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Mechanism and leaching kinetics of molybdenite concentrate in a hydrogen peroxide-acid system

Alvaro Aracena ¹, Alan Azocar ², Juan Patricio Ibáñez ², Oscar Jerez ³

¹ Escuela de Ingeniería Química, Pontificia Universidad Católica de Valparaíso, Avenida Brasil 2162, Cod. Postal 2362854, Valparaíso, Chile

² Departamento de Ingeniería Metalúrgica y de Materiales, Universidad Técnica Federico Santa María, Avenida España 1680, Valparaíso, Chile

³ Instituto de Geología Económica Aplicada (GEA), Universidad de Concepción, Casilla 160-C, Concepción, Chile

Corresponding author: alvaro.aracena@pucv.cl (Alvaro Aracena)

Abstract: The mechanism and leaching kinetics of a molybdenite concentrate in a H₂O₂-H₂SO₄ system were studied. The experimental work was performed in a batch reactor equipped with a condenser, a mechanical agitator and a temperature control system. The effects of the temperature, H₂O₂ and H₂SO₄ concentrations, particle size, liquid/solid ratio and agitation speed on the Mo recovery were investigated. The thermodynamic results showed that the leaching mechanism it was governed by several intermediate reactions; however, the influences of sulfuric acid and passivation were not observed in the reaction. The most predominant experimental result was the maximum Mo recovery of 81.3% by leaching 64 μm particles at 333 K (60 °C) for 5400 s (90 min). The molybdenum recovery was generally enhanced by increasing the H₂O₂ and H₂SO₄ concentrations. However, at H₂SO₄ concentrations higher than 1.0 mol/dm³, the Mo recovery decreased. Although the agitation speed affected the Mo recovery considerably, high recoveries could be still obtained without mixing. The experimental results and XRD analysis confirmed the reaction mechanisms. The leaching kinetics were analyzed using a shrinking core model in which the rate was controlled by diffusion through a porous layer with radius r_0 . The reaction rate orders were 1.0 and 0.2 for the H₂O₂ and H₂SO₄ concentrations, respectively, and the rate was inversely proportional to the square of the initial particle radius. The calculated activation energy was 75.2 kJ/mol in the temperature range of 278-333 K (5-60 °C).

Keywords: Molybdenite concentrate, hydrogen peroxide, kinetics, mechanism of reaction

1. Introduction

The main strategic advantages of the element molybdenum are its high durability, strength, and resistance to corrosion and temperature extremes. According to the International Molybdenum Association (IMOA), this element is typically used to produce high-strength steel alloys. In 2012, the production of molybdenum containing stainless steel accounted for approximately 20% of molybdenum use, and another 57% was employed in construction steel, tools, high speed steel and cast iron. The remaining molybdenum use was in enhanced products such as lubricant grade molybdenite (molybdenum disulfide, MoS₂), molybdenum chemical compounds and molybdenum metal. Although several different ores contain molybdenum, only molybdenite is suitable for industrial processing because it can be used to obtain marketable products. During metallurgical treatment, molybdenite is processed by ore flotation to produce a concentrate, which is then oxidized (roasted) in a multiple hearth furnace at temperatures between 773 K (500 °C) and 923 K (650 °C) to yield a molybdenum trioxide (MoO₃) concentrate, namely, molybdite, according to reaction:



During molybdenite roasting, toxic gases, such as SO_2 and SO_3 , are generated, depending on the oxidizing conditions, and these gases are subsequently emitted into the air. These pollutants can cause acid rain, thus harming the environment. The roasting process requires high energy (translated into heat) and generally reaches high temperatures, leading to increased production costs of molybdenum trioxide. Therefore, new mineral processing methods must be developed. Accordingly, a hydrometallurgical process was proposed as an alternative to MoS_2 roasting during molybdenum production. Because molybdenite is highly resistant to leaching, an oxidizing agent must be used to facilitate molybdenum extraction. This oxidizing agent must comply with the current global environmental regulations; in particular, its use must not result in the generation of chemicals that are harmful to humans or wildlife. In addition, the oxidizing agent should not create problems in stages subsequent to the leaching process (these stages are solvent extraction (SX) and electrowinning (EW)) mainly due to the use of agents such as ferric salts (Fe^{3+}), chlorides (Cl^-), and manganese (Mn^{2+}), causing damage to the equipment and serious problems with the chemical reagents used in the SX and EW stages. Therefore, in this study, hydrogen peroxide (H_2O_2) is proposed as a suitable oxidizing agent (with an oxidation potential of 1.7 V) because it decomposes into water and gaseous oxygen in aqueous solutions and is an environmentally attractive oxidizing agent.

The objective of this work is to analyze the feasibility of using hydrogen peroxide to leach molybdenite in an acidic solution. Unfortunately, at present, the leaching mechanisms of the molybdenite concentrate (or of crystallized or sintered molybdenite) with hydrogen peroxide are not clear. In this work, a critical study is conducted on the most recent stage in the development of molybdenite concentrate leaching, demonstrating the scarcity of information on this subject.

1.1. State of the art

Several studies on molybdenite concentrate leaching have appeared in the literature. Cao et al. (2009) leached molybdenum from molybdenite concentrate (41.40% Mo, 31.40% S, 2.20% Cu) using a NaClO_3 -HCl solution. The optimal operating temperature was determined to be 70 °C. Molybdenite was rapidly converted (leached), and a high recovery of approximately 98% was achieved, indicating that leaching could be a feasible alternative to roasting. However, a kinetic model could not be established due to insufficient data. Furthermore, the kinetic parameters for the molybdenum recovery rate at different temperatures were not determined.

