



RECOVERY OF MOLYBDENUM AND COBALT POWDERS FROM SPENT HYDROGENATION CATALYST

M.A. Rabah, I.F. Hewaidy and F.E. Farghaly

Industrial Wastes laboratory, Extractive Metallurgy Dept.
CMRDI, P.O.Box 87 Helwan 11421, Cairo, Egypt.

Abstract

Free powders as well as compact shapes of molybdenum and cobalt have been successfully recovered from spent hydrogenation and desulphurization catalysts. A process flow sheet was followed involving crushing, milling, particle sizing, hydrometallurgical acid leaching, roasting of the obtained salts in an atmospheric oxygen to obtain the respective oxides. These were reduced by hydrogen gas at 1100°C and 900°C respectively. Parameters affecting the properties of the products and the recovery efficiency value such as acid concentration, particle diameter of the solid catalyst, temperature, time, under a constant mass flow rate of the hydrogen gas, have been investigated.

A mixture of conc. sulphuric and nitric acids (3:1 by volume) achieved adequate recovery of both metals. The latter increased with the increase in acid concentration, time up to 3 hours and temperature: 100°C and with the decrease in particle diameter of the spent catalyst. The pH of the obtained filtrate was adjusted to 2 with ammonia to precipitate insoluble ammonium molybdate and a solution of cobalt sulphate. Cobalt hydroxide can be precipitated from the latter solution at a pH=7.6 using excess ammonium hydroxide solution.

The obtained results showed that the metallic products are technically pure meeting the standard specifications. Compact shapes of molybdenum acquire density values increasing with the increase of the pressing load whereby a maximum density value of 2280 kg/m³ is attained at ≥ 0.75 MPa. Maximum recovery efficiency amounts to 96%.

A model explaining the obtained results assume that molybdenum and cobalt in the spent catalyst cement to an alumina carrier. Deposition of carbon usually poisoned the catalyst during use. The weight ratio of carbon increases as the particle size of the catalyst decreases. Nitric acid helps dissolution of these metals to form complex sulphate salts. High oxide states of molybdenum and cobalt are formed by roasting in atmospheric oxygen. Reduction with hydrogen gas takes place in two steps, the overall activation energy of which amounts to 144.39 kJ.mol⁻¹ for molybdenum and 143.4 kJ.mol⁻¹ for cobalt.

Metal powders are rough surface with irregular shape. Densification of these powders by pressing takes place due to random movement of the metal particles. Under certain load, minimum void volume is achieved and the particle-particle friction resists and overweighs the magnitude and direction of the exerting load. An economic study has revealed that spent catalyst contains molybdenum and cobalt that are recoverable. Cost of recovery is significant and the process of recovery is simple.

1 INTRODUCTION

Recovery of metal powders and/or metal alloys have been a subject of investigations reported in the literature. Two methods were given. The first involved hydrometallurgical processing. Berrebi et al (1) showed that nickel and copper were separated by solvent extraction to obtain pure metal. The process started with regeneration of the catalyst to eliminate hydrocarbons, carbon and sulphur. After caustic roasting, the material was leached to obtain a solution containing mainly molybdenum and vanadium and a solid containing essentially alumina, cobalt and/or nickel. It has been also shown that Mo, Ni, V and W were recovered from spent hydroprocessing catalyst. The catalyst was roasted in an oxygen-containing gas by ammonia leaching and hydrogen peroxide (2, 3).

Molybdenum, cobalt, vanadium, cadmium and zinc metals were recovered by solvent extraction from spent hydrosulphurizing catalyst (4). Recovery of these metals from spent waste was carried out by anhydrous chlorination followed by caustic-acid leaching processes(5). Molybdenum was recovered by roasting followed by water leaching (6,7). Hydrogen peroxide leaching (8), sodium hydroxide and sodium aluminate followed by oxygen pressure leaching (9), were also reported. Rokukawa(10) extracted Mo and V by sodium carbonate containing hydrogen peroxide. Pyrometallurgically, Yong et al (11) roasted spent catalyst at high temperature to recover Mo, Ni, W, Cu and chromium. High yield of extraction of Mo and vanadium was effected by roasting the spent catalyst with sodium carbonate(12,13). Hubred (14) used ammonium carbonate and precipitated molybdenum sulphide by hydrogen sulphide gas. Sujata (15) showed that the density value of the pressed shapes made of compacted metal alloy powder was improved with increase in temperature. Mitkov (16) reported that densification and the micro structure development during hot isostatic pressing of AP1 superalloy powder were influenced with pressure and temperature. The influence of manufacturing parameters on the sintering of molybdenum alloy structure (17) and metallic powder compacts (18) had been showed.

