

**Recovery of molybdenum from (Co – Mo /  $\gamma$  - Al<sub>2</sub>O<sub>3</sub>) spent catalyst.**

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**استرداد المولبيديوم من مخلفات العامل المساعد (Co – Mo /  $\gamma$  - Al<sub>2</sub>O<sub>3</sub>)**

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**Abstract**

In the present research, hydro – desulfurization spent catalyst with an alumina base has been found to be as a source for molybdenum recovery. It was composed of 19 - 30 % of molybdenum as MoO<sub>3</sub>. Two methods were used for the recovery of molybdenum. First method was using H<sub>2</sub>S gas for precipitation of Co as CoS, and the precipitation of Mo has been done by HCl acid solution addition. The second method was the alkali leaching of spent catalyst and recovery of molybdenum using dilute NH<sub>4</sub>OH solution and then the precipitation of molybdenum as trioxide using HCl solution. The optimum conditions were predicated for the recovery of molybdenum, and different parameters were studied such as the alkali concentration and leaching time.

**Introduction**

The petroleum refining industry makes extensive use of catalysts for desulphurization of various fractions [1]. Molybdenum-containing catalysts are widely used in the petroleum refining industry for mild hydrogenation and removal of heteroatom such as nitrogen, oxygen, and sulfur, as well as metals like nickel and vanadium [2]. The most common hydrodesulphurization (HDS) catalysts are the Ni-Mo and the Co-Mo both on the  $\gamma$ -alumina support [3]. This process plays an important role in

the one stage type of liquefaction operation. A conventional petroleum-type Co - Mo/ $\gamma$  - Al<sub>2</sub>O<sub>3</sub> or Ni - Mo/ $\gamma$  - Al<sub>2</sub>O<sub>3</sub> catalysts can be used for rehydrogenation of the recycle solvent stream. In two-stage coal liquefaction processes, the initial liquefaction step uses only natural components of the coal ash as catalysts, but the second stage employs a Co - Mo/ $\gamma$  - Al<sub>2</sub>O<sub>3</sub> catalyst for upgrading [4]. Molybdenum has got a wide application as an alloying agent in steel, cast irons and super alloys. It has a typical property to enhance the hardness, strength of the lost material and also has a greater importance as a corrosion resistant [5]. The main source of molybdenum is molybdenite, fenite, etc. Extraction of molybdenum from these ores is mainly carried out by roasting the ore in multi-hearth furnaces (MHF) of Herroshoff type [6]. The MoO<sub>3</sub> produced after roasting contains plenty of impurities [7]. The impurities present in the sample such as copper, iron, nickel forms a non-volatile and insoluble molybdates during roasting [8]. Many processes have been developed by hydro as well as pyrometallurgical routes to extract molybdenum from low grade resources [9]. During hydrodesulphurization reactions, the catalysts are deactivated by compounds of S, C, V, Fe, Ni, Si and traces of As and P [10, 11, 12]. As a result, the spent catalysts are classified as hazardous materials [13]. Due to their toxic nature, the disposal of spent catalysts can pollute the environment since heavy metals are leached out. To avoid pollution in land disposal as well as to minimize landfill space, the spent catalysts are subjected to metal extraction by various solubilization processes and reused in a variety of applications [14, 15, 16]. However, such waste materials containing high metal concentrations may be considered as “artificial ores” since they can serve as secondary raw materials with a consequent reduction in the demand for primary mineral resources. Recycling of spent catalysts became an unavoidable task not only for lowering catalysts costs but also for reducing their waste to prevent the environmental pollution [3]. Spent HDS catalysts generally consist of 10–30% molybdenum, 1–12% vanadium, 0.5–6% nickel, 1–6% cobalt, 8–12% sulphur, 10–12% carbon and the balance is alumina, which makes it economically viable for recovery of valuable metals [17]. In the present study the recovery of molybdenum from the spent catalysts was investigated using two methods. First one by using hydrogen sulfide to precipitate Co from the leaching solution, and the other method was the alkali leaching without H<sub>2</sub>S. The molybdenum was precipitated as ammonium molybdate and then calcinated to molybdenum oxide.

## Experimental

### Apparatus

Heating mantle, beakers, mechanical stirrer, electrical grinder, muffle furnace, balance, chiller (water cooler) and vacuum pump were used in this study.

