (1) and (2), one mole of molybdenite requires nine moles of chloride gas, of which production needs eighteen moles of electrons. The amount of MoS_2 was 0.507, 2.535, and 5.07 g in mass and 0.003167, 0.01584, and 0.03167 mole for the pulp density of 1, 5, and 10%, respectively. Thus, the required amounts of electrons to produce hypochlorite ions for leaching of all MoS_2 were 0.05701, 0.2851, 0.5701 in mole, and 5501, 27,508, 55,010 in coulomb. The applied coulombs were 21,024, 105,120 and 210,240 C for the pulp density of 1, 5, and 10%. Therefore, applied coulomb was much higher by 3.8 times than coulomb required for all leaching of MoS_2 upon the assumption that all applied electrons were used to oxidize Cl^- and all oxidation products were OCl^- . It can be understood that the number of applied electrons is substantial enough. In addition, the solubility of sodium molybdate in water is also much higher, for example, 443 g/L at 20°C . Nevertheless, increasing pulp density from 1 to 10% induced great reduction in leaching yield of Mo at 240 min from 83.9 to 58.9%.

Table 2. The amounts of MoS₂ input, and electron required and applied.

Pulp Density	Input Amount of Feed		Electrons Required (C)	Electrons Input (C)	The Ratio of Electron Required to that Input
	Weight (g)	Mole (M)			
1	5	0.003167	5501	21,024	3.822
5	25	0.01584	27,504	105,120	3.822
10	50	0.03167	55,008	210,240	3.822

Naturally, higher pulp density is preferred upon leaching operation. Thus, the effects of several factors on the leaching of Mo were investigated to find a way to increase the leaching yield of Mo even at high pulp density. Figure 6 exhibits the leaching of Mo in 5 M NaCl of 500 mL at 50 °C and at a high pulp density of 5% at various current densities. Unexpectedly, the leaching yield of molybdenum was much affected only at the initial time. In other words, that of Mo at 30 min much increased by ca. time with rising current density from 0.146 to 0.584 A/g. However, current density little affected the leaching of Mo for all current densities at the prolonged time of 240 min. Even at a reduced current density of 0.146 A/g, a similar value as leaching at a higher current density was observed. As shown in Equation (3), hypochlorite ions play a sufficient role in oxidation for the leaching of MoS₂, but the result showed that their number is not significant in leaching MoS₂ when they are more plentiful. In other words, a rise in current density did not help improve the leaching of molybdenum at extended leaching time. Therefore, it was concluded that a lower current density is favorable considering current efficiency.

**Figure 5.** Leaching yields of Mo with time as a function of pulp density (current density: 0.292 A/g).**Figure 6.** Leaching yields of molybdenum with time as a function of current density (pulp density: 5%).

It is well known that electrochemical and chemical reactions can be improved by increasing temperature. The effect of temperature was also investigated under the condition of the current density of 0.292 A/g and pulp density of 5%. The obtained result is presented in Figure 7. The rise in temperature up to 50 °C facilitated the leaching of Mo, but further elevation over 50 °C again hindered its leaching. In other words, an increase in temperature did affect the leaching efficiency of molybdenum positively at a temperature below 50 °C, and rather negatively at a temperature above 50 °C. The production reaction of OCl^- is expressed in Equation (2), while to be more specific, one more equation should be added [41].

