

Selective Recovery of Molybdenum from Petroleum Industry Waste Spent Hydrodesulfurization Mo–Co–Ni/Al₂O₃ Catalyst in the Presence of Ammonia: Process Optimization and Kinetic Studies

H. Arslanoğlu^{a,*}

^a Kırşehir Ahi Evran University, Faculty of Engineering and Architecture, Department of Chemical and Process Engineering, Kırşehir, 40200 Turkey

*e-mail: hasan.arslanoglu@ahievran.edu.tr

Received May 25, 2020; revised August 14, 2020; accepted October 25, 2020

Abstract—Composite catalysts containing molybdenum are mostly used for the purpose of hydrogenation in the oil refining industries. These treatment processes leave behind a large amount of used catalyst. These worn-out catalysts can be a secondary source of metal recovery for molybdenum and increase environmental awareness. In this paper, molybdenum recovery from worn-out catalysts has been investigated by leaching method in alkali medium (ammonia, NH₃) after roasting process. The experimental data indicate that the roasting temperature and period, leaching temperature and duration are highly effective on the dissolution yield of molybdenum. The maximum dissolution rates of molybdenum (92.12%) was reached under optimum leaching conditions; roasting temperature, 600°C; roasting time, 120 min; particle size, +75–30 μm; liquid/solid ratio, 6 mL/g; ammonia concentration, 1 M; leaching temperature, 80°C; leaching time, 90 min and stirring speed, 400 r/min. Kinetic results indicate that the dissolution reactions of molybdenum is controlled by the liquid film diffusion mechanism. Activation energy value (E_a) of molybdenum was found to be as 10.89 kJ/mol.

Keywords: spent catalyst recovery, molybdenum (Mo), leaching, kinetic, ammonia

DOI: 10.1134/S0965544121020043

INTRODUCTION

In petroleum refineries, large amounts of inorganic solid catalysts are used to accelerate the chemical reactions occurring in various processes known as thermochemical catalytic processes [1]. These catalysts used to remove sulfur, nitrogen and other metals in the crude oil structure during the petroleum refining process are generally alumina based and contain metals such as molybdenum, cobalt and nickel [2]. A forementioned catalysts lose their catalytic activity over the time due to the accumulation of impurities come within the raw materials on the catalyst surface in different catalytic processes [3, 4].

It is estimated that the amount of catalyst consumed by the oil industry in the world is 170×10^3 ton per year [5]. Although spent catalysts produced in petroleum refineries constitute only 4% of the total refinery waste, they are classified by various organizations as hazardous,

harmful to the environment and human health [1, 6]. Therefore, the evaluation or disposal of these spent catalysts containing molybdenum gain importance today. There are different applications for storage, disposal, regeneration and recovery of these precious metals [7]. Due to the enforcement of environmental laws and regulations, and requiring for large space, storage is not preferred [3, 8]. Although regeneration is an attractive method, it is not preferred much because regeneration technology is not available for oil refineries and is feasible for a limited number of cycles [9]. However, regeneration process is not possible for those catalysts which have lost their activity, especially in processes where thermal decomposition and phase separation take place [10]. In this regard, metal recovery appears an attractive method rather than regeneration of the spent catalyst.

Molybdenum, one of the most important transition elements, has wide application areas as a composite in the steel industry. Intense consumption in countries

Table 1. Elemental composition of spent catalyst [17]