## Materials

The following chemical agents were used in the experiments:

\*Spent Co - Mo/  $\gamma$  -  $\text{Al}_2\text{O}_3$  catalyst was supplied from Al- Daura refinery. The shape of the catalyst was cylindrical (2.5 mm x 6 mm), the chemical analysis of selected samples was shown in Table. 1. The physical properties of the catalyst type extrudes before its using were illustrated in Table. 2.

**Table (1): Chemical analysis of spent catalyst**

Type of catalyst	Composition		
	% Co	% Mo	% Al
Extrudes	2.5	12.5	44.0
Ketjenfine 124	2.6	12.0	45.0

**Table (2): Physical properties of the catalyst**

Normal size	2.5 – 6 mm
Pore volume	0.6 ml / g
Surface area	270 – 280 $\text{m}^2$ / g
Estimated density	540 – 550 $\text{Kg} / \text{m}^3$
Average length	5.7 mm

\*Ammonium hydroxide solution, hydrochloric acid was supplied from Aldrich (Germany). Hydrogen sulfide obtained by decomposition of thiourea in acidic solution.

## Procedure

1. The spent catalyst was grinded to obtain fine powder using electrical grinder, then was sieved to obtain a powder have (less than  $100\mu\text{m}$  ) particle sizes.
2. 10 g of spent catalyst have (less than  $100\mu\text{m}$ ) particle size was taken and placed in the beaker of 200 ml volume.
3. 100 ml of (4 M) diluted ammonium hydroxide solution was added.
4. The mixture was heated at  $60\text{ }^\circ\text{C}$  for 2 h.
5. The solution was lifted for cooling at room temperature, after that the solution was filtrated. The solid residual is containing Co, Fe, Si, Al, V and Ni; while the solution is contain ammonium molybdate.
6. The solution was refluxed for one hour.

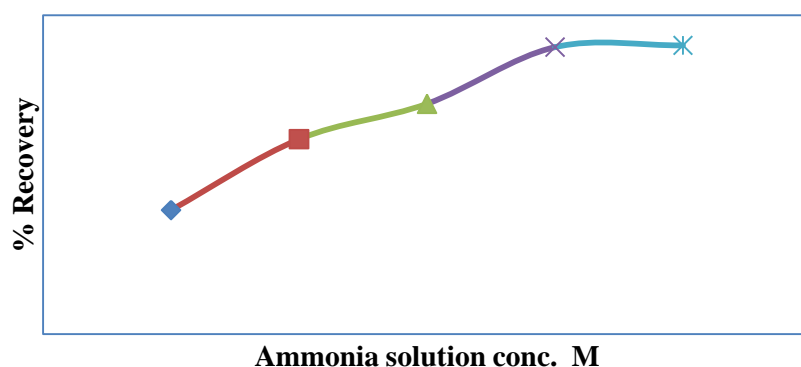
7. The solution was lifted for cooling until reaching 60 °C, add 5 ml of dilute HCl (0.5 M) , after that the precipitation can be done as follow:
  - a: Either evaporate of the solution under evacuated pressure until reach the dryness (the obtained ammonium hydrogen molybdate had technical grade).
  - b: Or evaporate of the solution under evacuated pressure at 60 °C until reach a half volume, then cold the solution to less than 5 °C using the chiller, left the solution a side until the appearance of the ammonium hydrogen molybdate crystals had high grade purity.
8. The solution was filtrated and separates the mother liquid which was used again for production of technical grade.
9. The ammonium hydrogen molybdate (two grades) was calcinated at 750 °C for two hours to obtain MoO<sub>3</sub> have technical (> 97%) and high grade purity (> 99%).

## Results and discussion

### Effect of extract concentration

In this set of experiments, the effect of extract concentration on Mo recovery was investigated. Different concentrations of diluted ammonium hydroxide with water (1, 2, 3, 4, and 5 M) were used for the recovery of molybdenum from the spent catalyst (Fig. 1). The results indicate that the recovery percentage was increased as the percent of ammonia solution was increased until reached the concentration of 4 M, after that the value of the increasing being small or near constant value. The recovery percent was calculated as follow:

