Extraction of molybdenite concentrates by leaching

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Abstract

Molybdenum concentrate, as Molybdenite (MoS_2), is nowadays obtained as a byproduct of the processing of porphyry copper ores, being molybdenite considered a minor component. The procedure for the commercial extraction of molybdenum from such a sulfide ore, involves the operations of roasting the concentrate, purifying the resulting calcination, either by distillation of molybdenum trioxide (MoO_3) or by a hydrometallurgical pathway, and finally reducing the trioxide of molybdenum with hydrogen to obtain the metal.

The objective of the present work is to study the production of molybdenum from molybdenite concentrates using aqueous solution of hydrochloric acid (HCl) as a lixiviant, sodium chloride (NaCl) as a catalyst, sodium hydroxide (NaOH) as a pH regulator, and lastly ferric chloride ($FeCl_3$) as an oxidant. The results show that working pH greater than 8, temperature of 50 °C, hydrochloric acid concentration of 5%, solid/liquid ratio of 10:1, stirring rate of 200-300 rpm and the addition of 2% ferric chloride. Mo leaching was 70% under experimental conditions at a time of 180 minutes, with a complete removal of iron.

Keywords: molybdenite; leaching; ferric chloride

Extracción de concentrados de molibdenita por lixiviación

Resumen

El concentrado de molibdenita (MoS_2) es obtenido actualmente como un subproducto en el procesamiento de minerales provenientes de un pórfido de cobre, siendo la molibdenita considerada un componente menor. El procedimiento para la extracción comercial de molibdeno desde un sulfuro, la molibdenita, implica tostar el concentrado, purificar el calcinado resultante, ya sea por destilación de tiroxido de molibdeno (MoO_3)o por una ruta hidrometalúrgica, y finalmente reducir el trióxido con hidrógeno para obtener el metal

El objetivo del presente trabajo es estudiar la producción de molibdeno desde concentrados de molibdenita usando una solución acuosa de ácido clorhídrico (HCl) como lixiviante, cloruro de sodio (NaCl) como catalizador, hidróxido de sodio (OHNa) como regulador de pH, y por último cloruro férrico ($FeCl_3$) como un oxidante. Los resultados muestran que trabajando en un pH más grande que 8 temperatura de 50ºC, con una concentración de ácido clorhídrico de 5% y una relación solida / liquido de 10:1, velocidad de agitación de 200- 300 rpm y la adición de un 2% de cloruro férrico, La lixiviación de Mo fue del 70% en condiciones experimentales en un tiempo de 180 minutos, con una remoción completa del hierro.

Palabras clave: molibdenita; lixiviación; cloruro férrico.

1 Introduction

Molybdenum, as main component or as a by-product, is found in low-grade ores and before its use as an industrial or metallurgical product, it must undergo in operations of concentration in order to liberate the mineral species, molybdenite (MoS_2), which is the most important one in terms of economics.

The conventional method for extracting Mo involves an oxidation-roasting-leaching process with ammonia.

Alternative processes such as oxidative pressure leaching, alkaline melting and alkaline hypochlorite leaching have gained increasing utilization in Mo production. Currently, ammonium molybdate is mainly reached by the ammonia leaching method [1]. This involves roasting molybdenite at high temperatures to obtain molybdenum calcine, which consists mainly of MoO_3 [2-4]. Subsequently, ammonium molybdate is produced through a series of processes, including leaching, purification and crystallization [5-6]. The ammonia leaching method imposes strict quality

requirements on molybdenum calcine due to the weak alkalinity of ammonia. Typically, the Mo content in calcine should exceed 55% (w/w), with iron (Fe) and copper (Cu) content below 2% (w/w). Furthermore, ideally the soluble Mo content should exceed 98% by weight [7]. Deviation from these specifications can result in high Mo content in the leach residue, negatively affecting Mo recovery. The shortage of high-quality molybdenite is increasing due to the continued exploitation of Mo resources, leading to an increasing proportion of low-grade complex molybdenite ore [8]. Typically, pyrite and chalcopyrite accompany low-grade complex molybdenite [9-10,11], easily transforming into insoluble iron molybdate and copper molybdate during the oxidation roasting process [12-14]. This formation of Fe molybdate and Cu molybdate significantly hinders the utilization of Mo, resulting in a considerable increase in the Mo content in the leach residue to approximately 15 %(w/w). Therefore, the efficient extraction of Mo from low-grade complex molybdenum calcine has become a critical bottleneck limiting wider application of molybdenum resources.

