

## STUDIES ON THE UTILIZATION OF SPENT CATALYST USED IN OIL REFINERY

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Enormous amount of the spent cobalt-molybdenum/alumina catalyst, used for the hydrodesulphurization process in the oil refineries, is locally available for its safe disposal. Studies were undertaken on this spent catalyst for the extraction of valuable metals contained in it. Its chemical evaluation indicated the presence of CoO 3.43%, MoO<sub>3</sub> 14.50%, Al<sub>2</sub>O<sub>3</sub> 79.67% and SiO<sub>2</sub> 2.40%. In view of the high prices of cobalt and molybdenum in the international market, the research and development work were mainly concentrated on the extraction of these metals. Leaching studies undertaken on the samples indicated the optimum recovery of cobalt up to 96% and 96.5% for molybdenum.

**Key words:** Catalyst, Hydrodesulphurization process, Leaching, Extraction.

### Introduction

A typical hydrogenation process developed for the refining of petroleum distillates is the cobalt-molybdate process (Berg *et al* 1947; Byrns *et al* 1943). The process is applicable to the desulphurization of both straight-run and cracked distillates. Cobalt-molybdenum/alumina catalyst is used for the Hydrodesulphurization process in oil refinery.

The catalyst contains metallic oxides and can be used for a certain definite length. It is used in the presence of hydrogen from catalytic reforming operations. Because the charge stock is liquid, heavy feedstock can be treated. The sulphur content reduces from 2.9% to 0.01% in the fraction boiling less than 430°F to 0.43% in the fraction boiling over 500°F (Hoog *et al* 1953; Vladimir and Kenneth 1956). With the passage of time, the activity of the catalyst is reduced and it has to be replaced with a new stock during plant shutdown/turnaround. Before this, used catalyst is replaced with a new one, it is generated to burn off all sulphur and carbon content to make it safe for storage and transportation through no extra precaution/packing.

Tonnes of the spent catalyst need safe and economical utilization without creating the environmental problem and severe health hazards by its prolonged exposure, if swallowed or inhaled. It may also cause sensitization by skin contact.

The chemical composition of the catalyst comprises the oxide of cobalt, which varies from 1-10% and the oxide of molybdenum from 10-20% with a balance amount of alumina indicating the potential for the extraction of these materials from the spent catalyst. Studies had been undertaken on the re-

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covery of cobalt-molybdenum-alumina by Grzechowiak *et al* (1986). The present studies were aimed at for the better recovery of these metals rendering it feasible.

### Experimental

**Sample preparation.** The catalyst sample was in the form of beads with an average size of 2.5x5.0 mm. The material was subjected to grind of an appropriate size. The sampling was undertaken by the standard Coning and Quartering technique and the final sample was prepared by pulverizing in the Teema Mill (Model, Jean Wirtz Dussel Dors, UK) for chemical evaluation and extraction studies.

**Chemical evaluation.** The sample was treated with an appropriate concentration of hydrochloric and hydrofluoric acids were heated on the sand bath. After cooling, water was added to it. The solution was filtered and its volume was measured in the measuring flask. Molybdenum and cobalt were estimated spectrometrically (Skoog and West 1971) using Atomic Absorption Spectrometer Model Hitachi, Z-8000. (Table 1), while alumina was evaluated using conventional method (Vogel 1961) by fusion with sodium carbonate.

**Leaching/extraction studies.** The catalyst was pulverized and then different techniques were applied for the leaching of molybdenum, cobalt and alumina on the sample. The conditions were optimized for the extraction of their respective salts. Following studies were undertaken on the samples.

(a) Acid leaching (b) Ammonia leaching (c) Soda leaching.

The brief description of the studies is given below:

*a) Acid leaching:* Different acids were tried for leaching by heating the sample with their different concentrations. The

**Table 1**  
Chemical composition of the catalyst

S. no	Compound (Oxide)	(%)
1	CoO	03.43
2	MoO <sub>3</sub>	14.50
3	Al <sub>2</sub> O <sub>3</sub>	79.67
4	SiO <sub>2</sub>	02.40

**Table 2a**  
Leaching with hydrochloric acid (1:1)

S. no	Compound (Oxide)	(%)
1	MoO <sub>3</sub>	14.29
2	CoO	03.07

**Table 2b**  
Leaching with aqua regia (1:1)

S. no	Compound (Oxide)	(%)
1	MoO <sub>3</sub>	09.49
2	CoO	02.97

**Table 2c**  
Leaching with sulphuric acid (1:4)

S. no	Compound (Oxide)	(%)
1	MoO <sub>3</sub>	09.67
2	CoO	03.07

**Table 2d**  
Leaching with ammonium hydroxide 32% (1:1)  
The sample was treated with ammonium hydroxide and filtered, the filtrate contains

S. no	Compound (Oxide)	(%)
1	MoO <sub>3</sub>	10.89
2	CoO	00.40

**Table 2e**  
Leaching with sodium carbonate

S. no	Compound (Oxide)	(%)
1	MoO <sub>3</sub>	5.96
2	CoO	1.92

solutions were then filtered. The filtrate contained three metals in the form of their respective salts, which were evaluated and the results are presented in Table 2a-2c.