Goodarzi et al. (2017) studied the leaching kinetics of a molybdenite concentrate using the Taguchi method (by experimental design). The effects of the leaching time, temperature, H_2O_2 concentration, H_2SO_4 concentration, pulp density and agitation speed on molybdenum extraction were investigated. Six control factors with 5 levels were employed in the analysis. In a classic full factorial experimental design, 5^6 (15,625) experiments would be required to study the selected space. Using the Taguchi L25 matrix, the number of required experiments was drastically reduced to 25. Analysis of variance (ANOVA) of the experimental results combined with practical observations of the leaching process indicated that an ash layer was not formed during leaching and that the particle decreased in size until it finally disappeared. Thus, the molybdenite concentrate dissolution process was chemically controlled, and diffusion models were not applicable. Furthermore, the activation energy of molybdenite dissolution in the presence of H_2O_2 and sulfuric acid was determined to be 46.5 kJ/mol. The most significant factors affecting molybdenite dissolution were the H_2O_2 concentration, pulp density and reaction temperature. Unfortunately, more tests were needed to conclusively establish these relationships; therefore, the information obtained could not be used to validate this hypothesis.

Madeja (2011) studied leaching of valuable minerals from catalysts used in partial oil hydrodesulfurization. The accumulation of metals, such as Mo, V, Ni, Co, Fe, Ti, Sn and As, on the catalyst surface results in a gradual decrease in its effectiveness until it is completely deactivated. Therefore, the leaching kinetics of molybdenum, nickel, vanadium and aluminum in an oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) system, in which soluble metal complexes can form, and in a H_2O_2 system were investigated. Based on the results, it was concluded that the molybdenum leaching rate was chemically controlled at the surface. The activation energy was determined to be 31 ± 2 kJ/mol at $\text{H}_2\text{C}_2\text{O}_4$ and H_2O_2 concentrations of 0.5 mol/dm³ and 3 mol/dm³, respectively. Unfortunately, conclusive chemical reactions representing the dissolution of the metals previously studied were not obtained.

In another study, Lasheen et al. (2013) investigated the leaching kinetics of low-grade ores containing 500 ppm molybdenum and 5000 ppm uranium. The leaching experiments were performed in a H_2SO_4 solution with H_2O_2 as the oxidizing agent, and the effects of the H_2SO_4 concentration, H_2O_2 concentration, leaching time, temperature, solid/liquid ratio, particle size and agitation speed on the extraction process were studied. The optimal conditions were determined to be a H_2SO_4 concentration of 2.5 mol/dm^3 , a H_2O_2 concentration of 0.5 mol/dm^3 , a leaching time of 7200 s (2 h), a temperature of 368 K (95°C), a solid/liquid ratio of 1:14, an ore particle size of $74 \mu\text{m}$ and an agitation speed of 600 r/min. The reaction was chemically controlled, and the calculated apparent activation energy of molybdenite leaching was 40.4 kJ/mol . In addition, other kinetic parameters (reaction order, particle size, etc.) that control the leaching process were determined. Unfortunately, the presence of other elements (such as uranium) may have interacted with the consumption of reagents.

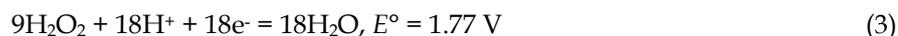
Therefore, in this study, a thermodynamic analysis was conducted to elucidate the possible dissolution mechanisms of molybdenite with hydrogen peroxide. Furthermore, the leaching kinetics of a molybdenite concentrate in a H_2O_2 -acid system was evaluated under different experimental conditions to develop a kinetic model and obtain the relevant kinetic parameters.

1.2. MoS_2 dissolution mechanism

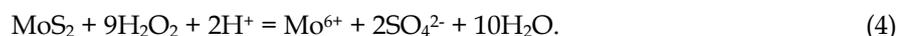
Molybdenite oxidation in an acidic solution ($\text{pH} \leq 1.0$) follows an electrochemical process that involves mineral leaching. During this process, the metal and sulfide ions are released into solution:



Molybdenite dissolution generates Mo^{+6} ions because the +6 oxidation state is the most stable of the 6 possible Mo oxidation states (0, +2, +3, +4, +5 and +6) (Gupta, 2000). This anodic process is confirmed by hydrogen peroxide reduction:



where E° is the standard electrode potential of the given reaction for the overall mechanism:



However, reaction (4) is incomplete because molybdenum ions (for example, Mo^{+6}) are thermodynamically unstable in solution (Gupta, 2000), and they react with water to form different molybdate and polymolybdate species. Fig. 1 shows the E_h -pH diagrams of the Mo-S- H_2O system at 293 K (20°C), 313 K (40°C) and 333 K (60°C). These diagrams were used to identify the molybdate species formed in solution at different pH values. To construct these diagrams, Mo and acid concentrations of 0.003 mol/dm^3 and 1.0 mol/dm^3 , respectively, were employed, and the equilibrium thermodynamic data were mainly obtained from the HSC Chemistry database (Roine, 1999).

As shown in Fig. 1, an increase in the temperature does not affect the MoO_2^{+2} stability region. In contrast, the equilibrium pH between the anionic polymetallic $\text{Mo}_7\text{O}_{24}^{-6}$ and MoO_4^{2-} complexes shifts toward more acidic values, from a pH of 5.9 at 293 K (20°C) to a pH of 5.0 at 333 K (60°C). This shift results in a decrease in the $\text{Mo}_7\text{O}_{24}^{-6}$ stability region and an increase in the MoO_4^{2-} stability region.

Furthermore, an increase in temperature leads to a more vertical line between molybdenite and its ionic species, which decreases the stability region of MoS_2 and increases that of the ionic species. In addition, at 333 K (60°C), MoO_2^{2+} is present in the solution when the pH is less than 1.0, whereas the predominant species is $\text{Mo}_7\text{O}_{24}^{-6}$ in the pH range of 1-5.0. Above a pH of 5.0, MoO_4^{2-} is present in the solution. Therefore, MoO_2^{2+} is formed under acidic pH conditions ($\text{pH} < 1.0$) by the following reaction:



The overall molybdenite electrochemical oxidation reaction is obtained by combining reactions (4) and (5):



Sulfuric acid is consumed in reaction (6) because, although H_2SO_4 does not react during molybdenite leaching, it acts as a stabilizer during hydrogen peroxide decomposition. Therefore, it helps to sustain reaction (6) (Antonijevic, 1997), thus stabilizing the molybdenite leaching reaction.