The molybdenum concentrate, depending on the cleaning and concentration scheme implemented in the selective flotation plant, may contain a proportion of copper and iron between 1.5% and 6%, acting as impurities.

With this copper content it can be sent to the maquila facility for processing and transformation into molybdenum trioxide (MoO_3) for commercial purposes. However, as the amount of copper and iron present in the concentration increases, processing costs increase. For many years, chloride-based leaching, particularly $FeCl_3$, has been applied to extract various metals from sulfide minerals. [14-15] Commonly, the ferric ion (Fe^{3+}) is the most effective oxidant with a redox potential of 0.77 mV in acidic media; the high solubility of the metal allows Mo to be extracted more quickly than with other oxidants. [16-17]

$FeCl_3$ is often used as an oxidant for sulfur in copper sulfides by the leaching method, and the efficiency is lower when no additional reagent is included.

Work to develop new leaching parameters has often involved bench-scale experiments testing a matrix of conditions. While important, especially in determining kinetic parameters, these efforts can be labor-intensive, time-consuming, and sophisticated thermodynamics.

Therefore, in this work, we resort to the application of leaching with hydrochloric acid with the addition of ferric salts, mainly ferric chloride ($FeCl_3$) with pH control with the purpose of reducing the concentration of copper and iron in the material, in order to find the optimal recovery parameters of the desired metal (Mo).

2 Experimental methodology

The sample used is a flotation concentrate of copper, iron and molybdenum from a deposit in northern Argentina. To obtain an idea of the nature of the sample, structural and chemical characterizations are carried out. Subsequently, a portion is separated for experimental testing.

2.1 Chemical analysis

The analytical technique for determining Mo is through acid digestion with H_2S and $HClO_4$, with an organic catalyst and subsequent determination in acid solution with Perkin Elmer ICP-OES (optical emission spectrometer), model 7300 DV, the standards used for measurement are certified, and using measurement blank. The measurements of the samples were carried out in triplicate and the average measurement was obtained as a result.

For the other elements, an analytical technique consisting of acid digestion is used, specifically for a multi-acid attack (HF, HCl, HNO_3, $HClO_4$) of the concentrated sample. All the reagents used were of analytical grade.

2.2 Structural analysis

The mineralogical characterization was carried out with the objective of identifying and describing the minerals present in the sample and thus knowing their physical and chemical properties. The mineralogical characterization was carried out through a number of techniques and methods including:

Macroscopic observation: mineral samples were visually examined, describing their appearance, color, brightness, among others.

Optical microscopy: a microscope is used to examine thin sections of mineral samples. The equipment utilized was an Olympus SZ61 TR stereoscopic magnifier and an Olympus GX 51 optical microscope with a Leco IA 32 image analysis system.

Electron microscopy: A SEM scanning electron microscope is utilized, employing the energy disperse spectroscopy (EDS) technique using Phoenix software to analyze the samples. Before observation under the microscope, these samples were coated with a conductive layer of gold palladium alloy

X-ray diffraction. This technique allows us to identify the minerals present in a sample and determine its chemical composition. The equipment utilized was a Philips WP 1011 Diffractometer.

2.3 Laboratory testing methodology

The method used to carry out leaching is via agitation. That is, acid leaching is carried out by stirring the samples where the acid reacts with the present minerals, dissolving the metal of interest and producing metal ions in the solution.

This medium allows us to evaluate important parameters, such as leaching rate, extraction efficiency and the influence of several variables such as lixiviant concentration, particle size, temperature and pH, all useful data to optimize and design leaching processes.

The steps followed in the agitation leaching tests in the laboratory were as follows:

Weighing samples: carried out on Mettler Toledo analytical scale.
- Preparation of the leaching solution and catalysts.
- Working pH conditioning.
- Mixing and stirring: The mineral samples and the

leaching solution are placed in a beaker (400 ml) and subjected to constant stirring using magnetic stirrers to ensure uniform distribution of the leaching solution. A "Fisatom, model 752A" magnetic stirrer was used, which allows to control both stirring speed and temperature.

- Contact Time Control: The sample is shaken for a certain period.
- pH control: by repeatedly measuring the pH value, it is carried out using a "Hanna, model HI 8424" pH meter.
- Temperature control: by repeatedly measuring the value, it is carried out with a "GERMAN" digital spike thermometer.
- Sampling: 20 ml rich solution samples are taken every 1 hour.
- Analysis: the resulting solution is analyzed to determine the concentration of the metals of interest via both AA and ICP techniques (after acid digestion).

