

# SPENT CATALYST WASTE MINIMIZATION AND UTILIZATION

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**SUMMARY:** Spent hydroprocessing catalysts form a major source of solid wastes in the petroleum refining industry. Because of their hazardous nature, increasing emphasis has been placed to minimize spent catalyst waste generation at source as well as to develop cost-effective methods for reprocessing and recycling the waste catalyst material as much as possible. Spent hydroprocessing catalyst waste reduction at source can be achieved by using improved more active and more stable catalysts, regeneration, rejuvenation and reuse of deactivated catalysts in many cycles, and by reusing in less severe hydrotreating units by cascading before the final disposal. The spent catalyst can be recycled by using them as raw materials for recovery of valuable metals and other products. This paper focuses on the recent advances in the above options for minimization and recycling of spent hydroprocessing catalyst wastes. In addition, details of three processes that were developed in this laboratory for spent catalyst reprocessing and utilization are presented and discussed.

## 1. INTRODUCTION

In the petroleum refining industry, the amount of spent hydroprocessing catalysts discarded as solid wastes has increased significantly in recent years because of a steady increase in the processing of heavier feedstocks together with a rapid growth in diesel hydrotreating capacity to meet the increasing demand for low sulfur fuels. The total quantity of spent hydroprocessing catalyst generated currently worldwide is estimated to be in the range of 150000-170000 t/y and it will continue to increase as new hydrotreating units are built [Dufresne, 2007]. The storage, transportation, treatment, and disposal of these spent catalysts require compliance with stringent environmental regulations because of their hazardous nature [USEPA, 2003]. As a result, increasing attention has been paid to minimize spent catalyst waste generation at source as well as to develop safe and cost-effective methods for recycling and disposal. In this article, an overview of spent catalyst waste minimization methods, and recycling in the production of useful materials including metals recovery is presented.

## 2. SPENT CATALYST WASTE MINIMIZATION METHODS

The quantity of spent hydroprocessing catalyst discarded as solid waste can be reduced, if the

useful life of the catalyst before disposal could be extended for a longer period. This can be done in three ways: (i) Regeneration / rejuvenation and reuse, (ii) Usage in less demanding hydrotreating processes or in other processes, (iii) Reduce catalyst consumption by using improved catalysts with longer life.

### **2.1. Regeneration / reactivation / rejuvenation and reuse**

Hydrotreating catalysts consist of sulfides of Mo and Co or Ni on  $Al_2O_3$  support. During use in a hydrotreating reactor, the catalysts deactivate mainly by the deposition of coke which covers the active sites. Catalysts deactivated by simple coke deposition can be reused after regenerating the catalyst by removing the deposited coke by combustion. This can be repeated a few times until the catalysts activity recovery is reduced below acceptable level because of loss of surface area caused by sintering during regeneration. Careful control of temperature and oxygen concentration during coke burning is critical to suppress the sintering of the active phase and support (Furimsky and Massoth, 1993). In the past, most refiners regenerated their catalysts in situ in fixed-bed reactors. Temperature runways and hot spots can occur in the in situ regeneration resulting in catalyst sintering and activity loss. Another problem is that catalyst fines stay in the catalyst bed which can cause reactor plugging and maldistribution when the reactor is restarted. Today a majority of the refiners use ex situ (off site) regeneration services offered by companies such as Tricat, Eurecat, Porocel etc. for regenerating their hydrotreating catalysts (Dufresne, 2007). Off site regeneration of hydrotreating catalysts results in better activity recovery because of close control of regeneration temperature, better evaluation of the catalyst's reusability by a variety of characterization and quality control tests, and removal of fines and chips that contribute to pressure drop problems. Environmental, safety and reduction of unit's shutdown and start up times are additional benefits of ex situ regeneration. Presulfiding services after regeneration are also offered by these companies.

In the case of some new generation diesel hydrotreating catalysts with high metals (Mo and Co or Ni) loading, additional chemical treatments of decoked catalysts with oxygen containing chelating agents are done to redispense the metals. Major catalyst manufacturing companies such as Albemarle, Criterion and Haldor Topsoe are licensing the technologies for reactivation of regenerated diesel hydrotreating catalysts. HDS activity recovery above 95% of fresh catalyst activity has been achieved in such reactivation process.

