

Research Article

# Kinetics Study on Molybdenum Leaching from Spent Catalyst in Ammonium Hydroxide Solution

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## Abstract

The aim of the present work is to study the kinetics of leaching process of spent catalyst Ni, Mo/Al<sub>2</sub>O<sub>3</sub> in order to recover the molybdenum using ammonium hydroxide. The investigation depends on the results of previous work (Mousa et al, 2012). The experiments were conducted in 1-liter stainless steel autoclave. Kinetics study showed that both the diffusion through ash layer and the reaction on the surface of particles between the molybdenum and the ammonium hydroxide effect on the kinetics. The activation energy for reaction model was found to be equal to 6.706 kJ/mol, while the activation energy when using the ash layer model was 24 kJ/mol. The values of activation energies indicate that the intermediate or mixed is controlled the process.

**Keywords:** Kinetics, Molybdenum recovery, Ammonium hydroxide, Leaching

## 1. Introduction

Catalysts are widely used in a chemical process such as hydrodesulfurization, cracking, ammonia production and many others. This study interested in investigation on the controlling steps of molybdenum recovery from spent Ni, Mo/Al<sub>2</sub>O<sub>3</sub> catalyst using leaching process. After many reused the catalyst deactivated by S, C, V, Fe, Ni and Si (Trim, 1989; Furimsky et al, 1999). The production will be unacceptable due to decline in the catalyst efficiency. After that, the catalyst has to be regeneration if it's feasible, finally, the spent catalyst discarded as solid waste. (Marafi, 2008) reported that about 15000-17000 tons of solid waste produce from the refinery plant only. Due to increasing in the world demand and few primary sources of molybdenum in addition to environmental limitation, the recovery of molybdenum from spent catalyst as a secondary source arose. A low waste generation and gas emission classified the hydrometallurgy processing method as environmentally friendly. Different of processing were proposed to recovery molybdenum from spent catalyst. (Raisoni et al, 1988; Kar et al, 2004; Barik et al, 2012; Sahu et al, 2013; Isabel et al, 2013) used a leaching process by acid or alkaline. Other researchers used the leaching process as a first step then solvent extraction was used as a second step to recovery the molybdenum from spent catalyst (Raju et al, 2013; Thi et al, 2015), while bio method was used by Roya et al, 2011; Mafi et

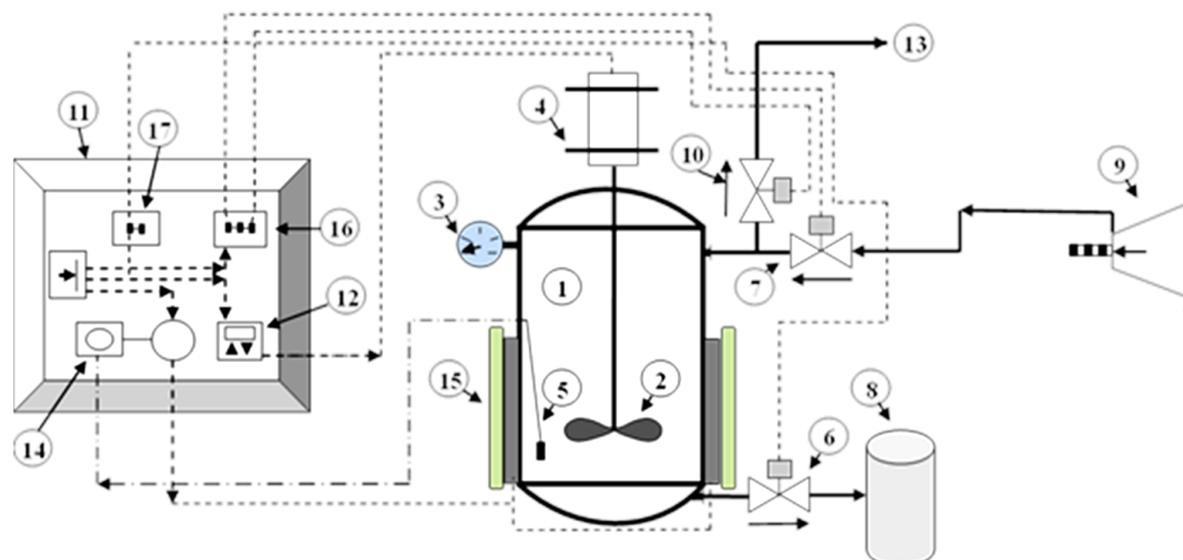
al, 2012). Bioleaching follows by the leaching process was conducted to recover the molybdenum from spent catalyst (Debabrata et al, 2013). Mechanochemical transformation of molybdenum sulfides into molybdate was conducted by (Zhao et al, 2016). Grinding the molybdenum with sodium carbonate and oxidants, then the reaction conducted in solid state without heating so the process considered as environment-friendly. Many researchers studied the kinetic of molybdenum from spent catalyst. (Anna et al, 2011) investigated the kinetics of molybdenum, vanadium, nickel and aluminum leaching from spent catalyst. The reaction mechanism for leaching the process of the spent catalyst was discussed in detailed. It was found that the activation energy of molybdenum is 31 KJ/mol.