A series of tests are diagrammed varying certain operational conditions of importance in the leaching process, to determine the influence of said variables, as well as determine the optimal conditions for it.

3   Tests results

3.1. Chemical analysis results

To carry out the instrumental determination after acid digestion, an Inductively Coupled Plasma Optical Emission (ICP-OES) device was used. Measurements are carried out as mentioned in 2.1 Obtaining the results of Table 1.

3.2. Mineralogical analysis results

In both optical and electronic microscopes, Figs. 1 and 2; it was possible to observe; the presence of fairly predominant grains of chalcopyrite as the predominant species and other elements present that were corroborated with quantitative chemical analysis.
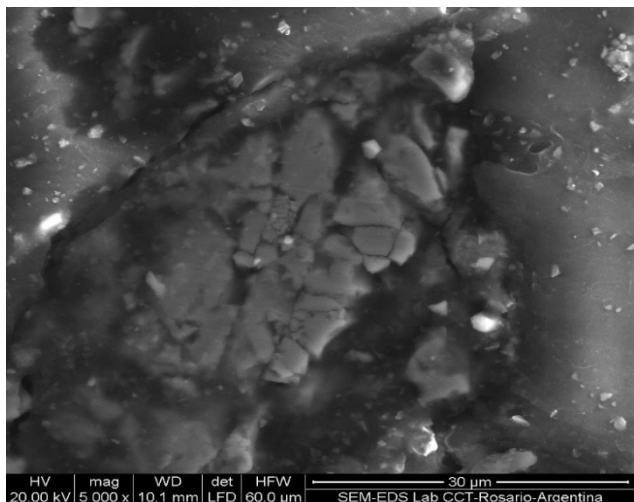

Figure 1. Scanning electron microscope (SEM) images of sample 1. Molybdenite with metal incrustation
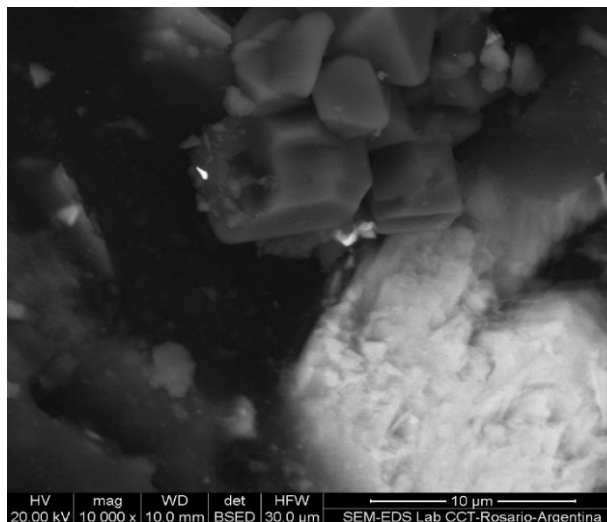Source: Bazan, Medina and Orozco, 2024.

Figure 2. Scanning electron microscope (SEM) images of sample 2. Molybdenite with the presence of pyrite
Source: Bazan, Medina and Orozco, 2024.

The diffractograms obtained are shown in Figs. 3 and 4. This allows us to qualitatively evaluate the differences that exist between each of the concentrates, in terms of the crystalline phases present in it.

The spectra obtained corroborate that in each sample the majority mineralogical species is chalcopyrite ($CuFeS_2$), it is also shown that the peaks are different due to the different concentrations of Molybdenite.

3.3   Experimental methodology results

According to studies carried out by Zhan-Fang Cao [18], it was concluded that the variation in the stirring rate, as well as in the amount of catalyst, does not yield significant changes in the results, so the stirring rate is maintained between 200-300 rpm and 1gr (one gram) of NaCl as catalyst. The effect of sodium chloride is attributed to the formation of stable sodium molybdate [19]

Table 1.
Chemical composition of samples.