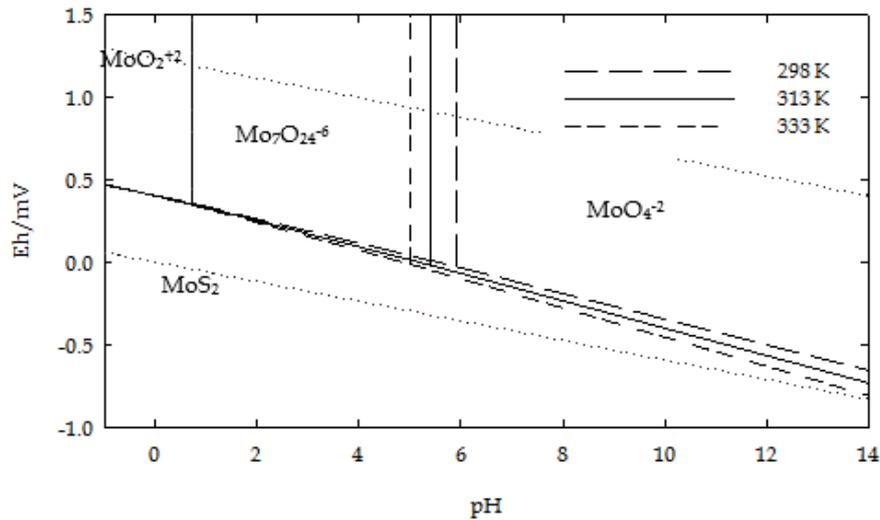


Fig. 1. E_h -pH diagram for Mo-S- H_2O system at 293, 313 and 333 K (20, 40 and 60°C) ($[\text{Mo}] = 0.003 \text{ mol/dm}^3$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol/dm}^3$)

2. Experimental procedure

Molybdenite concentrates were obtained by the selective flotation process at the Codelco concentrator plant (El Teniente Division). The elemental composition (% w/w) of the concentrate was 49.55% Mo, 1.92% Cu, 2.54% Fe and 37.40% S, and the rest was silica. Assuming that all of the molybdenum was in the form of molybdenite (MoS_2), the MoS_2 concentration would be 82.67%. To verify this assumption, the molybdenite concentrate was analyzed by X-ray diffraction (XRD). As shown in Fig. 2, only molybdenite peaks were observed in the diffraction pattern.

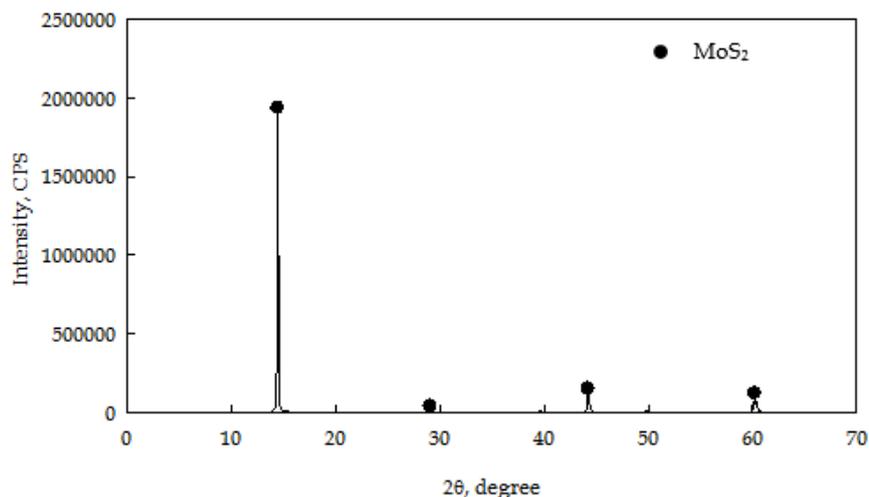


Fig. 2. XRD analysis of molybdenite concentrate

The concentrate was sieved with different meshes to obtain uniformly sized particles. The particle size ranges were 53-75 μm , 75-106 μm and 106-180 μm , corresponding to average particle sizes of 64, 90.5 and 143 μm , respectively.

The leaching experiments were performed in a 2 dm^3 glass reactor equipped with a mechanical agitator, a heat blanket, a thermocouple, a porous tube for extracting liquid samples, and a water-cooled

condenser to minimize solution losses due to evaporation. To maintain low temperatures (278 K), a thermoregulatory bath coupled to the glass reactor was used.

In a typical experiment, 1.0 dm³ of a sulfuric acid leaching solution and hydrogen peroxide with a given concentration were added to the glass reactor. Then, the solution was heated to the desired temperature, and 10⁻³ kg (1.0 g) of the molybdenite concentrate was subsequently added to the system. During the leaching reaction, liquid samples were extracted at different times, and the molybdenum concentration of the extracted solution was measured by atomic absorption spectroscopy (AAS). At the end of each experiment, the solution was filtered, and the solid residue was washed and dried before the X-ray diffraction analysis.

3. Result and discussion

3.1. Effect of agitation speed

The effect of the agitation speed on molybdenite concentrate leaching was studied under the following operating conditions: a temperature of 333 K (60 °C), a H₂O₂ concentration of 5 mol/dm³, a H₂SO₄ concentration of 1 mol/dm³, a liquid/solid ratio of 1429 dm³/kg and an average particle size of 64 μm. Agitation speeds of 200, 300 and 400 rpm were tested. Additionally, the leaching experiment was performed without agitation (0 rpm) for comparison. Fig. 3 shows the molybdenum extraction results as a function of time for all speeds tested.