Spent catalysts from residual oil hydroprocessing operations which are deactivated by coke and metal deposits (e.g. V) are not regenerated and reused currently since the technology for their regeneration and reactivation is not commercially available. Regeneration by conventional procedures using nitrogen-air or steam-air under controlled conditions does not result in complete reactivation of the catalysts. While the carbon deposit is removed completely, the metallic impurities (e.g. V) remain on the catalysts blocking the pores. Recently, a process was developed in our laboratory to rejuvenate the metal-fouled spent catalysts by selective leaching of the metals blocking the pores by chemical treatment (Marafi et al., 2000; 2003).

A schematic diagram of the process is shown in Figure. 1. The process consists of several operations such as deoiling, sieving, separation of heavily fouled catalysts from the partly fouled portions by jiggling, metal leaching and decoking to produce rejuvenated catalysts from partly fouled spent catalyst portions and sending the heavily fouled portion for metal recovery. Substantial improvements in the chemical and physical characteristics occurred in the rejuvenation process. The rejuvenated catalyst contained no coke and its vanadium content was 80% lower than that of the spent catalyst. Small amount of vanadium remaining in the rejuvenated catalyst was not concentrated near the outer surface of the catalyst pellets, but evenly distributed inside the pores. The surface area increased from 98 to 240  $m^2/g$ . A similar increase in catalyst pore volume was also noticed, HDS activity measurements showed that over 95% of the activity of the fresh catalyst was recovered by rejuvenation. Economic assessment of the

process revealed that rejuvenation and reuse of the catalyst is feasible with an internal rate of return (IRR) of 20%.

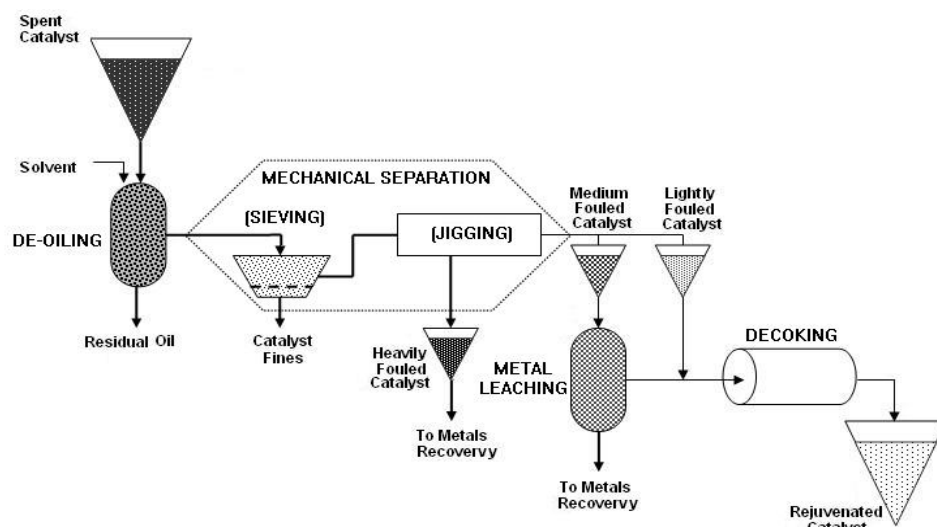


Figure. 1. Rejuvenation process for spent residue hydroprocessing catalyst.

## 2.2. Usage of spent hydrotreating catalysts in other processes

When the regenerated catalysts from high severity hydrotreating processes do not have sufficient activity recovery for reuse in the original process, it might be possible to use them in less severity hydrotreating processes or other process. Cascading spent catalyst from one unit to another unit after regeneration is commonly practiced in most refineries. Typically cascading could be gas oil hydrotreater → Kerosene hydrotreater → naphtha hydrotreater. In multi reactor residue hydrotreating units, it is often possible to shift a regenerated catalyst from the back-end reactors that are deactivated to a lesser extent by metal deposits to front-end reactors.

The reuse of spent hydrotreating catalysts in processes other than hydrotreating has been reported in some scientific papers and patents. Furimsky (1997) showed that spent  $\text{CoMo}/\text{Al}_2\text{O}_3$  and  $\text{NiMo}/\text{Al}_2\text{O}_3$  type HDS catalysts are highly active for decomposition of  $\text{H}_2\text{S}$  and suggested that they can be used for hot gas clean up ( $\text{H}_2\text{S}$  removal). Thorsten et al [2005] reported that spent  $\text{NiMo}/\text{Al}_2\text{O}_3$  and  $\text{CoMo}/\text{Al}_2\text{O}_3$  type HDS catalysts (from gas oil or naphtha HDS units) can be used as adsorbents for removal of sulfur, nitrogen and aromatic compounds from hydrocarbon feedstock.