The aim of the present study is to investigate the controlling step of molybdenum leaching from spent hydrodesulfurization catalyst in ammonium hydroxide. Due to well mixing, our study neglected the resistance of mass transfer in the interface between the solid (spent catalyst) and liquid (ammonium hydroxide). The study investigates on the mass transfer in the ash layer and the reaction on the surface of the solid particles.

## 2. Experimental work

3 kg of the spent catalysts which are used in these experiments was taken from Al-Dora refinery plant stores (Iraq). This sample was roasted at 600 °C. After that the sample was grinded and sieved to reach the desired particle size.

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1. An autoclave reactor 2. Three propeller turbine blades impeller 3. Pressure Gage (10 bar) 4. Electrical motor  
 5. Pt 100 thermocouple 6. Outlet product Solenoid valve (1/2 inch) 7. Inlet air Solenoid valve (1/4 inch) 8. leachate shell  
 9. Air compressor 10. Outlet air Solenoid valve (1/4 inch) 11. Autoclave board 12. The digital regulator of the mixer  
 13. Vent Gas 14. Temperature controller system (pt100) 15. Asbestos isolator layer 16. Power Switch of the inlet and outlet air valve  
 17. Power Switch of the leachate

**Figure 1** Schematic diagram of laboratory autoclave reactor system (Mousa *et al*, 2012)

A solution of 1 liter ammonium hydroxide (1-3 molar) was prepared. The heating system was switched on and the experiment's run temperature was fixed to (30-100 °C) in the temperature controller screen digit. The solution was heated to the desired temperature (30-100 °C) before charging it to the reactor to minimize the unsteady state time for heating. A mixing speed was setting to the desired values (100-600) rpm. After that 50 g of spent catalyst for each experiment was added to the ammonium hydroxide solution and fed to the reactor. A compressed air was supplied to the reactor to reach the desired pressure (1-7) bar. After the desired time (15-60min) was reached the solution was filtered to remove the unreacted molybdenum and impurities. Samples of solution were analyzed for molybdenum by means of Atomic Adsorption spectrometry. Fig.1 shows a schematic diagram of laboratory autoclave reactor system. A detail of experimental work was shown in (Mousa *et al*, 2012).

### 3. Results and discussion

An investigation for the kinetics study of leaching process to recover the molybdenum from spent hydrodesulfurization catalyst Ni, Mo/Al<sub>2</sub>O<sub>3</sub> was conducted. The optimum conditions were, pressure (P=7 bar), temperature (T=77 C<sup>0</sup>), ammonium hydroxide (C=2.333M), particle size (P.S=700 micrometer), agitation speed (rpm=600 min<sup>-1</sup>) and time (t=1 h).

The reaction between the molybdenum and ammonium hydroxide solution in leaching process can be represented as follow



The mechanism of leaching process using shrinking core model is well known. It is involved the following steps: the liquid reacted (NH<sub>4</sub>OH) transports from the bulk to the interface between the ammonium hydroxide and the spent catalyst. After that, overcome the resistance of interface. Then, NH<sub>4</sub>OH reacts with molybdenum compound at the surface of the catalyst. Furthermore, the products diffuse to overcome the ash resistance which increases due to increasing the thickness of the layer. The agitation system was designed perfectly so we assume no significant resistance in the interface and the bulk mass transfer. Our study interested to focus on the controlling steps in reaction and diffusion through ash layer only. If the chemical reaction between the liquid NH<sub>4</sub>OH and molybdenum compound is the controlling step, the fraction of molybdenum reacted can be represented by the following equation:

$$k_r t = 1 - (1 - x)^{1/3} \quad (2)$$

$$k_r = \frac{b k' C_M}{R_i \rho} \quad (3)$$

$$x = C_M / C_{Mi} \quad (4)$$

If the controlling step of the leaching process is the ash layer, the fraction of molybdenum reacted calculated from the following equation:

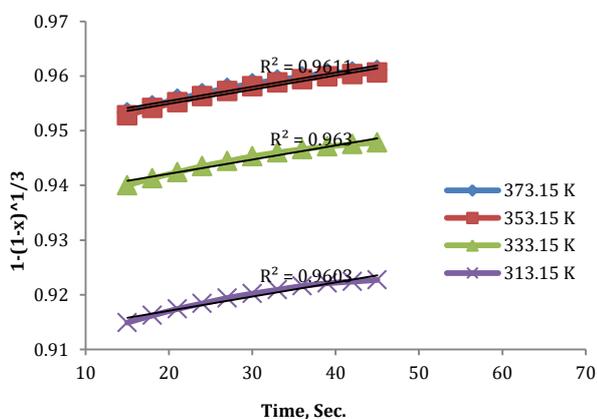
$$tk_d = 1 - 3(1 - x)^{\frac{3}{2}} + 2(1 - x) \tag{5}$$