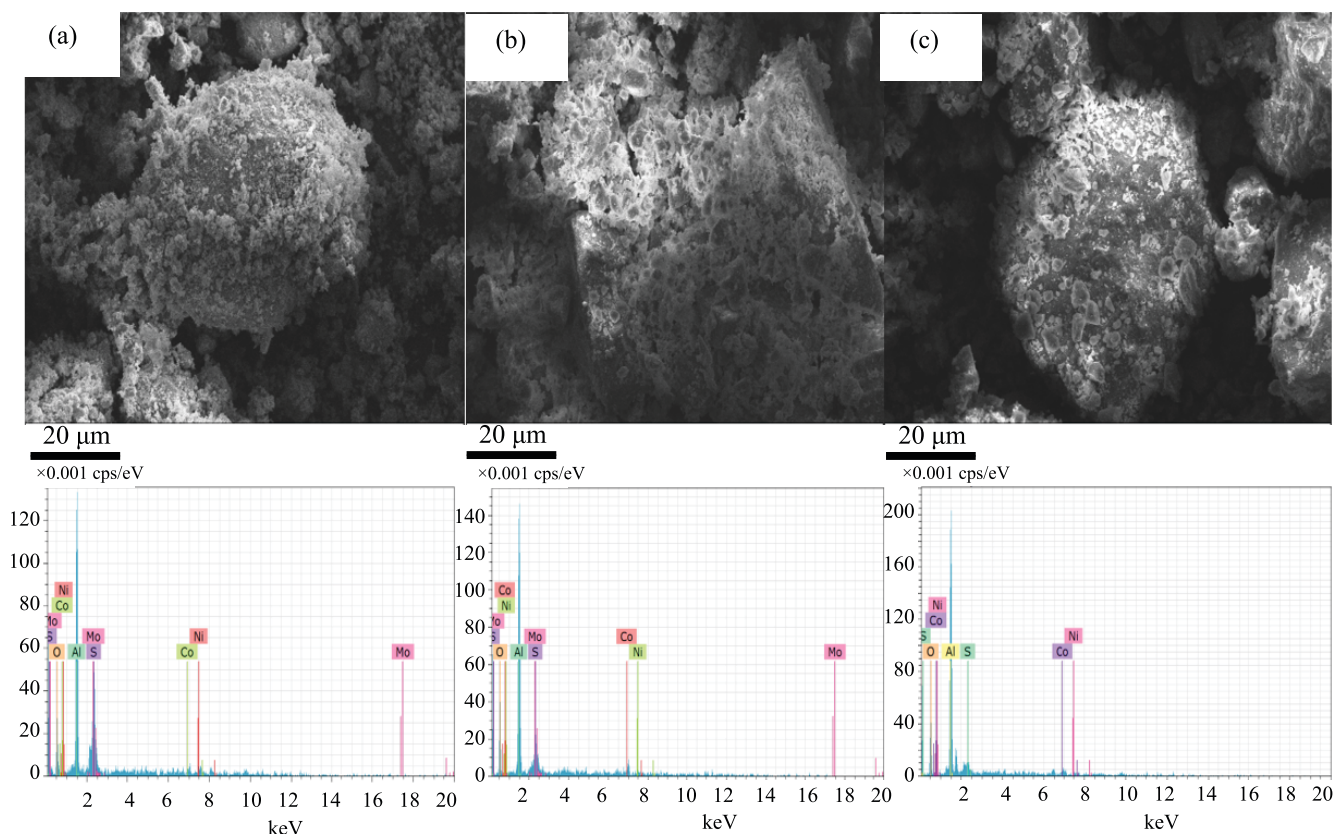
Component, wt %													
Al	Mo	Co	Ni	Ca	Fe	Zn	Cr	Cu	Cd	Pb	C	S	P
37.42	9.35	2.18	1.72	0.34	0.019	0.008	0.005	0.003	0.015	0.001	13.71	0.73	0.28

where the industry is developed is attributed to the countless beneficial effects it has on the metal industry. Molybdenum is not only used in steel industry, but also finds applications in the industry as a catalyst. The most intense usage of molybdenum-containing composite catalysts appear in the desulfurization of petroleum, petrochemical and coal-derived substances. By capturing sulphur, it is aimed to minimize sulphur dioxide emission during combustion of fuel. For example, catalysts spent in hydrogenation plants are disposed of as waste. These waste composite materials are a vital resource for metal recovery [11, 12].

Recovery of metals from spent catalysts. Reducing environmental pollution, minimizing the need for storage space and meeting the metal needs of the market, metal recovery is a very convenient method. Furthermore, spent catalysts are considered to be an important secondary source for metals since they contain valuable elements

such as Co, Mo, Ni and Al [13]. On the other hand, metal recovery from catalysts that have lost catalytic activities may allow for easier reconstruction of catalysts [2]. Currently, two different methods, hydrometallurgical and pyrometallurgical, are used for the recovery of precious metals from spent catalysts [14, 15]. Hydrometallurgical processes are more preferred than pyrometallurgical methods due to their low energy consumption and low gas emissions and high recovery of metals [16]. In the hydrometallurgical processes, pretreatments such as oxidation and roasting are used to ensure that the precious metals pass into the solution in high efficiency [17, 18]. However, leaching of the spent catalyst can be carried out directly in the presence of acidic or alkali solvents [16].

There are studies in the literature on the recovery of precious metals from spent catalysts that directly use different acid and alkali solvents as leaching reagents [1, 3, 4, 18]. The aim of this study is to recover molybdenum

**Fig. 1.** SEM-EDS results of (a) raw spent catalyst, (b) roasted spent catalyst and (c) leaching residue of spent catalyst.