Majority Elements	Sample	
	M1 (%)	M2 (%)
Mo	39,53	35,83
Cu	0,97	0,99
Fe	6,12	6,24
S	18,36	16,13
Trace Elements	Sample	
	M1 (mg/L)	M2 (mg/L)
Al	16,84	13,93
Na	0,62	0,56
K	0,49	0,43
Ni	0,40	0,40
Ag	0,20	0,20
Mn	0,60	0,60
Ca	25,50	25,90
Mg	6,40	6,00
Zn	0,60	0,60
Ba	3,20	2,70
Cd	0,60	0,60
As	0,13	0,14
Re	1,72	1,58

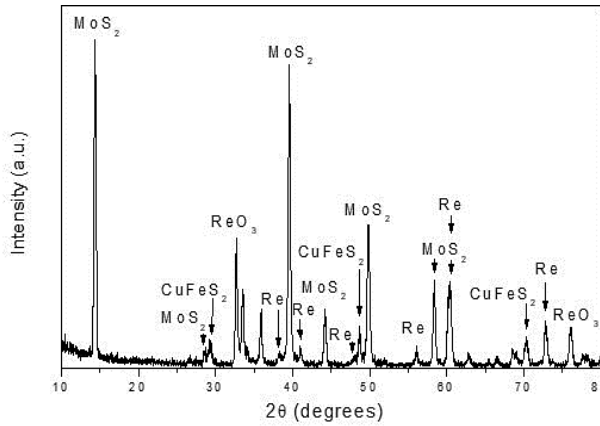Source: Bazan, Medina and Orozco, 2024.

Figure 3. Diffractogram of sample M1
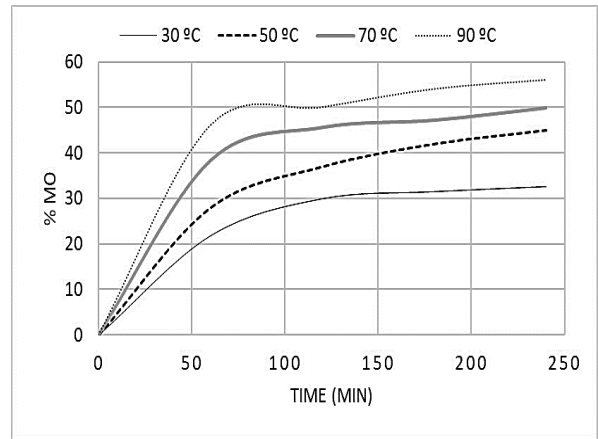Source: Bazan 2024.

Figure 5. Mo extraction at different temperatures.
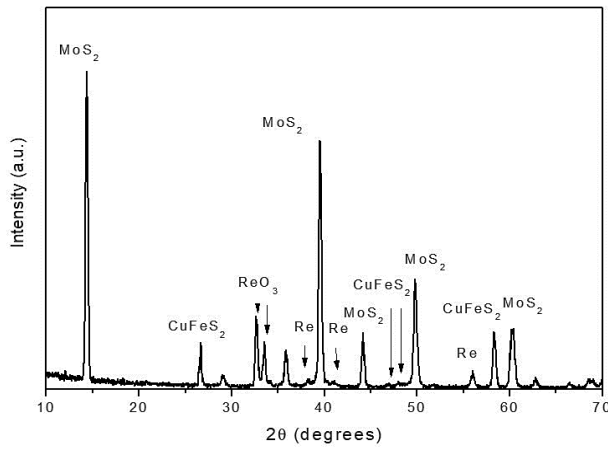Source: Bazan, Medina and Orozco, 2024.

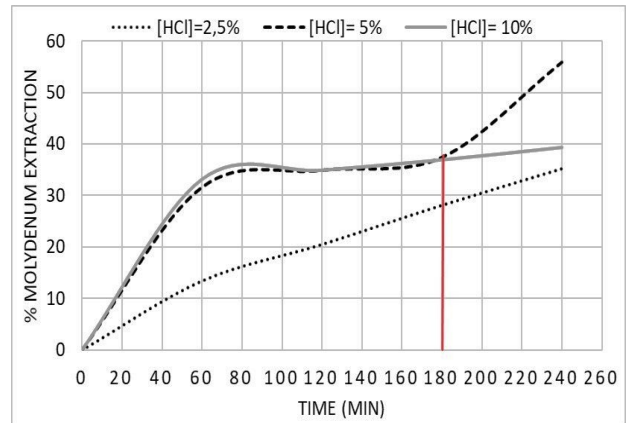Figure 4. Diffractogram of sample M2.
Source: Bazan 2024.

Figure 6. Mo extraction as a function of [HCl]
Source: Bazan, Medina and Orozco, 2024.

And according to Hesami [20], the pH oscillation around 8 due to the high dissolution rate of molybdenite in hypochlorite caused the production of hypochlorous acid. It seems that the presence of hypochlorous acid (strong oxidizing agent) in the pulp leads to the more extraction of molybdenum and copper.