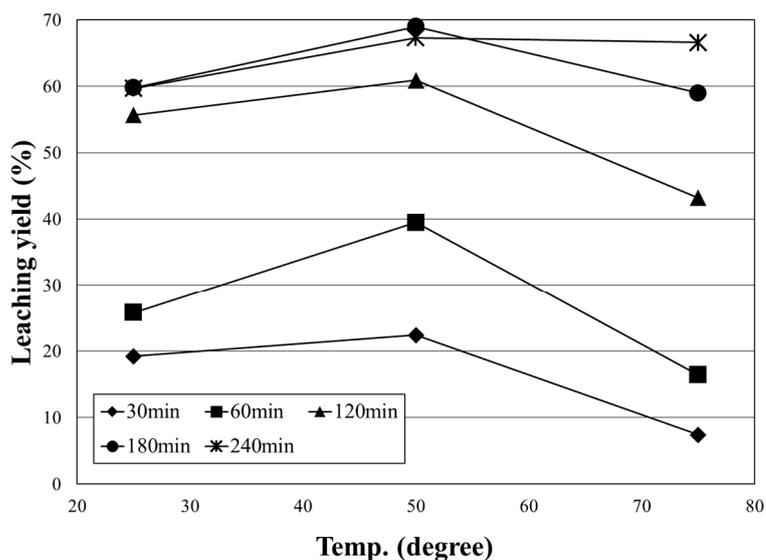


Figure 7. Leaching yield of molybdenum at various temperatures (current density: 0.292 A/g, pulp density: 5%).

In other words, the dissolution reaction of Cl_2 into an aqueous solution should occur before reaction with NaOH to produce OCl^- . It is well known that the solubility of a gas in the solution generally reduces with growing temperatures. The solubility of Cl_2 in water decreased sharply by more than half with an increase in temperature from 25 to 75 °C [39]. The reduction in dissolved Cl_2 should give rise to a lower number of OCl^- in the leaching solution. Consequently, the leaching of Mo became slower. It could be understood that the facilitation of leaching reaction by increasing temperature became dominant at a temperature below 50 °C. On the other hand, a slow-down in leaching reaction by a lower quantity of dissolved Cl_2 and subsequently OCl^- ions by increasing temperature was predominant at a temperature above 50 °C. An elevation in temperature was also ineffective in promoting Mo leaching at a high pulp density of 5%.

An increase in current density and temperature was not effective in obtaining a higher leaching yield of Mo. It was pointed out that applied electrons were theoretically enough to produce OCl^- to oxidize MoS_2 input. It indicates that a large portion of OCl^- made was not utilized for leaching of Mo. A possible reason for this is that the meeting of OCl^- with MoS_2 did not effectively occur due to its slow mass transfer of OCl^- . Therefore, the application of ultrasound was made to enhance the leaching of molybdenum. It has been found that sonication is a promising tool to enhance the chemical reaction in solution [42]. Upon ultrasonic irradiation in an aqueous solution, a process of cavitation in the shock waveform near a surface disrupts the interfacial boundary layers. It shortens the diffusion layer thickness by microjet into a solid surface. It facilitates the mass transfer of ions greatly. Figure 8 reveals the leaching of molybdenum in 5 M NaCl of 500 mL at 25 °C, a high pulp density of 5%, and the current density of 0.292 A/g under ultrasonic irradiation of

various powers. The ultrasonic irradiation can elevate the temperature of the solution. As mentioned above, local increase in temperature above 50 °C may rather retard the leaching of Mo. Therefore, the temperature was adjusted to 25 °C. Ultrasonic irradiation was observed to markedly improve the leaching of Mo. Specifically, the leaching yield at 240 min increased from 59.7 to 92.0%. It indicates that slow mass transfer of OCl^- to MoS_2 in the feed may be one of the primary reasons for low leaching yield and ultrasonic irradiation is much effective in its promotion.