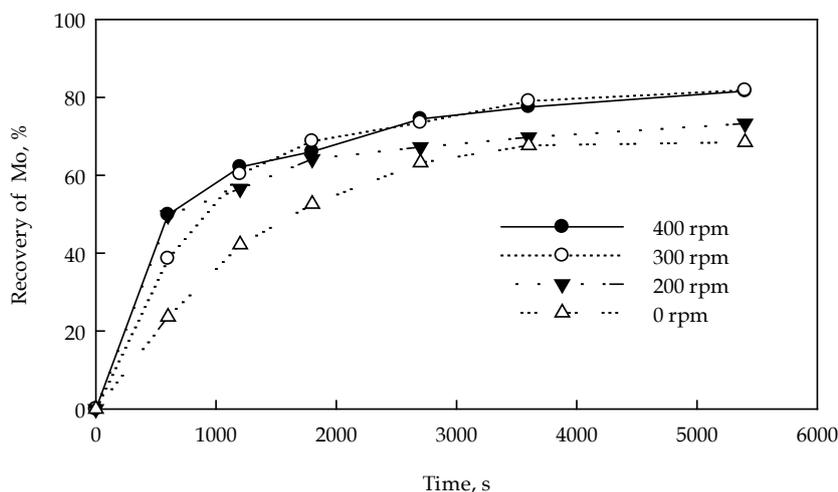


Fig. 3. Effect of the agitation speed on molybdenum recovery. Working conditions: Temperature = 333 K, [H₂O₂] = 5 mol/dm³, [H₂SO₄] = 1 mol/dm³, Average particle size = 64 μm, liquid/solid ratio = 1429 dm³/kg

Generally, the molybdenum recovery increased with increasing agitation speed. After 5400 s (90 min), the recoveries were 73.3% and 81.5% for the agitation speeds of 200 and 300 rpm, respectively. The molybdenite dissolution rate reached plateau at agitation speeds above 300 rpm. This result indicates that mass transfer does not play an important role in the leaching process at higher agitation speeds. Therefore, the following experiments were performed using an agitation speed of 300 rpm. Fig. 3 also shows that when the system was not agitated (agitation speed of 0 rpm), a good molybdenum recovery of up to 68.5% was still obtained after 5400 s (90 min).

3.2. Effect of solution temperature

Fig. 4 shows the Mo recoveries measured at different temperatures in the range of 278-333 K (5-60°C) under the operating conditions employed in the previous section. This temperature range was chosen based on previous studies (Antonijevic et al., 1997; Agacayak et al., 2014) mainly because hydrogen peroxide decomposes rapidly near 70 °C.

The temperature considerably affects the molybdenite concentrate leaching rate. Increasing the temperature from 278 to 333 K (5 to 60 °C) led to an increase in the molybdenum recovery from 11.5%

to 81.3% after 5400 s (90 min) of leaching due to the exponential growth of the apparent rate constant, as discussed below.

At the lowest temperature tested (278 K (5°C)), which is close to the freezing point of water, the Mo recovery was 10%. Hydrometallurgical plants in Chile currently operate at this temperature.

It is proposed that the molybdenite leaching mechanism in a $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ system is described by reaction (6). To verify this leaching mechanism, molybdenite was partially leached at 333 K (60°C) for 1200 s (20 min). The solid sample was subsequently filtered, dried and analyzed by XRD. The XRD results showed only the presence of MoS_2 in the solid sample. It is concluded that no intermediate molybdenum species are formed during molybdenite leaching, therefore, this process can be described by reaction (6).

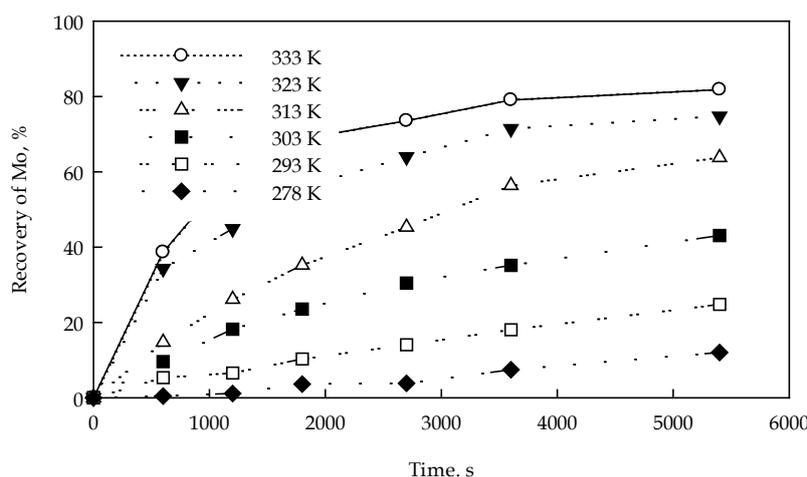


Fig. 4. Effect of solution temperature on molybdenum recovery. Working conditions: agitation speed = 300 rpm, $[\text{H}_2\text{O}_2] = 5 \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4] = 1 \text{ mol/dm}^3$, average particle size = 64 μm , liquid/solid ratio = 1429 dm^3/kg

3.3. Effect of H_2O_2 concentration

The H_2O_2 concentration was varied over the range of 0.1-5.0 mol/dm^3 under the conditions used in the previous sections. Fig. 5 shows the molybdenum recovery as a function of time for different H_2O_2 concentrations.

Even at a low H_2O_2 concentration of 0.1 mol/dm^3 , the molybdenum recovery of 24.0% was achieved in 5400 s (90 min). The Mo recovery nearly doubled to 44.0% when the concentration increased to 0.5 mol/dm^3 . At high H_2O_2 concentrations of 3 mol/dm^3 and 5 mol/dm^3 , the Mo recoveries were 75 and 81%, respectively, after 5400 s (90 min).

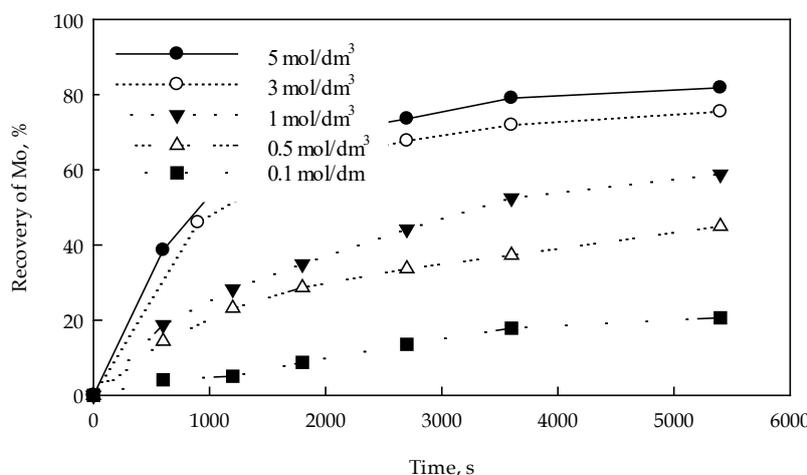


Fig. 5. Effect of H_2O_2 concentration on molybdenum recovery. Working conditions: Temperature=333 K, Agitation speed=300 rpm, $[\text{H}_2\text{SO}_4]=1 \text{ mol/dm}^3$, average particle size=64 μm , liquid/solid ratio=1429 dm^3/kg

3.4. Effect of H₂SO₄ concentration

The effect of the H₂SO₄ concentration (0.1, 0.5, 1.0, 2.0, and 3.0 mol/dm³) on the molybdenite recovery was investigated under the same conditions as those used in the previous sections, and the results are presented in Fig. 6.