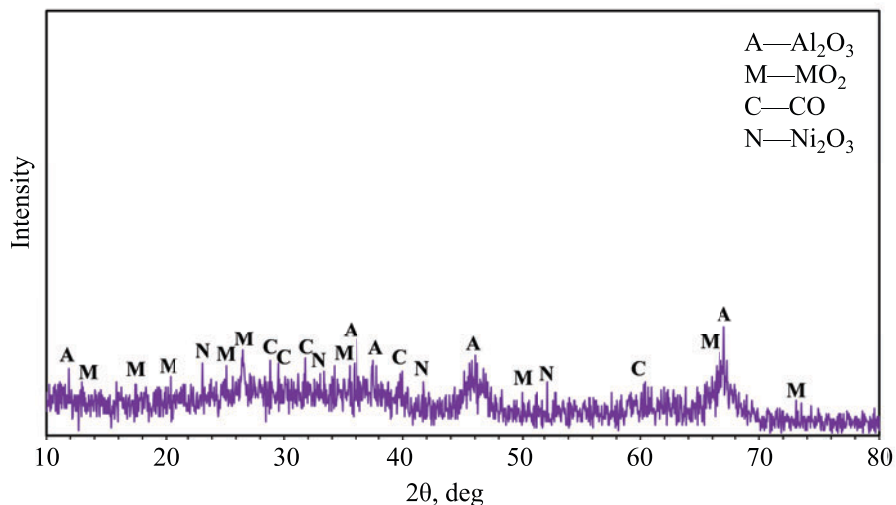


Fig. 2. XRD graph of spent (CoMoNi/Al₂O₃) catalyst.

metals from used hydrodesulfurization catalyst which is pre-roasted by using NH₃ solvent; to investigate the effects of roasting temperature, roasting time, particle size, liquid/solid ratio, ammonia concentration, leaching temperature, leaching time and mixing speed on the dissolution efficiency of metal and determine the optimum test conditions for maximum molybdenum recovery.

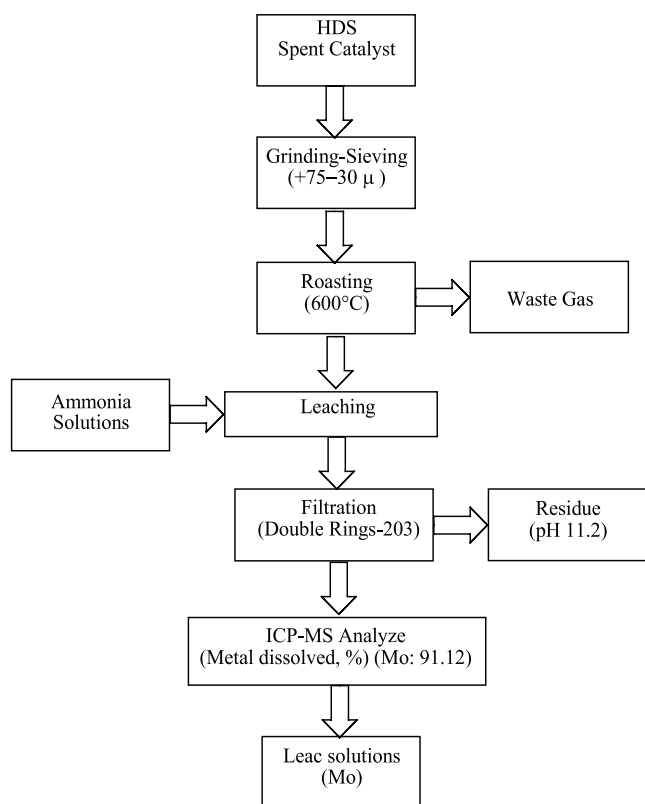


Fig. 3. Flow diagram of roasting and leaching processes applied to spent catalyst.

EXPERIMENTAL

The spent catalyst used in hydrodesulfurization (HDS) utilized in the experiments was obtained from an oil refinery industry in Romania. Analytical grade NH₃ used as leaching reagent was purchased from Merck (27% NH₃). Crushing, grinding and sieving processes were applied to the spent catalyst, respectively, to the desired particle size. The prepared powder samples were dried at 105°C for 2 h and stored in closed plastic containers for use in the experiments. The metal content of the sample is given in Table 1. The roasting was carried out at a heating rate of 10°C/min in an atmosphere controlled oven at different times (10–360 min) and temperatures (200–800°C), and the roasted samples were cooled to room temperature.

SEM images of the solid residue remaining after leaching of the spent catalyst before and after roasting and in the presence of ammonia solution are shown in Fig. 1. On the other hand, according to XRD results in Fig. 2, Co, Ni, Mo, and Al elements are found in the spent catalyst structure. The structure of the spent catalyst is quite complex and amorphous. In addition, it is seen that the main characteristic peaks belong to metal oxide and metal sulfur compounds (Al₂O₃, NiS₂, MoO₃). Moreover, the sulfur was found in elemental form (S) but no phases corresponding to carbon could be identified. However, the carbon is expected to be present in the form of hydrocarbons or oxides.