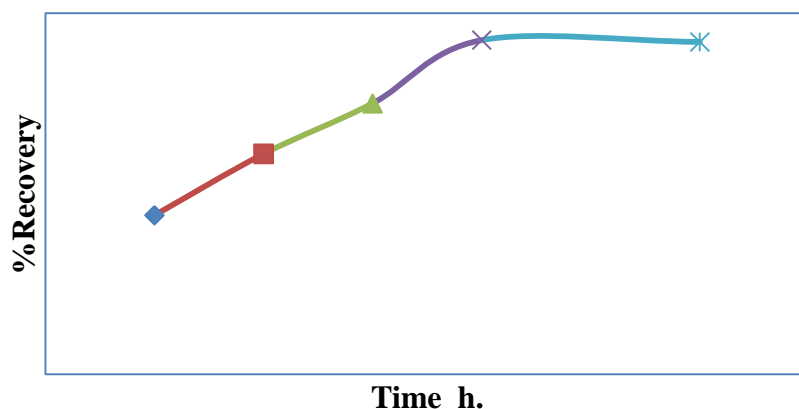
$$\% \text{ Recovery} = x \times 100$$



**Figure (1): Relationship between concentration and %Mo recovery**

### Effect of recovery time

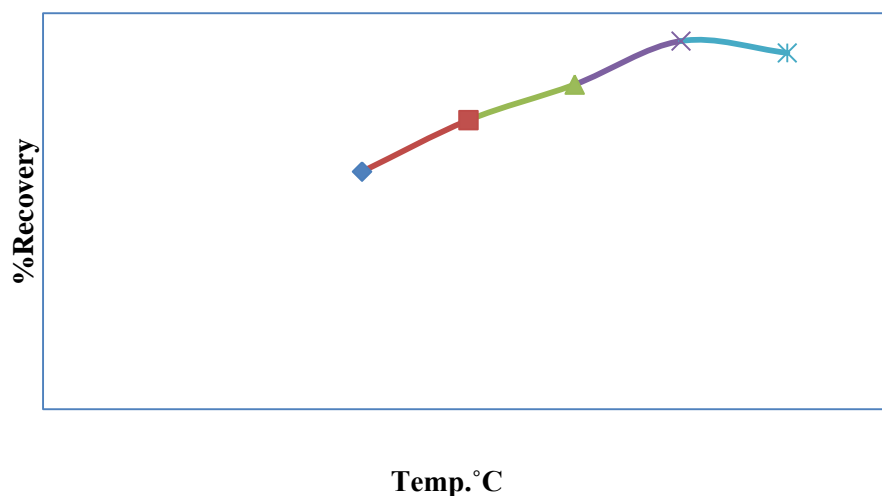
In this set of experiments, the effect of recovery time on Mo recovery was investigated. A sample of solution was taken at the end of each period (0.5, 1, 1.5, 2 and 3 hours). Operating conditions (room temperature, 4 M solution concentration and particle size = less than  $100\mu m$ ) were used. The results (Fig. 2) showed that the recovery percentage increase with increasing the time and the maximum percentage was reached at 2 h with 92.5%.



**Figure (2):Effect of time on %Mo recovery**

### Effect of temperature

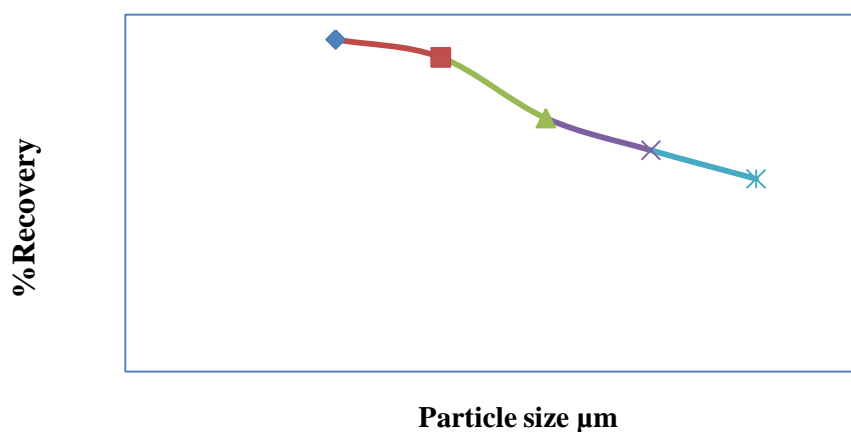
The effect of temperature on the recovery of Mo was investigated. The solution was heated to different temperatures (30, 40, 50, 60 and  $70^{\circ}\text{C}$ ). Other experiment conditions (recovery time, ammonium hydroxide concentration) were fixed from previous sections while particle size was kept constant less than  $100\mu m$ . The results obtain (Fig. 3) revealed that the maximum recovery was obtain at  $60^{\circ}\text{C}$  with 93%, while at  $70^{\circ}\text{C}$  the decrease of recovery percent was observed, that may be due to the liberation of ammonia from the leaching solution at high temperature, which is lead to decrease in the solution concentration and finally decrease the recovery percentage.