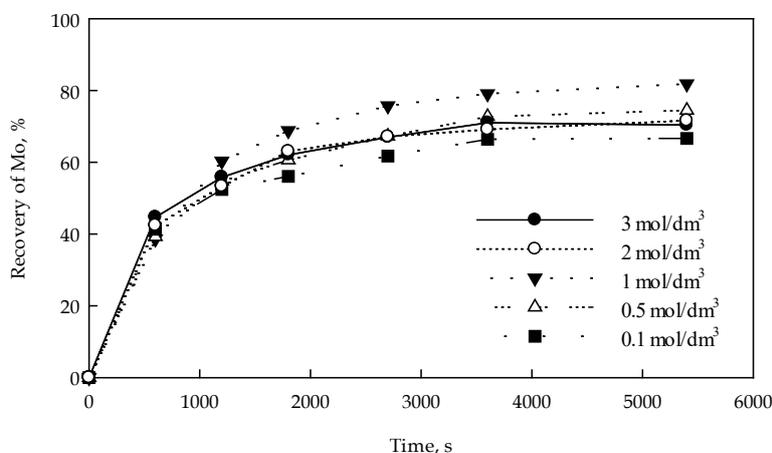


Fig. 6. Effect of the H₂SO₄ concentration on the molybdenum recovery. Working conditions: Temperature = 333 K, [H₂O₂] = 5 mol/dm³, agitation speed = 300 rpm, average particle size = 64 μm, liquid/solid ratio = 1429 dm³/kg

The results show that sulfuric acid was required for the molybdenum recovery. Even at low H₂SO₄ concentrations (0.1 mol/dm³), the molybdenum recovery was high, reaching 66% in 5400 s (90 min). The Mo recovery increased to 74.4% and 81.8% as the acid concentration increased to 0.5 mol/dm³ and 1.0 mol/dm³, respectively. However, at H₂SO₄ concentrations of 2 and 3 mol/dm³, lower recoveries of 72% and 70%, respectively, were obtained. This behavior was primarily due to the increase in the sulfate ion (HSO₄⁻ and SO₄²⁻) concentrations with increasing acid concentrations. Antonijevic et al. (1997) found that an increase in the sulfate concentration negatively affected the iron recovery from pyrite and concluded that the sulfate ions competed with H₂O₂ molecules for the adsorption sites on the particle surface, leading to a decrease in the pyrite dissolution rate. Therefore, although H₂SO₄ acted as a stabilizing agent during rapid H₂O₂ decomposition, the findings of Antonijevic et al. (1997) indicated that the decrease in the molybdenite leaching rate at high H₂SO₄ concentrations observed in this study might be due to the competitive adsorption between sulfate ions and H₂O₂ on the MoS₂ surface.

3.5. Effect of particle size

The effect of the average particle size on the MoS₂ leaching rate was studied using particles with average sizes of 64, 90.5 and 143 μm, and the results are presented in Fig. 7.

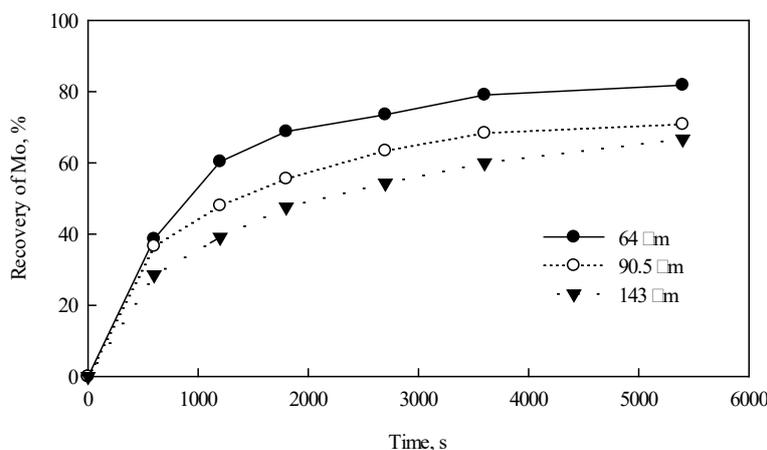


Fig. 7. Effect of average particle size on the molybdenum recovery. Working conditions: Temperature = 333 K, [H₂O₂] = 5 mol/dm³, H₂SO₄ = 1 mol/dm³, agitation speed = 300 rpm, liquid/solid ratio = 1429 dm³/kg

Generally, the molybdenum recovery increased with decreasing the particle size and can reach 81% in 5400 s (90 min). When the average particle size was 143 μm , the Mo recovery decreased to 67% at 5400 s (90 min) due to the decrease in the surface area with increasing the particle size.

3.6. Effect of liquid-to-solid ratio (dm^3/kg)

To study the effect of the liquid/solid ratio on molybdenite leaching, experiments were performed for 5400 s (90 min) using liquid/solid ratios in the range of 143-2000 dm^3/kg . Fig. 8 shows the molybdenum recovery as a function of dm^3 solution/kg particle for different liquid/solid ratios.