Leaching tests. The leaching experiments were carried out using 500 mL shaker (Zhcheng ZHWY-200D) with adjustable temperature and stirring speed. The

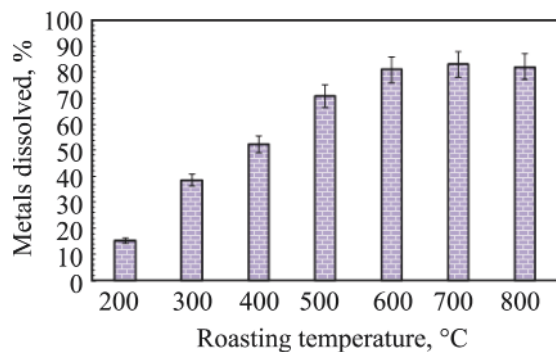


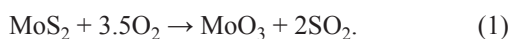
Fig. 4. Effect of roasting temperature on molybdenum leaching.

temperatures of ammonia solutions prepared at different concentrations (0.25–1.5 M) were adjusted to the desired values. The roasted powder samples were then added to the prepared solutions and mixed. Samples taken at certain times were filtered and the amount of metal in the filtrate was determined by ICP-MS (Agilent 7500ce Octopole). The flow diagram for the roasting and leaching processes applied for the recovery of precious metals from the spent catalyst is summarized in Fig. 3.

RESULTS AND DISCUSSION

Dissolution reactions. The pH of the leaching medium was measured to about 11.2 in the concentration range of ammonia in this study. Therefore, the reaction is pH dependent.

A series of preliminary tests were carried out for roasted spent HDS catalysts the above-mentioned reaction [1, 2, 10].



Dissolution reactions between the roasted spent catalyst and ammonia solution:



On the other hand, more metal was extracted per unit quantity of raw catalyst than from the spent catalyst in the roasted product. That is, when 25 g of catalyst is roasted at 600°C, a weight loss of about 23.4% occurs. It is probably due to the removal of moisture on alumina surface, carbonization reactions, burning of metal sulfides and dehydroxylation of alumina. In addition, the organic substances which are contaminated with the unroasted catalyst also pass to the solution during leaching. However, in the leaching process where roasted catalyst was used, the leaching solution was found to have lower pollution and the final pH of solution was measured as 11.2. For this reason, the roasting treatment was applied

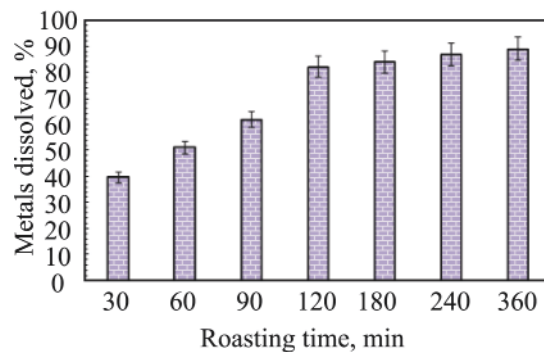


Fig. 5. Effect of roasting time on molybdenum leaching.

to the spent HDS catalyst and the affecting independent variables on the process are optimized.

Effect of roasting temperature and time. The results of the experiments performed at different roasting temperatures and times are given in Figs. 4 and 5, respectively. When the results are examined, it is seen that molybdenum leaching values generally increase due to the increase in roasting temperature and time. The dissolution rate of molybdenum was found to be 81.92% at 600°C roasting temperature and 120 min. However, since there was no significant increase in metal leaching efficiencies after 120 min, subsequent experiments were carried out at this roasting temperature and time [15, 17].

Effect of particle size. In order to investigate the effect of particle size on the leaching of molybdenum, the results of the experiments carried out at different particle sizes in the range of +30–20 μm and +600–300 μm are given in Fig. 6. As can be seen in Fig. 6, it is clearly seen that the increase in particle size adversely affects the dissolution efficiency of metals and that the smaller particle sizes lead to an increase in metal leaching efficiencies. This can be explained by the release of molybdenum with smaller particle sizes, and the maximum amount of metal introduced into the solution as a result of the reaction [19]. The metal dissolution values of molybdenum in particle size of +75–30 μm were obtained as 82.75%. On the other hand, there was no significant increase in the leaching efficiency of metal with particle sizes smaller than +75–30 μm, and subsequent studies continued on particle sizes of +75–30 μm.

Effect of liquid/solid ratio. Figure 7 shows the effect of different liquid/solid ratios in the 1–12 mL/g range on metal leaching yields. According to the data in Fig. 7, the dissolution efficiencies of the molybdenum generally increased up to 6 mL/g, while the higher liquid/solid ratios showed no significant increase in the molybdenum

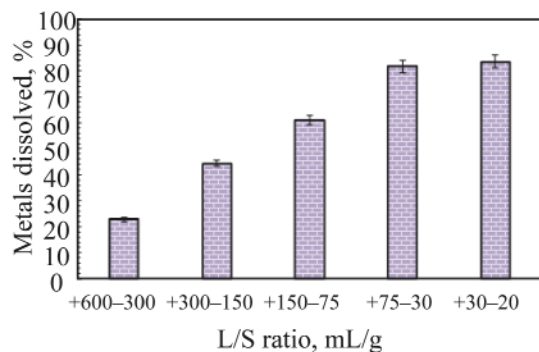


Fig. 6. Effect of particle size on molybdenum leaching.