$$k_d = \frac{2bDeC_M}{\rho R^2} \tag{6}$$

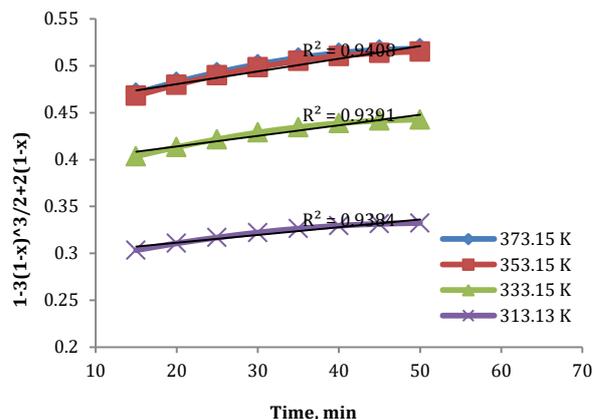
Where

- x = fraction of molybdenum reacted.
- C<sub>M</sub> = concentration of molybdenum at any time.
- C<sub>Mi</sub> = initial molybdenum concentration.
- k<sub>r</sub>, k<sub>d</sub> = apparent rate constants.
- k' = reaction rate constant.
- ρ = density.
- R<sub>i</sub> = initial radius of the particle.
- D<sub>e</sub> = effective diffusivity.
- b = stoichiometric coefficient.

According to previous work ( Mousa *et al*, 2012), one can see that the effect of temperature on molybdenum recovery can represent by the curve with two parts. The first part is the sharp one (in the first 50 min). Most of the molybdenum was recovered in the first 50 min. The second part is more sluggish on which the rest of molybdenum (not significant) was recovered. Our interest is to investigate the controlling step for the sharp curve. Equations 2 and 5 represent the controlling step for the reaction between the molybdenum compound and ammonium hydroxide and diffusion through ash layer respectively. The correlation coefficient (R<sup>2</sup>) and rate constants resulting from the fitting of shrinking model were calculated. Table one illustrates the values of correlation constants and rate constant. It's worthy to state that the apparent rates constant represented the slopes of figures 2 and 3, which result from plotting the right-hand side of equation 1 and 5 versus time at different temperatures.



**Figure 2** Reaction model versus time at optimum conditions pressure (P=7 bar), ammonium hydroxide (C=2.333M), particle size ( P.S=700 micrometer), agitation speed (rpm=600 min<sup>-1</sup>) at different temperature

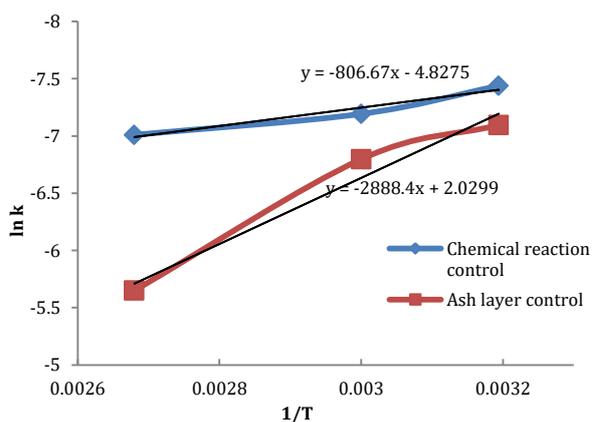


**Figure 3** Ash layer model versus time at optimum conditions pressure (P=7 bar), ammonium hydroxide (C=2.333M), particle size (P.S=700 micro meter), agitation speed (rpm=600 min<sup>-1</sup>) at the different temperature

**Table 1** the correlation constants (R<sup>2</sup>) and rate constants resulting from the fitting of shrinking model were calculated at optimum conditions

Temperature (K)	R2 for reaction control	R2 for ash control	K for reaction control	K for ash control
313.15	0.936	0.938	0.0005885	<b>0.0008285</b>
333.15	0.938	0.939	0.0007514	<b>0.001117</b>
353.15	0.940	0.940	0.0009028	<b>0.00351</b>

Examining figures 2 and 3 one can see that no effect of temperature when it becomes greater than 353.15 K on both reaction and ash layer controlling steps. The values of R<sup>2</sup> in table 1 indicate that no significant difference between the mass transfer through the ash layer and reaction steps. Due to the comparable values of R<sup>2</sup> further evaluation was conducted. As shown in figure 4 on which the rate constant at different temperature was used to predicated the activation energy.



**Figure 4** Arrhenius plots for the leaching process at optimum conditions

For reaction model, the activation energy equal to 6.706 kJ/mol, while the activation energy when using the ash layer model equal to 24 kJ/mol. The calculated activation energy indicated that both the mass transfer through ash layer and the chemical reaction are effects on the leaching process. (Habashi, 1999) stated that if the activation energy of magnitude (20.92-33.44 kJ/mol), then intermediate or mixed controlled processes.

## Conclusion

The experimental data well fitted by the equation represented the diffusion through ash layer of the reaction products accumulates on the surface of the particles when using the shrinking core model. The calculated activation energies were 6.706 kJ/mol and 24 kJ/mol for reaction model and the mass transfer through ash layer respectively. It's clear that the values of activation energies consistent with intermediate or mixed- controlled processes.

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