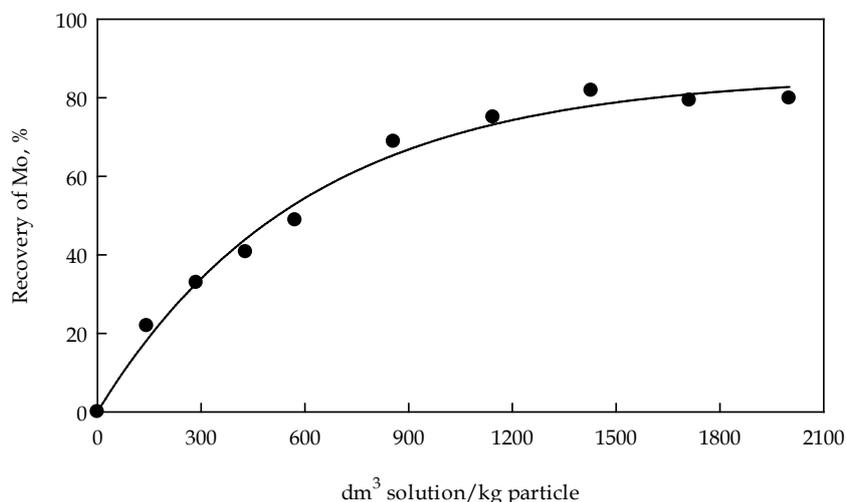


Fig. 8. Effect of the liquid/solid ratio on the molybdenum recovery. Working conditions: Temperature=333 K, $[\text{H}_2\text{O}_2]=5 \text{ mol}/\text{dm}^3$, $[\text{H}_2\text{SO}_4]=1 \text{ mol}/\text{dm}^3$, average particle size=64 μm , agitation speed=300 rpm, time=5400 s (90 min)

As the ratio increased from 0 to 857 dm^3/kg , dissolution of MoS_2 increased rapidly, and the Mo recovery was equal to 68.8%. At higher liquid/solid ratios, the molybdenum recovery increased gradually, reaching 81.5% when the ratio was 1429 dm^3/kg .

3.7. Molybdenite leaching kinetics

The behavior of the molybdenite leaching results as a function of temperature (Fig. 4) suggests that MoS_2 dissolution in a H_2O_2 -acid system can be described by the porous layer model. Therefore, assuming that the reactant concentrations are constant and that the rate is controlled by diffusion through a porous layer with radius r_o , the rate equation for the shrinking core model can be written as follows (Shon and Wadsworth, 1979):

$$1 - 3(1 - \alpha)^{\frac{2}{3}} + 2(1 - \alpha) = k_{app}t \quad (7)$$

where a is the fraction of reacted molybdenite. The apparent rate constant k_{app} is a function of temperature, H_2SO_4 concentration, H_2O_2 concentration and particle size, and it is related to the intrinsic rate constant of the system by the following equation:

$$k_{app} = k \frac{C_{\text{H}_2\text{O}_2}^q C_{\text{H}_2\text{SO}_4}^p}{r_o^2} \quad (8)$$

where k is the intrinsic rate constant; $C_{\text{H}_2\text{O}_2}$ and $C_{\text{H}_2\text{SO}_4}$ are the H_2O_2 and H_2SO_4 concentrations, respectively; b is a stoichiometric constant; q and p are the reaction orders with respect to the H_2O_2 and H_2SO_4 concentrations, respectively; and r_o is the particle radius.

Fig. 9 shows the fit of the porous layer model (equation (7)) to the experimental data in Fig. 4. The model curves exhibit a good linear fit to the kinetic data with regression coefficients, R^2 , greater than 0.90, indicating that equation (7) describes this system well. Table 1 shows the apparent rate constants at different temperatures obtained from the slopes of the linear fits.

The linear fits of the model to the experimental data are very good, with R^2 values of 0.95-0.99. The slopes of these curves (k_{app}) are plotted as a function of the square of the inverse initial particle radius in Fig. 11.

The good linear relationship ($R^2 = 0.99$) between k_{app} and the square of the inverse initial particle radius validates the proposed kinetic model (equation (7)).

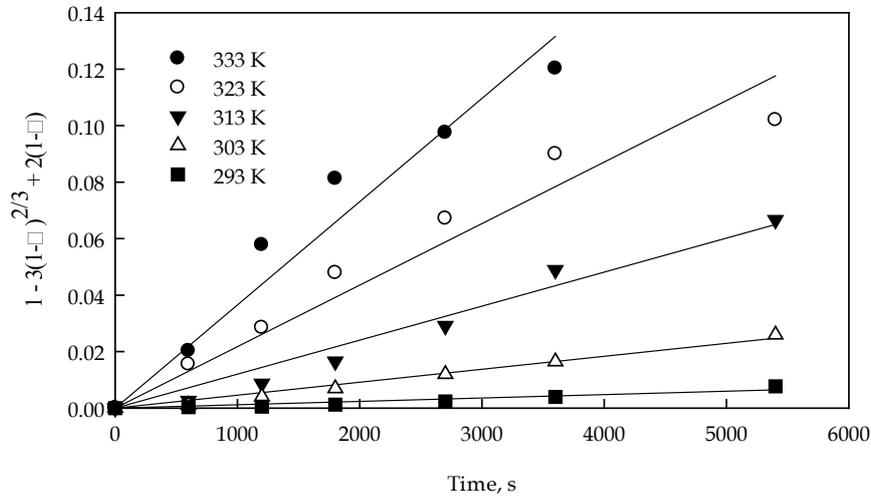


Fig. 9. Molybdenite dissolution kinetics for 64 μm particles in a H_2O_2 - H_2SO_4 system under conditions given in Fig. 4

Table 1. Rate constants for molybdenite dissolution with H_2O_2 and H_2SO_4

$T, ^\circ\text{C}$ (K)	$10^3/T, 1/\text{K}$	$k_{app}, 1/\text{s}$
20 (293)	3.413	0.1×10^{-5}
30 (303)	3.300	0.4×10^{-5}
40 (313)	3.195	1.1×10^{-5}
50 (323)	3.096	2.5×10^{-5}
60 (333)	3.003	4.0×10^{-5}