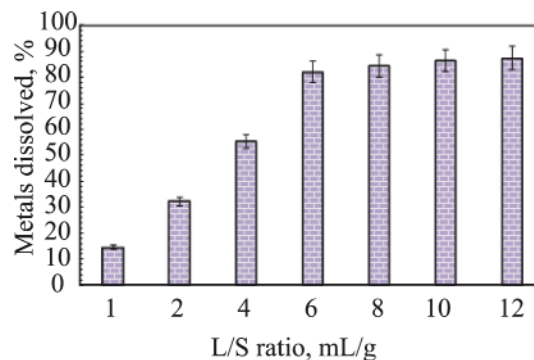


Fig. 7. Effect of liquid/solid ratio on molybdenum leaching.

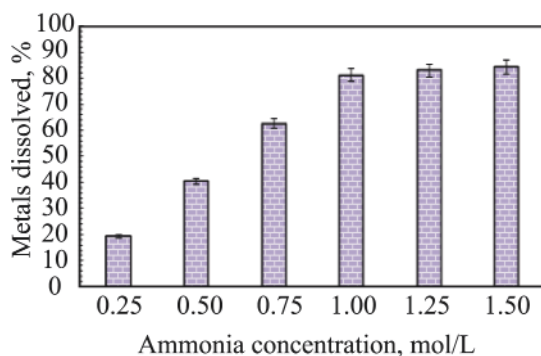


Fig. 8. Effect of ammonia concentration on molybdenum leaching.

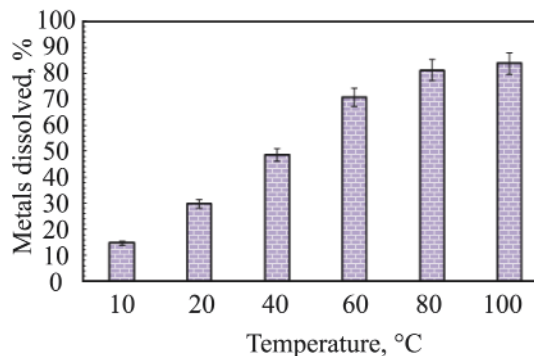


Fig. 9. Effect of leaching temperature on molybdenum leaching.

leaching value. This is due to the fact that the amount of ammonia limits the leaching efficiency due to the lack of sufficient solvent to dissolve metals [20]. Consequently, in the following experiments, the liquid/solid ratio was continued at 6 mL/g.

Effect of ammonia concentration. The results obtained from leaching experiments performed at different ammonia concentrations (0.25–1.5 M) are shown in Fig. 8. The results indicate that the dissolution efficiencies of molybdenum increased up to 1 M ammonia concentration, and the highest leaching values of molybdenum at 0.5 M ammonia concentration was 83.56%. At ammonia concentrations higher than 1 M, there was no significant increase in metal leaching efficiencies [3, 4]. Since it is known that increase in solvent concentration increases reaction efficiency in any leaching process, it is possible to say that increase in ammonia concentration will increase the dissolution rate of metals. Other experiments were carried out at a concentration of 1 M ammonia.

Effect of leaching temperature and time. Experiments were carried out at different temperatures (10–100°C) and times (15–180 min) in order to examine the effect of leaching temperature and time on the

dissolution yields of the molybdenum and the results obtained are given in Figs. 9 and 10. The results show that the increase in temperature leads to an increase in metal leaching efficiencies. When the leaching temperature rises from 10 to 80°C, it is seen that the dissolution percentage of molybdenum increase significantly and after 60 min molybdenum pass into the solution at 83.27%. On the other hand, temperatures higher than 80°C caused a slight increase in molybdenum leaching efficiencies. In light of these findings, it can be said that this increase rate is relatively decreased at temperatures above 80°C although the increase in temperature causes an increase in the amount of metal passing into the solution [16]. For subsequent experiments, the leaching temperature and time were selected as 80°C and 90 min, respectively.

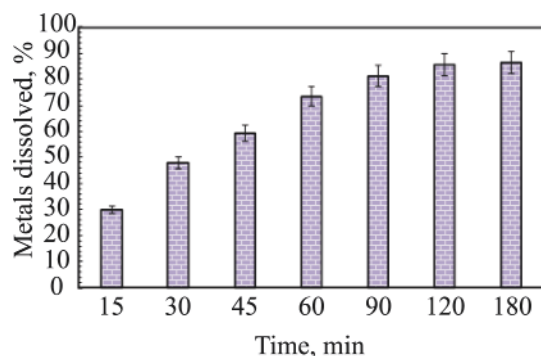
Effect of stirring speed. Leaching experiments were carried out in the mixing speed range of 50 to 600 rpm and the results are given in Fig. 11. According to the experimental results, it can be clearly seen that by increasing the mixing speed from 50 rpm to 400 rpm, dissolution efficiency of molybdenum rises up to (92.54%) from the spent catalyst. At the mixing speed of 500 rpm, molybdenum leaching yield reached 93.25%.