**Figure (3): Effect of temperature on %Mo recovery**

#### Effect of particle size

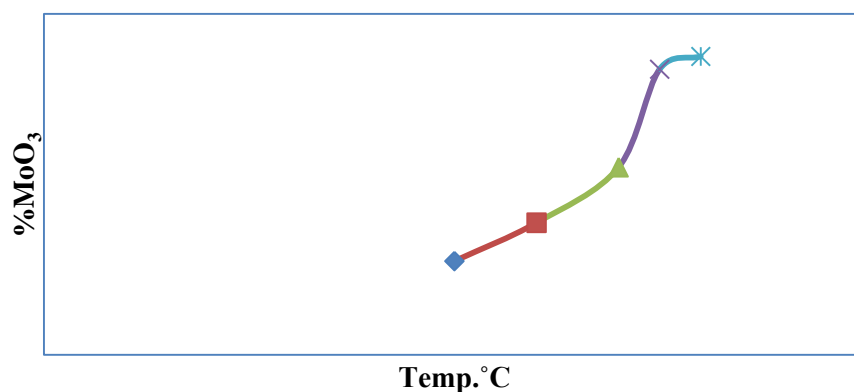
The effect of particle size on recovery of Mo was investigated. Particle size of catalyst (less than 100, 150, 200, 250 and more than 250  $\mu\text{m}$  or (300  $\mu\text{m}$ ) was used. Operating conditions (recovery temperature, solution concentration and recovery time) were fixed from previous sections. Fig. 4. shown that the recovery of molybdenum was increased as the particle size decrease. That may be due to the increase in the surface area, which is lead to increase of the contact area between the solid sample and the solution.



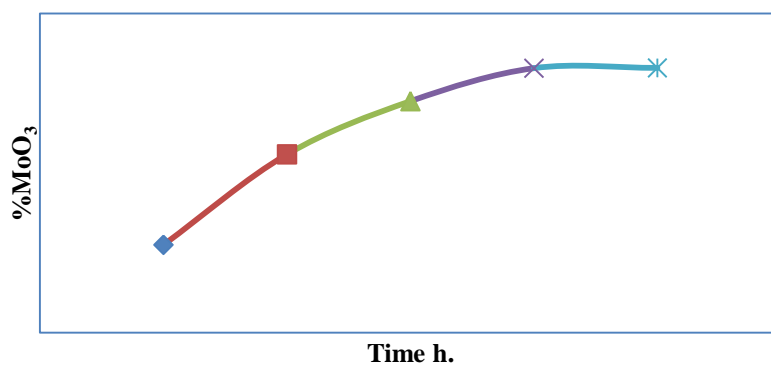
**Figure (4): Effect of particle size on %Mo recovery**

### Optimization of calcinations conditions

The parameters affecting the calcinations of ammonium hydrogen molybdate (AHM) to obtain molybdenum trioxide ( $\text{MoO}_3$ ) such as temperature and time were investigated in this study. Fig. 5 and Fig. 6, shown the results obtain, which are indicate that the maximum decomposition of AHM was occur after two hours at 750 °C.



**Figure ( 5): Relationship between temperature and % MoO<sub>3</sub>**



**Figure (6): Relationship between time and %MoO<sub>3</sub>**

## Conclusions

In the present investigation and operating conditions, it may be concluded that the alkali leaching for Mo recovery by using  $\text{NH}_4\text{OH}$  and HCl was achieved and the equilibrium was reached after two hours of contact time. The percent of Mo recovery increased with increasing in  $\text{NH}_4\text{OH}$  concentrations until reached 4 M. The results indicate that increasing the temperature from 30 to 60 °C lead to an increasing in the Mo recovery from 60% to 93%. The recovery of Mo was increased with decreasing the particle size. The particle size which is less than 100  $\mu\text{m}$  gave the highest recovery percent. Also can be concluded that the spent catalyst can be considered as a rich source for Mo and other metals in its composition.

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