3.3.1 Effect of operating temperature

The effect of temperature 30°C, 50°C, 70°C and 90°C has been studied with the following fixed conditions: ratio L/S:10/11 time:240 min, [HCl]=5%; pH:8.

The results obtained are shown in Fig. 5.

Temperature has an important effect on the dissolution rate of molybdenum; the highest extraction of Mo was reached at 180 minutes and 90 ºC.

For operational purposes, according to the results obtained, 50 ºC is energetically adequate to reduce energy cost. This effect of temperature on the dissolution rate of Mo tells us that increasing the reaction temperature increases the average kinetic energy of the reactants, thus accelerating the diffusion rate and the rate of the chemical reaction, which ultimately facilitates the chemical reaction.[21]

3.3.2 Effect of hydrochloric acid concentration

The next series of tests investigates the effect of the concentration of the leaching solution. Tests are carried out at different concentrations of the leach solution: 2.5%, 5% and 10% HCl, with the fixed conditions of: T.50°C, time: 240 min, L/S ratio: 10/1; pH:8. Results are shown in Fig. 6.

The highest percentage of molybdenum extraction was found at a HCl concentration of 5% for a time of 240 min.

The curve shows in Fig. 6 that for a concentration of 2.5% the rate of molybdenum dissolution is slow. The Mo extraction at the beginning of the tests for 5% and 10% shows a similar behavior until 180 min, then the Mo extraction increases rapidly for a concentration of 5% while for a concentration of 10% it remains asymptotic.

The decrease in the leaching percentage of Mo when HCl concentration was higher than 5% may be ascribed to the formation of passive film on the surface of the ores like elemental sulfur. In general, these passive films can be dissolved by a pitting mechanism in the presence of chloride ions.[22]

The lower dissolution of molybdenite (MoS_2) at a concentration of 2.5% is related to the stability of this mineral in acidic media. The quantitative extraction observed of HCl might be due to the ease with which MoO_2^{2+} is formed at high

acid concentration and the large presence of Cl⁻ ions required for the formation of an extractable complex. The complex might be further solved by HCl molecules thereby increasing its extractability.[23]

The graph suggests that HCl solutions in concentrations greater than 5% have no apparent effect on Mo extraction. Therefore, the dissolution of metals can be decreased by the formation of passivation layers of sulfides, metal oxides and hydroxides [24] on the surface of the mineral.

Therefore, the 5% HCl concentration is chosen as the optimal concentration for subsequent tests.

3.3.3 Effect of the liquid-solid relationship

The effect of the liquid-solid ratio (mass/volume) from 5:1 to 25:1 was studied with the following fixed conditions T:50°C, time:240 min, [HCl]=5%; pH:8.

Fig. 7 shows the effect of liquid-solid ratio on molybdenum leaching ratios. As a low liquid-solid ratio can inhibit the diffusion of ions in solution [23]. When the liquid-solid ratio is 25:1 ml/g, the maximum extraction obtained at 240 min is 41.1%. The maximum percentage of Mo extraction at 240 minutes was achieved with a solid-liquid ratio of 10:1 of 49.9%. As the percentage of solids increases, metal recoveries decrease, since there would be less hydrochloric acid available to leach a greater amount of solid.[26].

Based on bibliographic research, it has been verified that researcher Joseph D. Lessard has demonstrated that the incorporation of additional reagents, such as $FeCl_3$ (iron (III) chloride) solutions, in the acid molybdenum leaching procedure, leads to significant improvements in process effectiveness. This is because $FeCl_3$ reacts with copper (Cu) and iron (Fe) following a specific chemical reaction eq. (1):