2 EXPERIMENTAL

The experimental part of this study included the preparation of the materials, the testing rig and equipments, and measurements of the physico-chemical properties of the input and output products

2.1 The Materials

2.1.1 The spent catalyst.

A spent catalyst sample weighing about 50 kg was supplied by Coke and Basic chemicals company, Cairo, Egypt. The catalyst is usually used in industrial hydrogenation and

ammonia fixation as well as desulphurization processes. The sample was visually inspected whereby foreign contaminants were removed. It was then classified with respect to particle size by mechanical sieving with a set of sieves having 4, 2.40, 1.20 and 0.35 mm opening diameters. Five cuts were obtained (-4 down to -0.35 mm in diameter).

2.1.2 The chemicals

Mineral acids as well as caustic soda of pure grade were used as follows.

- Conc. sulphuric acid (98%) and nitric acid (70%) were used for acid leaching processes (3:1 by volume).
- Caustic soda (60% concentration by weight) was used for the hydrometallurgical recovery of metal hydroxide.
- Lead acetate 4%, EDTA 0.1N, and zinc sulphate 0.1N were used for the determination of molybdenum, cobalt and alumina respectively.

2.2 Methods of Preparation of Molybdenum and Cobalt Powders

Figure [1] shows the process flow sheet followed for the preparation of metal powders of molybdenum and cobalt. However, reduction step was carried out in a tube furnace fitted with hydrogen gas cylinder and gas purification system. Reduction was monitored at a temperature range 500-900 °C for 1-3 hours. The metal oxide was charged in a porcelain boat (25 g). After the temperature of the hot zone of the furnace have been brought at the required level, the boat with the charge was introduced into the reaction zone. Hydrogen gas was allowed to flow at a flow rate 0.5-1.5 liter/minute.

After each experiment, the furnace was switched off meanwhile hydrogen gas was flowing. When the temperature of the furnace and the sample were cooled down to $\approx 100^{\circ}\text{C}$, hydrogen gas cylinder was closed. The boat was then discharged and placed in a desiccator. The obtained metal powder was weighed and investigated. Plate [1] shows a photograph of the used reduction test rig.