## 2.3. Development of improved hydrotreating catalysts

Spent catalyst waste generation in catalytic hydrotreating units can be reduced through the use of more active and stable catalysts in the process. Remarkable improvements have been made in recent years in the performance of catalysts used in distillate and residual oil hydrotreating units (Stanislaus and Absi-Halabi, 2002; Furimsky, 2007). A list of high-active new generation hydrotreating catalyst developed and marketed by various catalyst manufacturing companies for diesel deep HDS is presented in Table. 1. Development of improved hydrotreating catalysts has been possible through a clear understanding of the key properties namely, nature of the active sites and their structure, and the textural characteristics of supports, more specifically pore size, that have significant influence on the catalysts performance (Topsoe et al., 1996; 2007). In the case of diesel deep HDS catalysts, increased active metals loading to increase the number of active sites, higher dispersion of the active phase (e.g. Type II  $\text{CoMoS}$  or  $\text{NiMoS}$ ) by optimizing

preparation procedures and enhancement of hydrogenation function of the catalyst by additives and by optimized catalyst formulation have been used to improved HDS activity.

In addition to the development of highly active and more stable new generation hydrotreating catalysts, improvements in feed (oil) distribution in reactors by using better trays, better catalysts loading and process revamps and optimization have been made in recent years to improve hydrotreating reactor performance. These improvements have increased run-lengths significantly and thereby reduced spent catalyst waste generation.

Table. 1. Improved new generation diesel hydrotreating catalysts.

Catalyst Manufacturer	Improved New Generation Deep HDS Catalysts
Albemarle	STARS: KF 756, KF 757, KF 767, KF 848, NEBULA
Haldor Topsoe	TK 573, TK 574, TK 575 Brim, TK 576 Brim TK 605 Brim TK 911, TK 915
Criterion	CENTINEL Gold Series CENTINEL Ascent Series
Axens	HR 448, HR 526 HR 548, HR 568
Grace / ART	SMART – Catalyst system
Kuwait Catalyst Co. (KCC)	HOP - 414, HOP - 467
Cosmo Oil Co.	C – 606A

### 3. RECOVERY OF METALS

Spent, hydroprocessing catalysts contain alumina and metals such as Mo, Ni, Co and V in appreciable concentrations. These metals are highly valuable and are used extensively in the steel industry and in the manufacture of special alloys. Spent hydroprocessing catalysts could be used as a cheap source for these valuable metals. This will result in recycling and reutilization of the waste catalysts and reduce their environmental problems. In view of the environmental and economic benefits, increasing attention has been paid to develop processes for recovering metals and other valuable materials from hydroprocessing catalysts.

#### 3.1 Laboratory studies on metal recovery from spent hydroprocessing catalysts

Several methods such as chlorination, acid leaching, alkali leaching, bioleaching, roasting with soda salts etc. have been studied and reported in open literature and patents for the recovery of Mo, Ni, Co and V from the spent catalysts. Metal recovery efficiencies for different methods are compared in Table. 2.

Once in the solution, the metals can be isolated in a pure form using established methods based on selective precipitation and solvent extraction. In the case of solvent extraction, a high selectivity of extraction can be achieved by merely adjusting the pH of the solution containing an extracting agent (Inoue et al., 1993).

Table. 2. Metal recovery by different leaching and roasting methods (Marafi and Stanislaus, 2008).