Table 2. The best-fit equations and correlation coefficient values (R^2) between leaching time and metal extraction values of kinetic models

Model	Temperature, °C					
	10	20	40	60	80	100
Liquid film diffusion control	$R^2 = 0.9909$ $y = 0.00004 - 0.055$	$R^2 = 0.9978$ $y = 0.00009 - 0.074$	$R^2 = 0.9900$ $y = 0.00010 - 0.063$	$R^2 = 0.9939$ $y = 0.00025 - 0.088$	$R^2 = 0.9918$ $y = 0.00045 - 0.099$	$R^2 = 0.9952$ $y = 0.00075 - 0.084$
Surface chemical reaction control	$R^2 = 0.9564$ $y = 0.00097 - 0.054$	$R^2 = 0.96712$ $y = 0.0027 - 0.068$	$R^2 = 0.9826$ $y = 0.00081 - 0.041$	$R^2 = 0.9794$ $y = 0.00097 - 0.054$	$R^2 = 0.9872$ $y = 0.0027 - 0.068$	$R^2 = 0.9802$ $y = 0.0035 - 0.035$
Film diffusion control through product layer	$R^2 = 0.9819$ $y = 0.079 - 0.174$	$R^2 = 0.9694$ $y = 0.091 - 0.134$	$R^2 = 0.9813$ $y = 0.066 - 0.119$	$R^2 = 0.9909$ $y = 0.079 - 0.174$	$R^2 = 0.9734$ $y = 0.091 - 0.134$	$R^2 = 0.9874$ $y = 0.097 - 0.172$

This can be attributed to a reduction in the boundary layer thickness around the particle and an increase in the amount of metal passing into the solution due to an increase in the stirring speed [17]. The highest leaching values of molybdenum metal reached 94.75% at 600 rpm stirring speed.

It is known that all the metals in the spent HDS catalyst structure are dissolved in a certain amount in the acidic medium. Also, some metals such as Mo and Al were dissolved in the presence of alkali leaching agent. Since Mo metal is amphoteric, they is readily soluble in both acidic and basic leaching mediums. However, Co and Ni are only dissolved in the acidic conditions. Leaching experiments were performed at low ammonia concentrations (0.25–1.5 M) and at pH range of 10–13. Therefore, the solubility of Mo is high while the solubility of Co and Ni is quite low for these leaching conditions. The solution medium also has a high rate of molybdenum. It also contains little dissolved aluminum. In addition, there are cobalt and nickel that pass into solution medium as much as resolution equilibrium constant values. The solution also contains 96% molybdenum, about 3.5% aluminum and 0.5% Cobalt + Nickel.

**Fig. 10.** Effect of leaching time on molybdenum leaching.

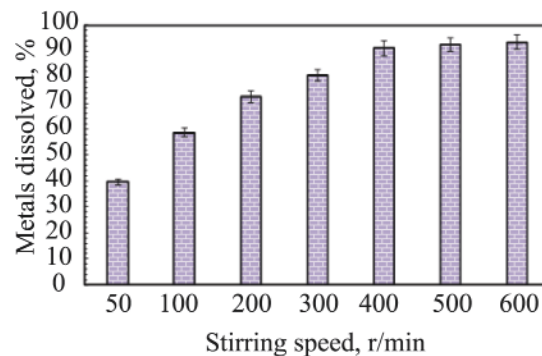
Kinetic studies. The kinetics of leaching processes consisting of solid and liquid phases are explained by heterogeneous reaction models [18, 20, 21]. This study was carried out in the presence of ammonia leaching reagent, the shrinking core model was used to determine leaching kinetics. According to this model, increasing the diffusion layer thickness around the solid particle during the dissolution reaction significantly reduces the dissolution rate. In the shrinking core model, the reaction rate is controlled by different mechanisms such as liquid film diffusion [Eq. (3)], film diffusion [Eq. (4)], and surface chemical reaction [Eq. (5)], which are given below. Accordingly, the reaction rate is controlled by the slowest step in all leaching reactions.

$$t = [1 - (1 - x)], \quad (3)$$

$$t = k[1 - 3(1 - x)^{2/3} + 2(1 - x)], \quad (4)$$

$$t = k[1 - (1 - x)^{1/3}]. \quad (5)$$

In the above equations k is the reaction rate constant (min^{-1}), t is the reaction time (min) and x is the ratio of the metal to the solution. In addition, correlation coefficient values of dissolution reactions are calculated by taking these equations into consideration. It is