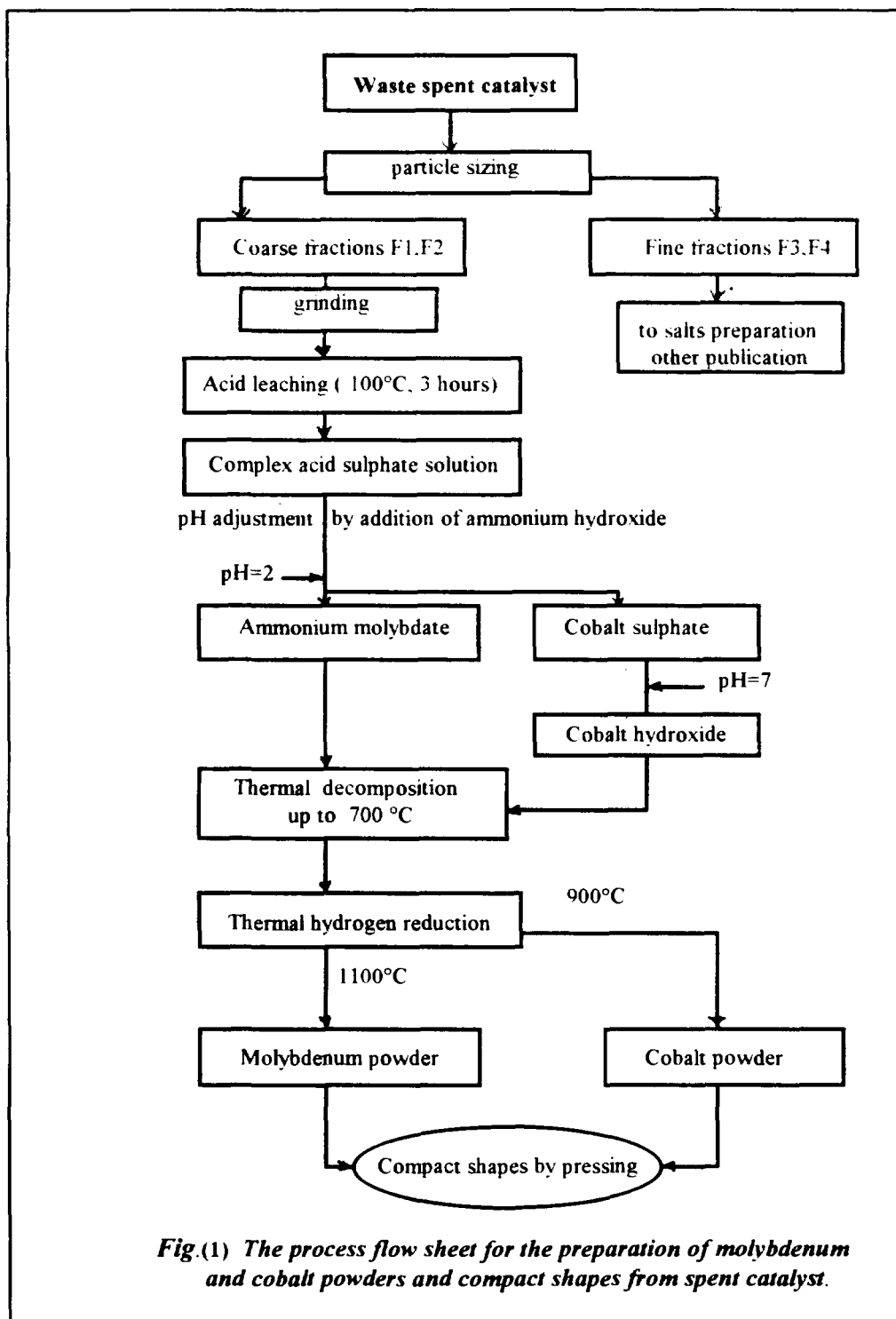


Fig.(1) The process flow sheet for the preparation of molybdenum and cobalt powders and compact shapes from spent catalyst.

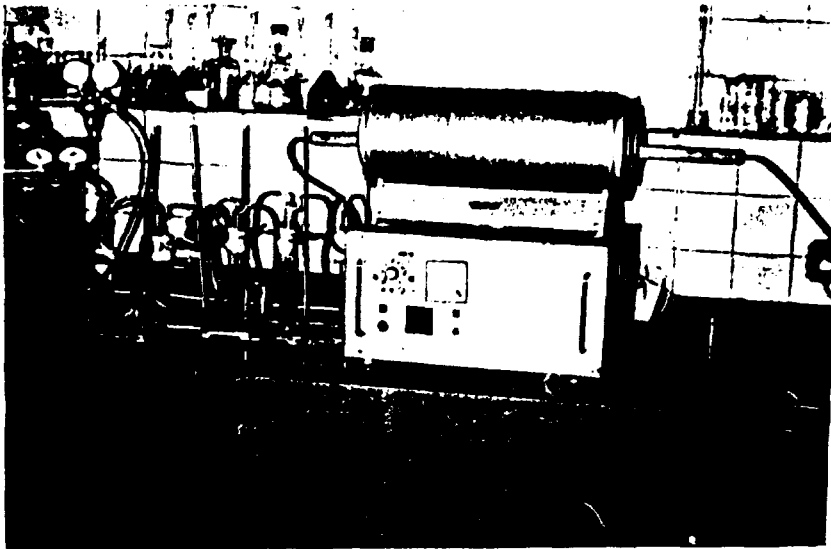


Plate (1) A photograph of the used test rig for hydrogen reduction.

2.3 Methods of Measurements of the Physico-Chemical Properties of the Input and Output Products.

- Particle size (mean value) was determined by a sieve shaker type VEB MLW Labortechnik iL Menau, Germany.

- Specific surface area was determined by isothermal liquid nitrogen adsorption method (BET).
- Density of the powder and compressed shapes were determined with the help of density bottle using kerosene as a displacement fluid.
- Molybdenum was determined as lead molybdate (19).
- Cobalt was determined complexometry with 0.1N EDTA and meroxide indicator (20).
- Recovery efficiency of molybdenum and cobalt from spent catalyst was determined according to :-

$$(\xi_{\text{rec}}) = \frac{\text{weight of recovered metal} \times 100}{\text{weight determined of the metal in the sample}}$$

Efficiency of reduction was determined according to

$$(\xi_{\text{red}}) = \frac{\text{weight loss (at a given T \& t)} \times 100}{\text{weight loss due to complete reduction}}$$