$$CuFeS_2 + 4FeCl_3 \rightarrow CuCl_2 + 5FeCl_2 + 2S \qquad (1)$$
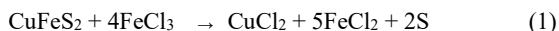
This reaction is of the redox type where: Both S^{-2} and Cu^{+1} are oxidized to SO_4^{-2} and Cu^{+2} by the Fe^{+3} of $FeCl_3$. Fe is reduced to Fe^{+2} to form $FeCl_2$, whose compound is stable and does not interfere with the Mo leaching reaction.
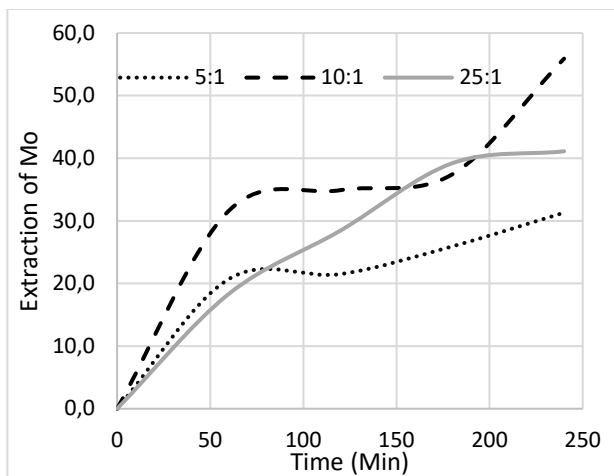
Figure 7. Mo Extraction as a Function of S/L Ratio
Source: Bazan, Medina and Orozco, 2024.

Consequently, a new series of tests are planned to use the ideal conditions previously identified, in addition to the incorporation of this specific reagent.

3.3.4 Effect of adding ferric chloride

In this series of tests, the concentration of $FeCl_3$ is varied from 2.5-5 and 10%, with the following fixed conditions: T:50°C, time: 240 min, [HCl]=5%; pH:8 and an S/L ratio= 10.1. Obtaining the results of Fig. 8.

The optimal molybdenum extraction conditions are temperature of 50°C, a HCl concentration of 5%, a $ClFe_3$ concentration of 2%, an S/L ratio of 10:1 and a reaction time of 60 minutes.
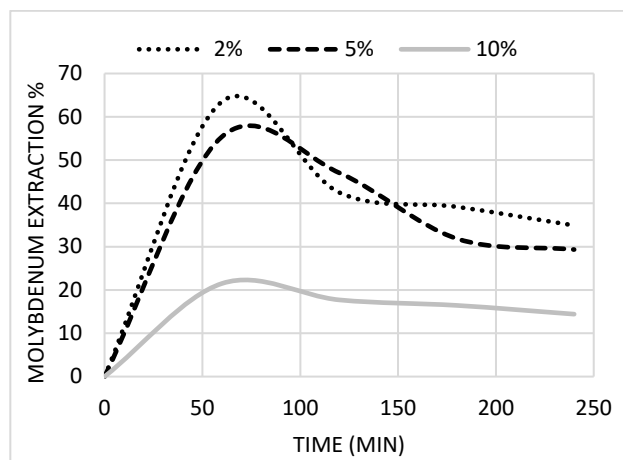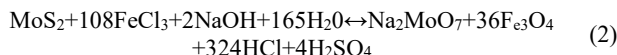
Figure 8. Mo extraction, as a function of ferric chloride ($FeCl_3$).
Source: Bazan, Medina and Orozco, 2024.

In Fig. 8 a greater recovery of Mo occurs with the addition of $FeCl_3$ at a pH greater than 8, controlling with NaOH, with a time of 60 minutes of operation, producing the following proposed chemical reaction. Eq. (2):

$$MoS_2+108FeCl_3+2NaOH+165H_2O \leftrightarrow Na_2MoO_7+36Fe_3O_4 \\ +324HCl+4H_2SO_4 \qquad (2)$$

This can be corroborated according to the Eh-pH diagrams in Fig. 9, determined experimentally during the leaching processing where the Eh value was around =-0.127 Volt.

Although the recovery of Mo was found, under optimal operating conditions, it is important to analyze the effect of leaching on copper and iron metals in molybdenite so that it can be a marketable product.

The copper content in molybdenite concentrates is crucial since the steel industry is the primary consumer of molybdenum produced from molybdenite. Therefore, molybdenum compounds produced for the steel industry must contain very little copper to minimize the deleterious effect of this impurity on the physical properties of the resulting alloy steels [18].
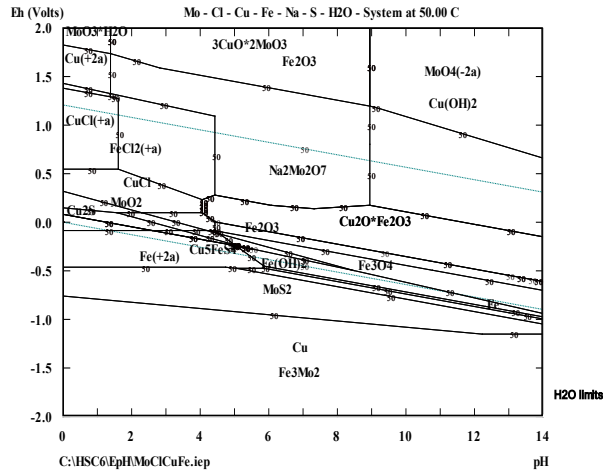
Figure 9. Eh-pH diagram of the leaching process with FeCl$_3$.
Source: Bazan, Medina and Orozco, 2024