**Fig. 11.** Effect of string speed on molybdenum leaching.

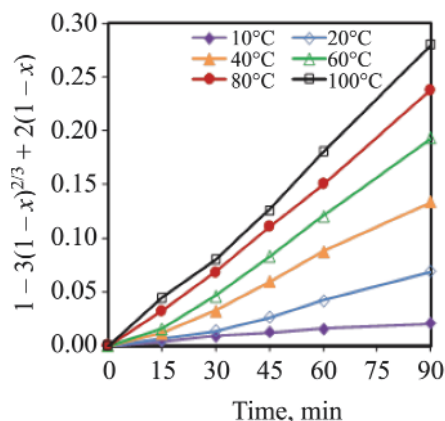


Fig. 12. Liquid film diffusion model [Eq. (4)].

understood from the correlation coefficient values that the experimental results are more compatible with Eq. (4) ($R^2 = 0.9948$) (Table 2). Accordingly, the dissolution rate of molybdenum can be expressed by the film diffusion mechanism in the shrinking core model (Fig. 12).

The activation energy (E_a) of the leaching process can be calculated by plotting as shown in Fig. 13 using the Arrhenius equation [Eq. (6)] using experimental results at different temperatures (10–100°C).

$$k = Ae^{-\frac{E_a}{RT}} \quad (6)$$

In the Arrhenius equation, k is the reaction rate constant (min^{-1}), A is the frequency factor, E_a is the activation energy of the reaction (J/mol), R is the ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The magnitude of the E_a gives information about the mechanism by which heterogeneous reactions are controlled. Namely; the heterogeneous reactions that occur are controlled by the surface chemical reaction when $E_a > 40 \text{ kJ/mol}$, and by the film diffusion mechanism when $E_a < 20 \text{ kJ/mol}$ [19, 21, 22]. In this study, activation energy value for molybdenum were calculated as 10.89 kJ/mol . The results show that the leaching process is controlled by the surface chemical reaction mechanism.

CONCLUSIONS

In this study, the effects of roasting temperature, roasting time, particle size, liquid/solid ratio, ammonia concentration, leaching temperature, leaching time and stirring speed parameters of molybdenum used in the catalyst were investigated. Experimental results show that the roasting temperature and time are highly effective in the solution of metals. The highest molybdenum (82.58%) leaching value was achieved at 500°C roasting

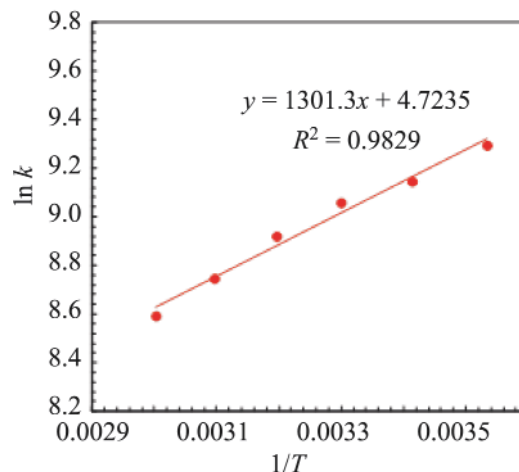


Fig. 13. $1/T$ vs $\ln k$ graph.

temperature and 120 min roasting time. On the other hand, it is seen from the experimental findings that leaching time and temperature significantly affect the metal leaching efficiencies. Maximum molybdenum (92.74%) dissolution values under optimum test conditions (roasting temperature 600°C , roasting time 120 min, particle size $+75-30 \mu\text{m}$, liquid/solid ratio 6 mL/g , ammonia concentration 1 M , leaching temperature 80°C , leaching time 90 min and stirring speed 400 rpm. Kinetic results show that the dissolution reactions of molybdenum in the presence of ammonia are controlled by the liquid film diffusion mechanism. The activation energy value for molybdenum was 10.89 kJ/mol . As a result, the results show that ammonia can be used as solvent in leaching molybdenum from spent catalysts.

ADDITIONAL INFORMATION

H. Arslanoğlu, ORCID: <http://orcid.org/0000-0002-3132-4468>

CONFLICT OF INTEREST

The author declares that there are no conflicts of interest regarding the publication of this paper.