3- RESULTS

Table (1) shows the particle size distribution of the obtained spent catalyst sample. It can be seen that the major part of the sample has a particle diameter of -0.35 mm whereas the coarser fraction (+4 mm) amounts to 13.4 % by weight. The chemical composition of the obtained four fractions (F1 through F4) is given in Table (2). It can be seen that the coarser fractions > 1.2 mm contain the highest content of molybdenum and cobalt and lowest carbon content. Figure (2) shows the weight loss percentage (ΔW) as a function of heating the

catalyst fractions F1 through F4. It is seen that ΔW values increase rapidly with increase in temperature up to 500°C. With further rise in temperature, ΔW values slightly increase approaching a constant value at 700°C. However, coarse fractions (F1 and F2) acquire lower ΔW values (42%) as compared to the finer fractions F3 and F4 (60%).

Figure (3) shows the efficiency of recovery (ξ_{rec}) value of molybdenum and cobalt metals achieved at $\approx 100^\circ\text{C}$ as a function of leaching time and acid concentration. It is seen that (ξ_{rec}) values are insignificant with dilute acid mixture. With conc acid mixture, (ξ_{rec}) values amount to 74% after 30 minutes. It then increases gradually with increase in time approaching a constant value of 92% after about 300 minutes.

Figure (4) shows that (ξ_{rec}) value increases with increase in particle diameter of the catalyst sample. Maximum and constant (ξ_{rec}) value of 94% is acquired with particle size of ≥ 1.2 mm.

Figure (5) shows the effect of leaching temperature on the (ξ_{rec}) value of molybdenum and cobalt from coarse particles (F1 and F2) of the catalyst. It can be seen that parabolic relationship curves are obtained. At the lower temperature level $< 50^\circ\text{C}$, (ξ_{rec}) value is insignificant ($< 1.5\%$). With rise in temperature, a drastic increase in (ξ_{rec}) value takes place passing through a maximum at 100°C amounting to 80% and 96% after 120 and 240 minutes respectively. With further rise in temperatures up to 150°C , (ξ_{rec}) value decreases rapidly down to an insignificant value. Figure (6) is the Arrhenius plot devoted to the hot acid leaching process. An activation energy value of 674.9 kJ.mol^{-1} is obtained.

Figure (7) illustrates the effect of temperature on the decomposition percentage and the magnitude of loss in weight of ammonium molybdate to obtain molybdenum trioxide. It is seen that up to 300°C only 23% weight loss is achieved. However at 500°C , 54% weight loss that corresponds to 94% decomposition is achieved. Complete decomposition takes place at

600°C. Figure (8) shows the reduction efficiency of molybdenum trioxide and cobalt oxide with hydrogen gas to obtain molybdenum and cobalt metal powders. It can be seen that with molybdenum, a flat portion of the curve is achieved within the temperature range 600-800 °C corresponding to (ξ_{red}) value of 11%. Increasing the temperature bring about higher values of (ξ_{red}) whereby complete reduction is matched at 1100°C. With cobalt oxide, complete reduction takes place at 775-800°C.

Figure (9) shows the surface area of the obtained molybdenum and cobalt powders. It can be seen that similar set of curves as given in Fig. (8) with a maximum surface area of 120 square meters is obtained. Figure (10) shows the density values (ρ_p) of the prepared powders as a function of compression load. It can be seen that ρ_p value increases gradually with the increase in pressing load. Maximum and constant ρ_p value of 2420 kg.m⁻³ is obtained for powder pressed at 570 kPa.

4- DISCUSSION

The spent catalyst under discussion is one of the recurring waste material that contains valuable metals such as molybdenum and cobalt. The catalyst is manufactured by coating alumina carrier with active molybdenum and cobalt metals probably by impregnation technique. The catalyst is used for hydrogenation and desulphurization of coal gas as well as in ammonia fixation processes. The fresh catalyst is cylindrical pellets having 5 mm in diameter and pale green in colour. During the catalytic action, coal gas undergoes excessive cracking so that carbon particulates are one of the resultant species. Deposition of carbon smoke on accessible surface of the catalyst is liable to take place. Legitimately, the catalyst becomes black in color and is poisoned whereby its catalytic efficiency gradually diminishes. Also, part of the catalyst deforms to fines with no practical catalytic effect. Under these conditions,

cokeries usually remove the immaterial part of the catalyst by sieving. The under size part is discarded. It is our input waste material.