Table 2.
Analysis of variance (ANOVA)

Anova for Response Surface Quadractic Model					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob>F
Model	422.12	5	84.42	43.36	0.0004
A-Temperature	134.26	1	134.46	69.06	0.0004
B-Tiempo	148.37	1	148.37	76.2	0.0003
AB	28.62	1	28.62	14.7	0.0122
A^2	101.7	1	101.7	52.23	0.0008
B^2	0.011	1	0.011	5.55E+00	0.9435
Residual	9.74	5	1.95		
Lack of Fit	8.7	3	2.9	5.57	0.1559
Pure Error	1.04	2	0.52		
Cor total	431.86	10			
Std Dev	1.4		R-Squared		0.9775
Mean	41.18		Adj R-Squared		0.9549
C.V. %	3.39		Pred R-Squared		0.8514
PRESS	64.17		Adeq Precision		20.738

Source: Bazan, Medina and Orozco, 2024.

The next stage was to focus on the percentage of iron and copper extraction. Fig. 10 shows the results obtained

Lessard investigates that the residual Cu remaining in the concentrate is found to exist as Cu$_2$S, lending further credence to the hypothesis that CuFeS$_2$ is decomposed and trivalent Fe is selectively reduced while most Cu, Fe, and S are removed during leaching. Increasing the FeCl$_3$ concentration also leads to an increase in the MoO$_2$ production, likely due to the decreased pH.[27]

Table 3.
Equation coefficients

a	-29.472720
b	1.622150
c	0.189800
d	-0.001980
e	-0.009430
f	-1.08E-05

Source: Bazan, Medina and Orozco, 2024.

3.3.5 Optimization of significant variables

To obtain maximum information from a minimum number of experiments, a Box-Behnken experimental design (BBD) was implemented using the Design-Expert software. Using the experiments mentioned above, with 2 center points of two factors (A and B) at three levels,

A: Temperature (30°C, 60°C, 90°C),
B: Time (60min, 150min and 240min).
The variables that remain fixed are:
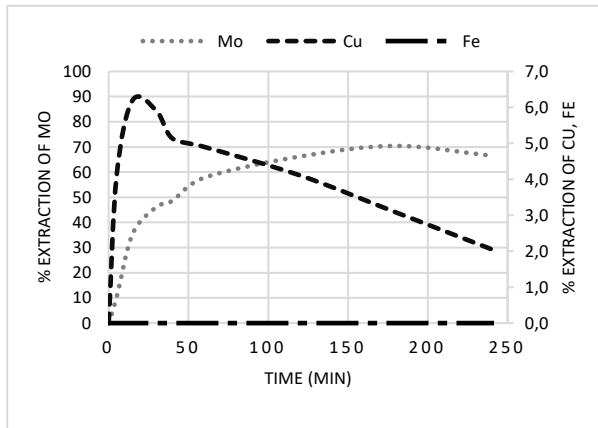pH ≥ 8; HCl concentration 5%; S/L ratio 10:01; stirring speed 200-300rpm.

Figure 10. Mo extraction compared to Cu and Fe.
Source: Bazan, Medina and Orozco, 2024.

The optimization criterion was to maximize Mo extraction at different temperatures and time.

The data obtained were fitted to a Quadratic vs 2FI model with regression analysis. From the analysis of variance (ANOVA) in Table 2, it can be corroborated based on F value of 43.36 that the model is significant; with an R and an adjusted R^2 of 0.9775% and 0.9549%, respectively.

In this way, the 3D response surface serves to graphically visualize the interaction effects of independent variables. Fig.11 shows that the optimal working conditions were found for a temperature of 60°C and a time of 220min. Source: Bazan, Medina and Orozco, 2024.

Resulting in a regression eq. 3 as shown below:

$$\%Extraction\ Mo = a + b \cdot T + c \cdot t - d \cdot T \cdot t - e \cdot T^2 - f \cdot t^2 \quad (3)$$

Where:

T is the temperature and t is the time. The coefficients are shown in the Table 3.