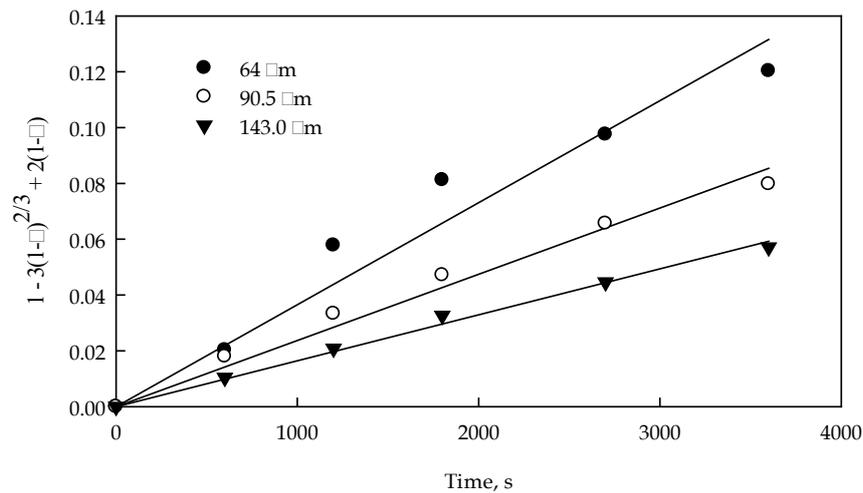


Fig. 10. Molybdenite dissolution kinetics for different particle sizes (data from Fig. 7)

According to equation (8), k should vary linearly with the square of the inverse initial particle radius if the kinetics are indeed controlled by diffusion through a porous layer. To confirm this mechanism, the particle size data shown in Fig. 8 were replotted according to equation (7), and the results are shown in Fig. 10.

In addition, the reaction order q was calculated from the kinetic data obtained using different H_2O_2 concentrations (Fig. 5). These data were plotted according to equation (7) in Fig. 12. As shown in Fig. 13, the $\ln(k_{app})$ values, which were derived from Fig. 12, exhibited a good linear dependence on $\ln(C_{H_2O_2})$ ($R^2 = 0.99$). The slope of the linear relationship in Fig. 13 indicates that the reaction order is 1.0 with respect to the H_2O_2 concentration.

To calculate the reaction order p for the H_2SO_4 concentration, a concentration range of 0.1-1.0 mol/dm³ was used; concentrations greater than 1.0 mol/dm³ were not considered due to the atypical behavior of the Mo recovery curves at high H_2SO_4 concentrations (Fig. 6). The experimental data in Fig. 6 were plotted according to equation (7) in Fig. 14, and the corresponding $\ln(k_{app})$ versus $\ln(C_{H_2SO_4})$ plot is shown in Fig. 15.

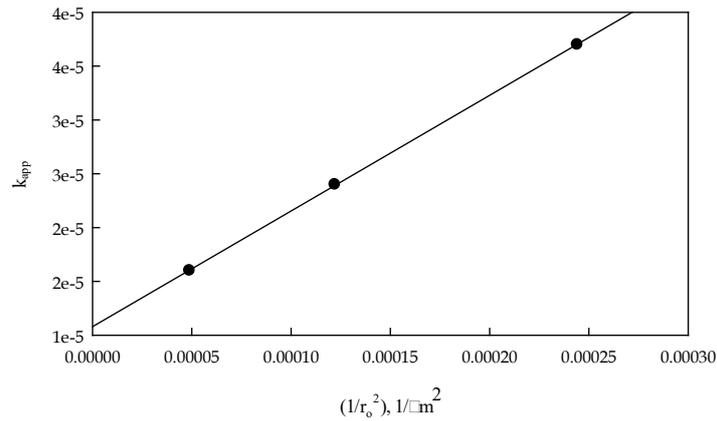


Fig. 11. Dependence of the apparent rate constant on the particle radius

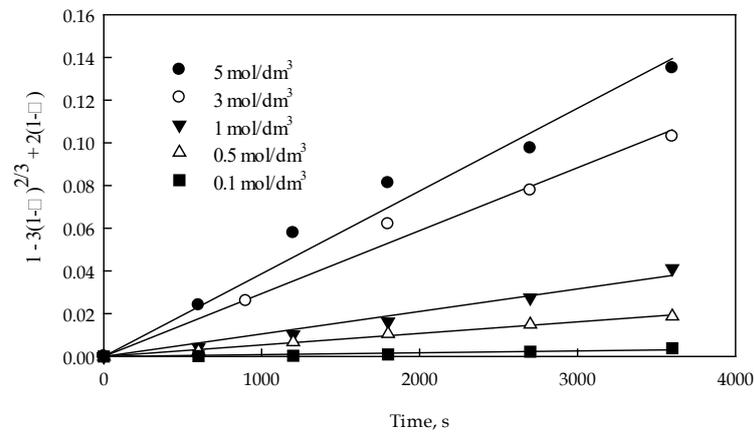


Fig. 12. Molybdenite concentrate leaching kinetics for different H_2O_2 concentrations