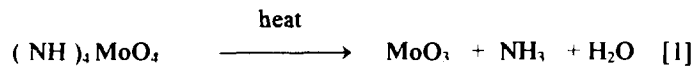
In the light of making use of industrial wastes, recovery of molybdenum and cobalt powders from spent catalyst shed a special consideration. The investigated catalyst sample of this work contains grains having different particle diameters as given in Table (1). The major part of the sample (40% by weight) is under 0.35 mm size. Analysis of that part reveals it is composed of 97.95 % by weight of carbon and alumina. In other words, only $\approx 2\%$ of the sample contain molybdenum and cobalt metals. This finding may be reasonable. The coarse fractions (F3 and F4) contain higher weight ratio of the two metals. These are more feasible for metals recovery.

The gradual increase in recovery efficiency (ξ_{rec}) with increase in particle diameter is self explanatory. The fine catalyst part bears excessive carbon deposits per unit weight as compared to the unbroken grains. That coating carbon deposit may establish a barrier to the attack of the acidic leachant. Such effect becomes more pronounced with fine fractions. With the coarse ones, however, incomplete coverage with carbon helps dissolution of the more available metals in the corrosive fluid.

Under the conditions undertaken in this work, the effect of acid diffusion to the particle boundary has been controlled by adequate stirring. The gradual increase of recovery efficiency with increase in time stands for the corrosion resistance property of these metals. The maximum recovery value amounts to nearly 92% after 300 minutes. Complete recovery (100%) is not liable to take place. Minor part of the metals lies on the bottom of surface contour of the alumina carrier. Diffusion of the attacking fluid through the alumina pores to the metal lying on the bottom is controlled by a concentration gradient established across the pore system of the carrier.

Acid dissolution of molybdenum and cobalt oxides is enhanced by increasing the temperature of the system. From our measurements, ΔE amounting to $674.9 \text{ kJ.mol}^{-1}$ would be applied to promote acid dissolution. Such energy value might be satisfied at 100°C . At higher temperatures (corresponding to highly concentrated sulphuric acid) the leaching process is gradually decreasing as the required aqueous medium is lacking.

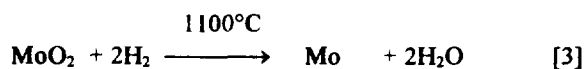
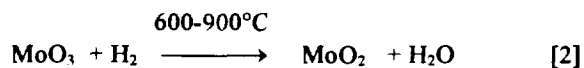
Results given in Fig (7) can be ascribed on the premise that ammonium molybdate is decomposed to molybdenum trioxide according to



The initial horizontal part of the curve achieved at $\approx 300^\circ\text{C}$ can be anticipated to the dehydration of the input molybdate salt. The drastic increase in loss in weight value with increase in temperature up to 700°C illustrates the formation of molybdenum trioxide.

Most of the molybdenum metal is used as an alloying element in steels and certain nonferrous alloys. According to the Bureau of Mines, United States production of molybdenum metal powder is approximately 416 tonnes. The largest consumption of cobalt is in magnetic alloys, cutting and wear-resistant alloys and catalysts production. (21,22).

Therefore, reduction of the prepared oxide with hydrogen to produce molybdenum metal is our final goal. Reduction process takes place in two steps. The first involves reduction to a lower oxide state. The second produces metal. Thus ;



With cobalt oxide, reduction with hydrogen takes place at 850°C . The low value of reduction efficiency obtained at $\leq 600^\circ\text{C}$ may be due to the formation of lower oxides of

cobalt. The obtained molybdenum and cobalt metals powders are needle-shaped crystals with different shape and size. These are investigated metallurgically. Plate (2) represents the crystal structure of these two preparations. Particle size measurement shows that the major part of these powders is 10-50 micron in size. This product find industrial applications as pressed shapes. So we have prepared molybdenum and cobalt shapes by pressing their powders. The bulk density values of these preparations are shown in Figure (10). However pressing of these powders does not bring about a density value of the casted metal (10200 kg.m^{-3} for molybdenum and 8900 kg.m^{-3} for cobalt). This is logic as the prepared particles are irregular in shape and size as is judged from metallography and surface area measurements. During pressing, random orientation of these particles is effected. In other words, voids and pores cannot be satisfied by solid particle rearrangement. However, the particle-particle friction resist the magnitude and direction of the exerted pressing load. With further increase in the latter, the aforesaid resistance may overweigh extra pressing load. In this case, constant bulk density values are acquired.