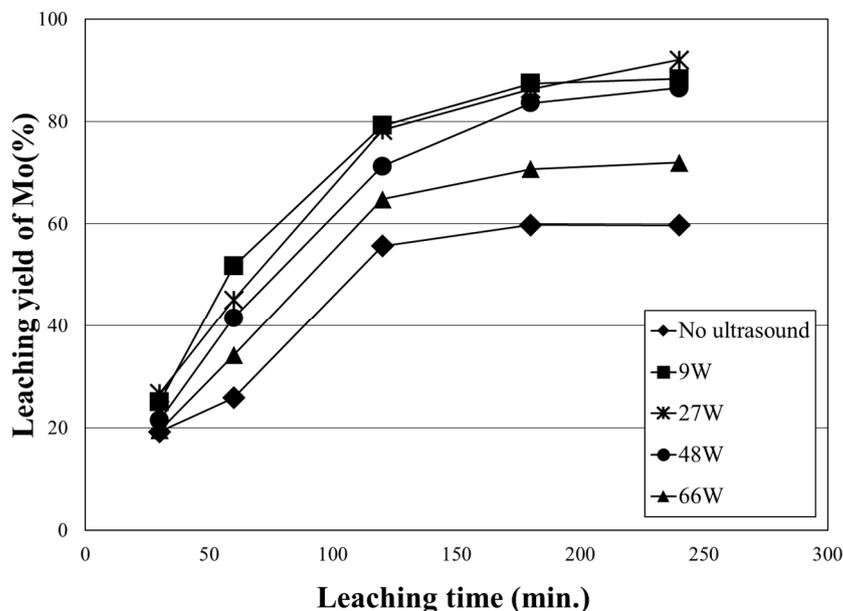
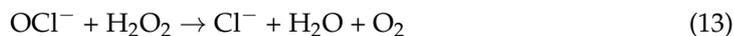


Figure 8. Leaching yields of molybdenum with time at various sonication powers (current density: 0.292 A/g, pulp density: 5%, temperature: 25 °C).

Nevertheless, it should be pointed out that the dependence of leaching yield on sonication power showed a different behavior as expected. Higher leaching yield was observed at lower sonication power. In other words, an increase in Sonication power induced a negative effect on the leaching of Mo, which may be due to the increased reduction in the number of hypochlorite ions at a high sonication power. Reportedly, extremely high pressure (~500 atm) and temperature (~5000 K) are generated during the violent collapse of the bubble by ultrasonic irradiation, where excited species such as $\text{OH}\cdot$ and H_2O_2 are formed, released into solution and react with substrates in solution, yielding products [42]. Hydrogen peroxide has both oxidation and reduction power, and its redox potential is lower than that of OCl^- in basic solution [43]. Thus, Hydrogen peroxide acts as a reducing agent in basic solution as follows:



Ultrasonic irradiation is understood to enhance the leaching of molybdenum by the acceleration of mass transfer and simultaneously hinder it by consuming the hypochlorite ions more. Under the condition used in this study, the former effect prevailed in the leaching reaction at low ultrasonic power, but the latter effect predominated that reaction at high ultrasonic power. It indicates that ultrasonic irradiation can affect the leaching of Mo both positively and negatively. Therefore, sonication power should be optimized to obtain a high leaching yield of Mo.

As shown in Figure 3, XRD analysis of the residue obtained by ultrasonic leaching revealed that chalcopyrite was unreacted and chalcopyrite concentrates may be obtained by selective leaching of Mo with an aid of ultrasound using the electro-oxidation method.

4. Conclusions

The selective leaching of Mo from Mo/Cu complex bulk concentrates in a 5 M NaCl solution using the electro-oxidation method was studied at various pHs, pulp densities, current densities, and temperatures. It was found that impurities of zinc and/or copper and Mo simultaneously dissolve and dissolved ions again decreased with time at pH 5 and 7. At pH 9, the highest leaching yield of Mo without the leaching of Zn and Cu was obtained, while CuFeS₂ remained unreacted. A rise in pulp density suppressed Mo leaching even though the ratio of applied current to the mass of feed input was maintained constantly. An increase in current density little affected the leaching of Mo at the prolonged times. Elevation of temperature enhanced the leaching of Mo at a temperature below 50 °C, but further increase above 50 °C again reduced its leaching. It was understood that the rises in current density and temperature were not effective in promoting Mo leaching. Instead, ultrasonic application of optimum power facilitated its leaching. However, increasing ultrasonic power above 27 kW retarded the leaching of Mo. Ninety-two percent of leaching yield was obtained upon leaching of Mo in 5 M NaCl at 25 °C, pulp density of 5%, and the current density of 0.292 A/g under ultrasonic irradiation with a power of 27 kW. XRD patterns showed that MoS₂ disappeared, and CuFeS₂ concentrates were obtainable.

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Conflicts of Interest: The authors declare no conflict of interest.

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