*b) Ammonia leaching:* The sample was treated with Ammonia in a conical flask covered with a watch glass to reduce the loss of ammonia and the solution was filtered. The results are shown in Table 2d.

*c) Soda leaching:* The sample was fused with sodium carbonate at 950°C and was treated with Hydrochloric acid. The results are shown in Table 2e.

*Extraction process.* After leaching with different reagents, molybdenum and cobalt were extracted from the mother liquor using different separation and extraction methods.

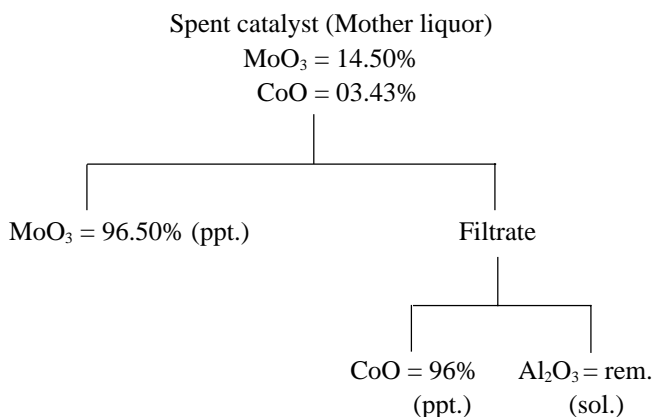
Two methods were applied for the extraction of the metals:

1. From the mother liquor, first molybdenum was separated as molybdenic acid, which was separated through filtration as the residue; the recovery of MoO<sub>3</sub> was about 96.5% Scheme-1. Cobalt was separated as its sulphide from the filtrate. Its extraction was 96%.

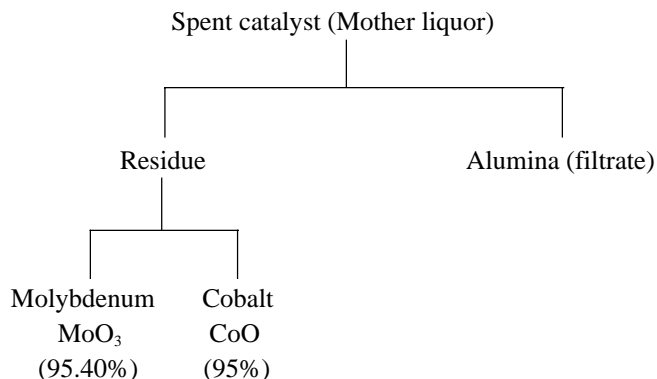
2. In the second process, both MoO<sub>3</sub> and CoO were precipitated as sulphides from the mother liquor while alumina remained in the solution form. The solution was filtered and the residue was treated with acid, precipitating molybdenum as molybdenic acid while cobalt remained in the solution form. By this method the extraction was 95.4% for MoO<sub>3</sub> and 95% for CoO (Scheme 2).

## Results and Discussion

The results of the studies indicate that cobalt and molybdenum can be extracted from the spent catalyst with a reasonable recovery and grade. These studies were not useful only



**Scheme 1.** Separation and extraction of molybdenum and cobalt from mother liquor (Method-I).



**Scheme 2.** Separation and extraction of molybdenum and cobalt from mother liquor (Method-II).

for the safe disposal of the spent catalyst but also were economically feasible as the prices of these metals in the international market are 400 \$ and 300 \$ per kg for cobalt and molybdenum, respectively (Aldrich catalogue). Therefore, the studies were mainly concentrated on these (cobalt and molybdenum) valuable elements. Earlier studies conducted on the extraction of these metals exhibit the recovery of 95% for molybdenum and 80-85% for cobalt. The results of the leaching studies indicate the enhanced recovery of cobalt and molybdenum i.e. 96.5% and 96%, respectively. These values represent that the studies are fairly successful. Moreover, the chemical processes, under normal industrial conditions have no hazard in aqueous phases, with normal safety

measures. The generation of fines (which is a possible hazard) can be controlled by wet grinding/closed circuit grinding.

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