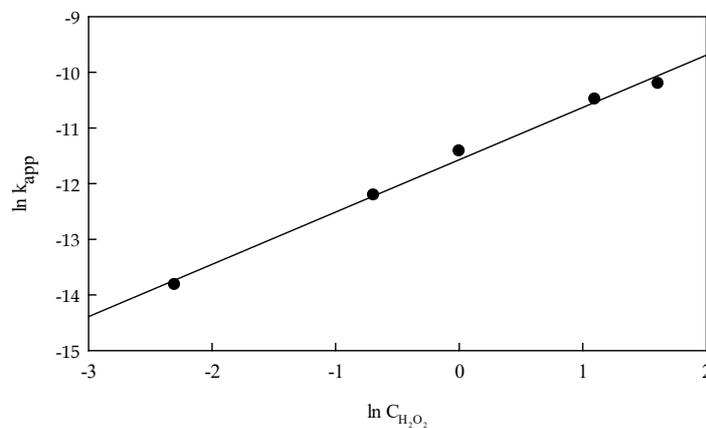


Fig. 13. Reaction order with respect to the H_2O_2 concentration

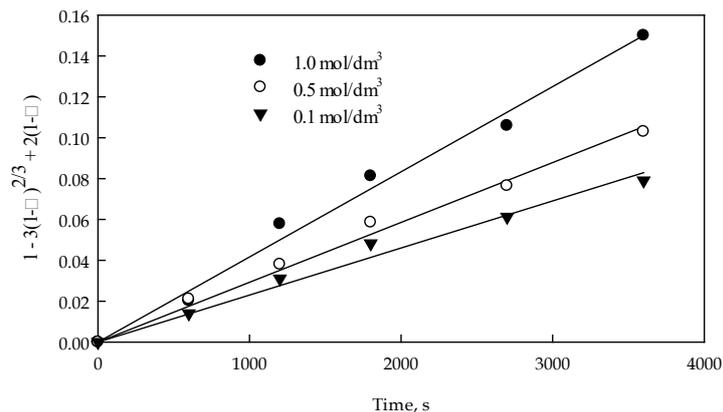


Fig. 14. Molybdenite dissolution kinetics for different H_2SO_4 concentrations

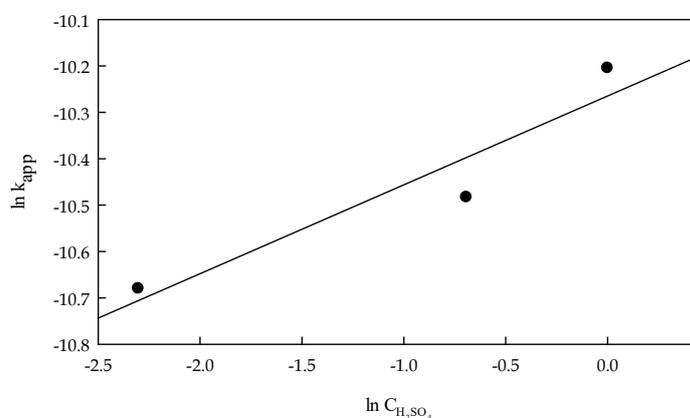


Fig. 15. Reaction order with respect to the H_2SO_4 concentration

A good linear relationship between $\ln(k_{app})$ and $\ln(C_{\text{H}_2\text{SO}_4})$ is observed ($R^2 = 0.91$), and a reaction order of 0.2 with respect to the H_2SO_4 concentration is obtained from the slope.

After the kinetic parameters were obtained, the activation energy of reaction (6) was determined using the apparent rate constants (k_{app}) obtained from Fig. 9. The following parameter values were employed in the calculations: the q value of 1.0, p value of 0.2, particle radius of 32 μm , a H_2O_2 concentration of 5.0 mol/dm³, a H_2SO_4 concentration of 1.0 mol/dm³ and b value of 1/9 (based on the stoichiometry of reaction (6)). Table 2 lists the apparent and intrinsic rate constants for the temperature range used in this study.

Table 2. Molybdenite dissolution rate constants in the temperature range of 293-333 K (20-60°C)

T , K	k_{app} , 1/s	k , 1/((1/s) μm^2 / (mol/dm ³))
293	0.1×10^{-5}	0.0018
303	0.4×10^{-5}	0.0074
313	1.1×10^{-5}	0.0203
323	2.5×10^{-5}	0.0461
333	4.0×10^{-5}	0.0737

The calculated intrinsic rate constants k were used to construct the Arrhenius plot shown in Fig. 16. A good linear relationship ($R^2 > 0.96$) was observed in the temperature range studied. The calculated activation energy was 75.2 kJ/mol, which is typical for a process controlled by diffusion through a porous layer.

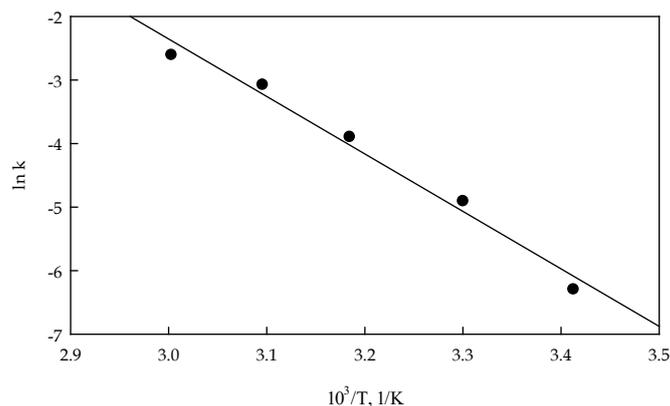


Fig. 16. Arrhenius plot for molybdenite leaching with hydrogen peroxide in the temperature range of 293-333 K (20-60°C)

Thus, the kinetics of molybdenite concentrate leaching in a H_2O_2 -acid system can be described by the following equation:

$$1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = 5.84 \times 10^{10} \frac{e^{-\frac{73.5}{RT}} C_{H_2O_2}^{1.0} C_{H_2SO_4}^{0.2}}{r_0^2} t \quad (9)$$

where $R = 8.314 \text{ J}/(\text{mol K})$, $k = 5.84 \times 10^{10} \text{ } \mu\text{m}^2 \cdot 1/((\text{mol}/\text{dm}^3)^{1.2} \text{ s})$, and the units of r_0 , t and the concentrations are μm , s and mol/dm^3 , respectively.

4. Conclusions

The conclusions of this study are summarized as follows:

1. Molybdenite concentrate leaching in a H_2O_2 - H_2SO_4 system generated molybdate (MoO_4^{2-}) ions, sulfate, H_2O and protons.
2. The molybdenite leaching rate was affected by the temperature, H_2O_2 and H_2SO_4 concentrations and particle size.
3. H_2SO_4 concentrations higher than $1.0 \text{ mol}/\text{dm}^3$ negatively affected the Mo recovery mainly due to competitive adsorption on the particle surface that resulted in a decrease in the adsorbed H_2O_2 concentration.
4. Molybdenite leaching was controlled by diffusion through a porous layer and can be described by the following rate equation:

$$1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha) = 5.84 \times 10^{10} \frac{e^{-\frac{75.2}{RT}} C_{H_2O_2}^{1.0} C_{H_2SO_4}^{0.2}}{r_0^2} t$$

5. The calculated activation energy was $75.2 \text{ kJ}/\text{mol}$, which is typical for processes controlled by diffusion through a porous layer.
6. The reaction orders were 1.0 and 0.2 with respect to the H_2O_2 and H_2SO_4 concentrations, respectively, and the reaction rate was inversely proportional to the square of the particle radius.

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