REFERENCES

1. Akcil, A.F., Vegliò, F., Ferella, F., Okudan, M.D., and Tuncuk, A., *Waste Manage.*, 2015, vol. 45, p. 420. <https://doi.org/10.1016/j.wasman.2015.07.007>
2. Marafi, M. and Stanislaus, J. *Hazard. Mater.*, 2003, vol. 101, no. 2, p. 123. [https://doi.org/10.1016/S0304-3894\(03\)00145-6](https://doi.org/10.1016/S0304-3894(03)00145-6)
3. Marafi, M. and Stanislaus, A., *Resour. Conserv. Recycl.*, 2008, vol. 52, no. 6, p. 859. <https://doi.org/10.1016/j.resconrec.2008.02.004>
4. Marafi, M. and Stanislaus, A., *Resour. Conserv.*

- Recycl.*, 2008, vol. 53, no. 1–2, p. 1.
<https://doi.org/10.1016/j.resconrec.2008.08.005>
5. Dufresne, P., *Appl. Catal. A: Gen.*, 2007, vol. 322, p. 67.
<https://doi.org/10.1016/j.apcata.2007.01.013>
6. Liu, C., Yu, Y., and Zhao, H., *Fuel Process. Technol.*, 2005, vol. 86, no. 4, p. 449.
<https://doi.org/10.1016/j.fuproc.2004.05.002>
7. Asghari, I., Mousavi, S.M., Amiri, F., and Tavassoli, S., *J. Ind. Eng. Chem.*, 2013, vol. 19, no. 4, p. 1069.
<https://doi.org/10.1016/j.jiec.2012.12.005>
8. Macaskie, L.E., Mikheenko, I.P., Yong, P., Deplanche, K., Murray, A.J., Paterson-Beedle, M., and Vaughan, D., *Hydrometallurgy*, 2010, vol. 104, nos. 3–4, p. 483.
<https://doi.org/10.1016/j.hydromet.2010.01.018>
9. Pradhan, J.K. and Kumar, S., *Waste Manage. Res.*, 2012, vol. 30, no. 11, p. 1151.
<https://doi.org/10.1177/0734242X12437565>
10. Marafi, A., Fukase, S., Al-Marri, M., and Stanislaus, A., *Energy Fuels*, 2003, vol. 17, no. 3, p. 661.
<https://doi.org/10.1021/ef020177+>
11. Arslanoğlu, H. and Yaraş, A., *Petrol. Sci. Technol.*, 2019, vol. 37, no. 19, p. 2081.
<https://doi.org/10.1080/10916466.2019.1618867>
12. Yaraş, A. and Arslanoğlu, H., *Sep. Sci. Technol.*, 2020, vol. 55, no. 11, p. 2037.
<https://doi.org/10.1080/01496395.2019.1673412>
13. Motaghed, M., Mousavi, S.M., Rastegar, S.O., and Shojasadati, S.A., *Bioresour. Technol.*, 2014, vol. 171, p. 401.
<https://doi.org/10.1016/j.biortech.2014.08.032>
14. Mishra, D., Chaudhury, G.R., Kim, D.J., and Ahn, J.G., *Hydrometallurgy*, 2010, vol. 101, nos. 1–2, p. 35.
<https://doi.org/10.1016/j.hydromet.2009.11.016>
15. Mohapatra, D. and Park, K.H., *J. Environ. Sci. Heal. Part A*, 2007, vol. 42, no. 4, p. 507.
<https://doi.org/10.1080/10934520601188409>
16. Chaudhary, A.J., Donaldson, J.D., Boddington, S.C., and Grimes, S.M., *Hydrometallurgy*, 1993, vol. 34, no. 2, p. 137.
[https://doi.org/10.1016/0304-386X\(93\)90031-8](https://doi.org/10.1016/0304-386X(93)90031-8)
17. Ognyanova, A., Ozturk, A.T., De Michelis, I., Ferella, F., Taglieri, G., Akcil, A., and Vegliò, F., *Hydrometallurgy*, 2009, vol. 100, nos. 1–2, p. 20.
<https://doi.org/10.1016/j.hydromet.2009.09.009>
18. Visaliev, M.Y., Shpirt, M.Y., Kadiev, K.M., Dvorkin, V.I., Magomadov, E.E., and Khadzhiev, S.N., *Solid Fuel Chem.*, 2012, vol. 46, no. 2, p. 100.
<https://doi.org/10.3103/S0361521912020127>
19. Arslanoğlu, H. and Yaraş, A., *Petrol. Sci. Technol.*, 2019, vol. 37, no. 19, p. 2081.
<https://doi.org/10.1080/10916466.2019.1618867>
20. Ferella, F., Ognyanova, A., De Michelis, I., Taglieri, G., and Vegliò, F., *J. Hazard. Mater.*, 2011, vol. 192, no. 1, p. 176.
<https://doi.org/10.1016/j.jhazmat.2011.05.005>
21. Yaraş, A. and Arslanoğlu, H., *Can. Metall. Quart.*, 2018, vol. 57, no. 3, p. 319.
<https://doi.org/10.1080/00084433.2018.1473136>
22. Arslanoğlu, H. and Yaraş, A., *Trans. Indian Inst. Met.*, 2020, vol. 73, no. 3, p. 785.
<https://doi.org/10.1007/s12666-020-01896-x>