5-THE ECONOMIC STUDY

An economic study has been conducted to evaluate the techno-economic feasibility of recovery of molybdenum and cobalt powders as well as pressed shapes from spent catalyst. The study is based on cost centers principle by grouping two or more steps in one center to achieve certain basic process. The prices of the materials ,chemicals ,power, manpower...etc. are taken as the home prices of the year 1994. The \$US price equals to 3.399 Egyptian pounds. Table (3) shows the cost elements and economy norms of the recovery process.

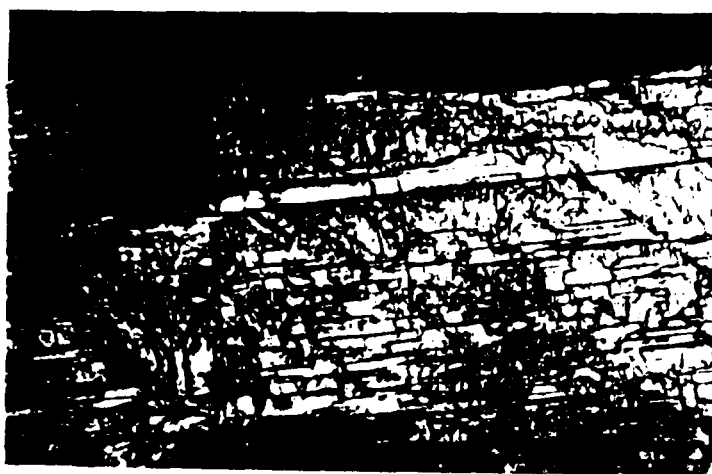


Plate (2) A photograph showing the metal molybdenum crystal as obtained from the prepared spent catalyst by reduction of molybdenum trioxide with hydrogen gas at 1100°C. (Mag.x 100). Etching solution was 15 ml nitric + 3 ml HF and 80 ml water.

6- CONCLUSION

The investigated sample of spent catalyst contains molybdenum and cobalt metals that can be recovered. The obtained metals powders meet the standard specifications. Compact shapes of these powders have been successfully prepared by pressing under ≥ 570 kPa. The recovery efficiency amounts to 97% and the applied technology of recovery is simple. The recovery process is costly significant and the price of the products is competitive to the market price.

Table (1) The particle size distribution of the used spent catalyst

sample	particle size ,mm (weight %)			
	F1, +4	F2,-4+1.2	F3, - 1.2+0.35	F4, - 0.35
1	13.6	24.2	22.5	40.0
2	13.24	24.0	22.34	40.0
Mean value	13.412	24.1	22.42	40.0

Table (2) The chemical composition of the catalyst fractions

fraction size,mm	Metal content , weight %			
	molybdenum	cobalt	alumina	carbon
F1 (+4)	9.70	7.95	40.35	42.0
F2 (-4 +1.2)	8.40	6.60	43.00	41.90
F3 (-1.2 + 0.35)	1.29	1.23	37.38	60.10
F4 (-0.35)	1.03	1.02	37.85	60.10

Table (3) Cost elements and economic norms

Item	quantity		sub	total
	units	price.\$	price\$	price.\$
Raw materials. kg	2500	20		
Chemicals . kg	1159	3101		
energy. kWh	10576	312		
power. kWh	8237	243		
equipments		1240		
labour . x 2weeks	6	640		
overhead charges 8%		77	5633	
Banking rate. 12%. 1 month		512		
others 38%		235	747	
subtotal				6380
End products :				
MO metal powder.kg	95.32	75	7147	
Co metal powder .kg	34.20	54	1846	8993
Net gain (profit)				2613

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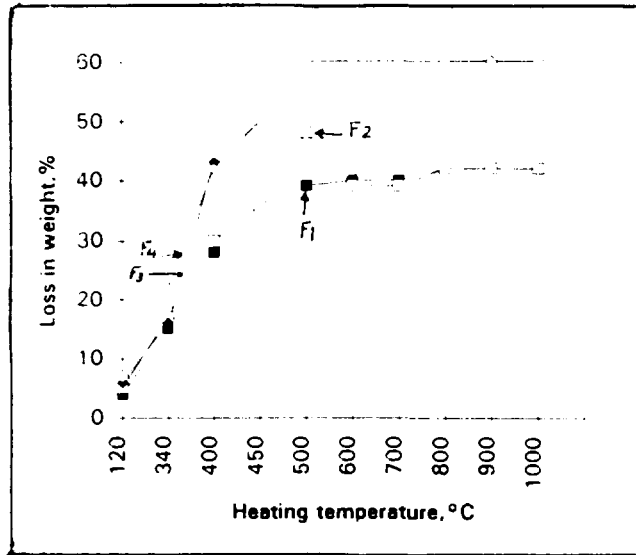


Fig. (2) Effect of thermal treatment temperature on the loss in weight of the spent catalyst.