In Fig. 11, experiments were applied that allow the cells to move quickly; proximity to the optimum sought for the response, studying each factor at least two levels for analysis of curvature, having several points that allow estimating all the terms of the model of equation (3); providing a stable prediction error in the experimental environment. With the leaching carried out, the dissolution of molybdenum was insignificant, 100% of the iron was dissolved, but the dissolution of copper was not important or significant to meet market requirements.

An optimization of significant variables was carried out using the Design-Expert software. It can be confirmed that the model is significant since it gives an R value and an adjusted R^2 of 0.9775% and 0.9549% respectively. The optimal working conditions according to the model are a temperature of 60°C and a time of 220min.

4 Conclusions

Based on the discussion presented above, the following conclusions were reached:

Regarding the chemical and mineralogical characterization carried out, it is concluded that the data provided by the chemical analyzes (Mo, Cu and Fe) coincide with the mineralogical analysis, confirming the presence of Molybdenite (MoS_2), Pyrite (FeS_2), Chalcopyrite ($CuFeS_2$), Bornite (Cu_5FeS_4) and Covelline (CuS), minerals of said elements.

The high proportion of sulfur S confirms that these are sulfide mineral species.

Figure 11. 3D response surface plots for Mo extraction at different temperatures and times.
Source: Bazan, Medina and Orozco, 2024.

It is also evident that the concentrations of the elements present in each sample are similar, corroborating good homogenization and quartering of the sample. The novel molybdenum extraction process was developed from a concentrate of molybdenite and chalcopyrite mainly, using hydrochloric acid as a leaching solution, sodium chloride as a catalyst, sodium hydroxide as a pH regulator to be able to work in a basic environment (pH>8).

Experiments show that it is an effective technique for extracting molybdenite concentrate by using hydrochloric acid. The experimental results show that leaching time, pH, liquid-solid ratio, leaching temperature and hydrochloric acid concentration have a significant effect.

The use of $FeCl_3$ solutions produces a positive effect on leaching, since they allow better recovery of Mo to be achieved in less operating time and allows selective leaching of the desired element.

The optimal technological parameters were determined for molybdenum leaching as follows: working pH greater than 8, temperature of 50 °C, hydrochloric acid concentration of 5%, solid/liquid ratio of 10:1, stirring rate of 200-300 rpm and the addition of 2% ferric chloride. Mo leaching was 70% under experimental conditions at a time of 180 minutes.

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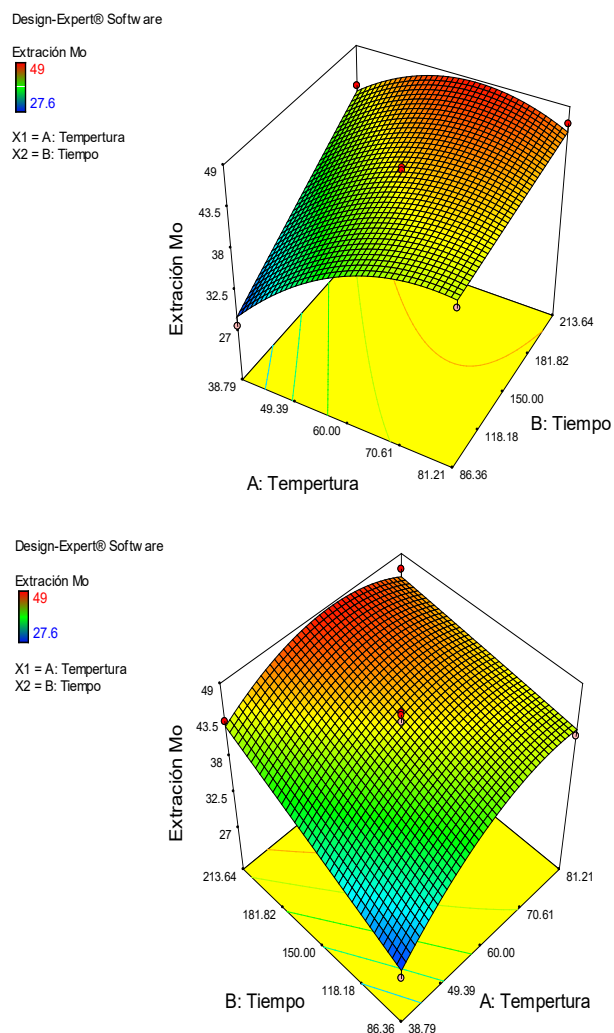
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