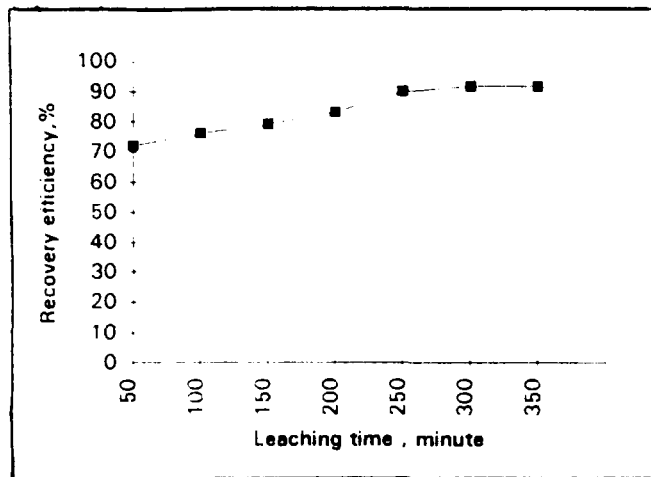


Fig. (3) Effect of acid leaching time on the recovery efficiency of molybdenum and cobalt metals.

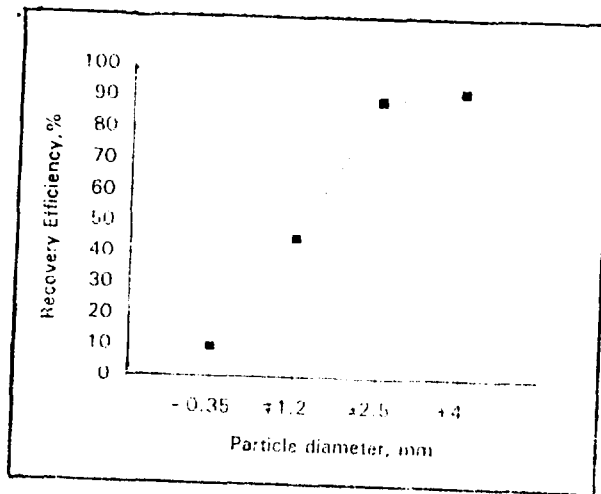


Fig.(4) Effect of particle diameter of the spent catalyst on the recovery efficiency of molybdenum and cobalt metals.

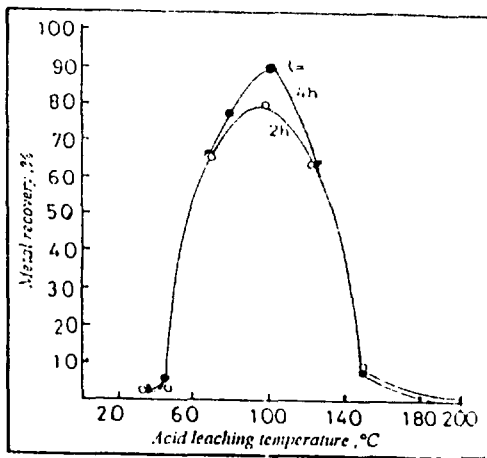


Fig.(6) The recovery percentage of metals from spent catalyst as affected by temperature.

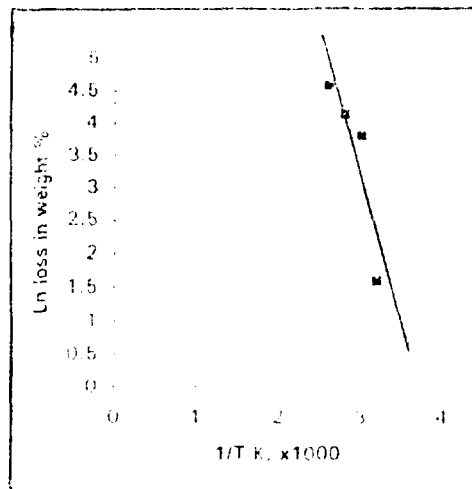


Fig.(6) The Arrhenius plot for acid leaching of the spent catalyst.

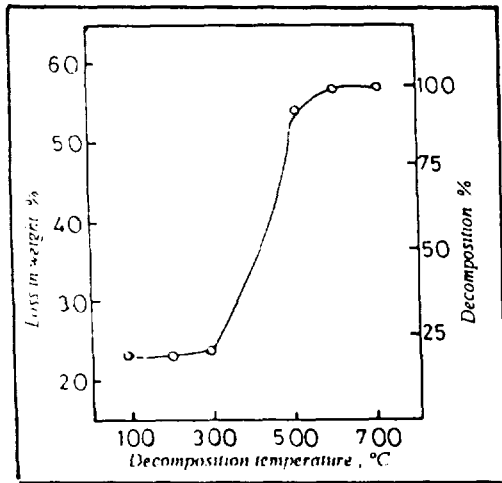


Fig.(8) Thermal weight loss and decomposition percentage of Ammonium molybdate as affected by temperature.

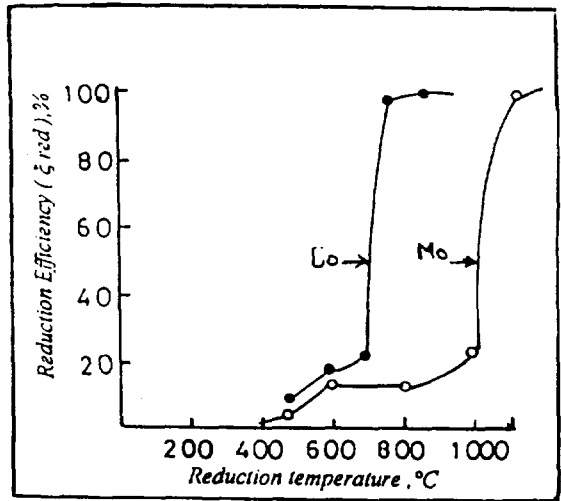


Fig.(9) Effect of reduction temperature on the (ξ red) values.

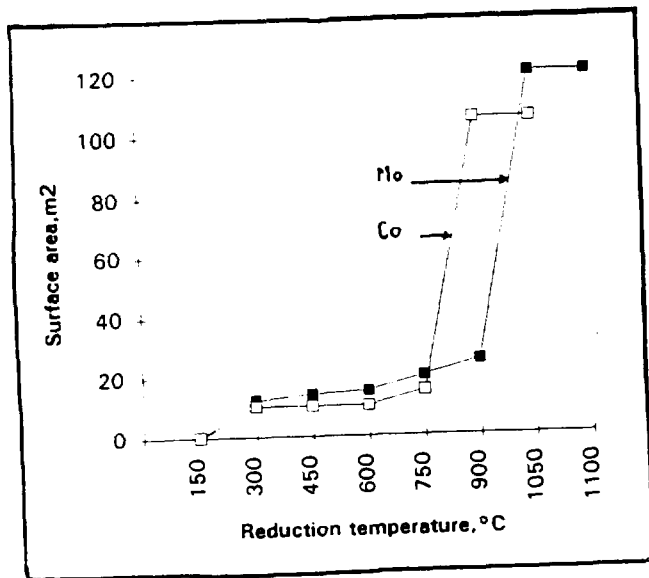


Fig.(9) The surface area of the produced metal powders as affected by the reduction temperature.

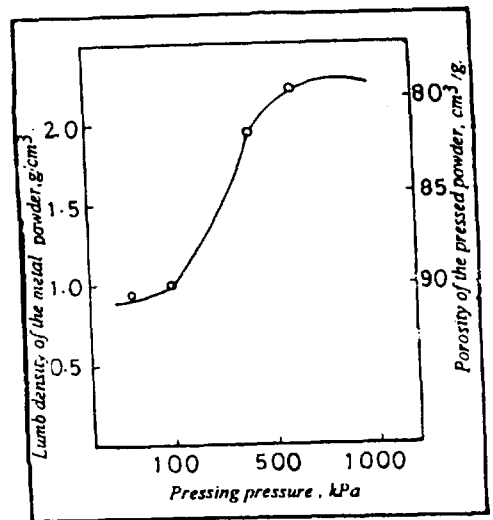


Fig. (10). Effect of pressure on lumb density and porosity values of the metals powder.