Metal present in spent catalyst	Reagent	Metals Recovered (wt %)			
		Mo	V	Ni	Co
V, Mo, Ni, Co, Al	Na <sub>2</sub> CO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	99	85	-	-
Mo, Ni, Al, C, S	Na <sub>2</sub> CO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	85	-	65	-
V, Ni, Mo, Al	NaOH (10%), pH 8.8	91.8	88.5	20	-
V, Ni, Mo, Al	NaOH (10%), pH 8.4	98.8	92.7	10	-
V, Ni, Mo	NaOH (atmospheric & pressure leaching in two steps)	97	92	-	-
V, Ni, Mo, Al	Aqueous NH <sub>3</sub> Solution (17M)	-	98.8	-	-
Ni, Mo, Al	NaOH (1 <sup>st</sup> stage) & H <sub>2</sub> SO <sub>4</sub> (2 <sup>nd</sup> stage)	84	-	98	-
Ni, Co, Mo, Al	NaOH (1 <sup>st</sup> stage) & H <sub>2</sub> SO <sub>4</sub> (2 <sup>nd</sup> stage)	97	-	92	92
V, Mo, Co, Ni, Al	Na <sub>2</sub> CO <sub>3</sub> (Roasting + leaching with H <sub>2</sub> O	90-95	90-95	-	-
Co, Mo, Al	NaOH roasting (1 <sup>st</sup> stage)	90	-	-	90
	H <sub>2</sub> SO <sub>4</sub> Leaching (2 <sup>nd</sup> stage)				
V, Mo, Ni Co, Al	NaOH roasting (1 <sup>st</sup> stage)	98.9	95.8	98.2	98.5
	H <sub>2</sub> SO <sub>4</sub> Leaching (2 <sup>nd</sup> stage)				
Mo, Ni, Al <sub>2</sub> O <sub>3</sub>	NaCl roasting + water extraction	90	-	-	-
Mo, Ni, Co, Al	KHSO <sub>4</sub> fusion + water extraction	96	-	90	90
V, Mo, Ni, Co	Aqueous NH <sub>3</sub> + NH <sub>4</sub> CO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	93	88	80	78
Mo, V, Ni	Citric acid	94	94	85	-
V, Mo, Ni, Al	Oxalic acid + H <sub>2</sub> O <sub>2</sub>	90	94	65	-

### 3.2 Commercial processes

There are several companies in the world which specialize in the recovery and reprocessing of spent catalysts. Following are the main companies involved: Gulf Chemical & Metallurgical Corporation (GCMC) USA, Cri-met (USA), Taiyo Koko Co. (Japan), Eurecat (France), Spent Catalyst Recycling (Germany), Taiyo Mining and Industrial Co. (Japan), Aura Metallurgic (Germany), Sadaci (Belgium), Full Yield Industries (Taiwan) Metallurgy Vanadium (USA), Metal-Tech, Nippon Catalyst Cycle Co. (Japan), Moxba-Metrex (The Netherlands), and Quanzhou Jing-Tai Industry Co. (China).

Metal reclaimers use one of two methods: hydrometallurgy or pyrometallurgy. Hydrometallurgy dissolves the metals by leaching the catalyst with an acid or base. The metals are then recovered as marketable metal compounds or metals. Pyrometallurgy uses a heat treatment such as roasting or smelting to separate the metals. It melts the spent catalysts at high temperatures, often with the aid of a flux to lower the melting temperature and viscosity of the slag. The metals sink to the bottom of the melt and are recovered and sold. The catalyst base/substrate floats on the surface as a slag that can be recovered and sold as a commercial commodity. In the case of spent hydroprocessing catalysts, all components can be recovered without leaving any residue by these processes. The recovered metals such as Mo, V, Ni and Co could be used in steel manufacture and the alumina could be used for the manufacture of refractories, ceramics and abrasives.

## 4. PREPARATION OF USEFUL MATERIALS FROM SPENT CATALYSTS

Utilization of spent catalysts as raw materials in the production of valuable products is an attractive option for their recycling from environmental and economic points of view. The use of

spent fluid catalytic cracking (FCC) catalysts in cement and concrete production has been reported in many studies. The use of spent hydroprocessing catalyst in cement production appears to be restricted because of its hazardous nature. However, many other useful materials such as fused alumina, synthetic aggregates, Anorthite glass-ceramics, refractory cement and refractory brick have been prepared from spent hydroprocessing catalysts.

Two processes, one for producing non-leachable synthetic aggregate materials with high compressive strength and the other for the preparation of active hydrodemetallization catalysts from spent hydroprocessing catalysts were developed in our laboratory. The process for synthetic aggregate production involved mixing the spent catalyst in the form of a fine powder (particle size less than 180nm) with clay, gatch, sand and water, shaping the wet mix into small balls of about 20mm diameter, drying the balls at 110°C for 12 hours and then heating them at high temperature in the range 1150 - 1300°C. Synthetic aggregate materials with minimum leaching (<1mg/l) and maximum compressive strength were produced when the firing temperature was around 1175°C (Figure. 2a and 2b).

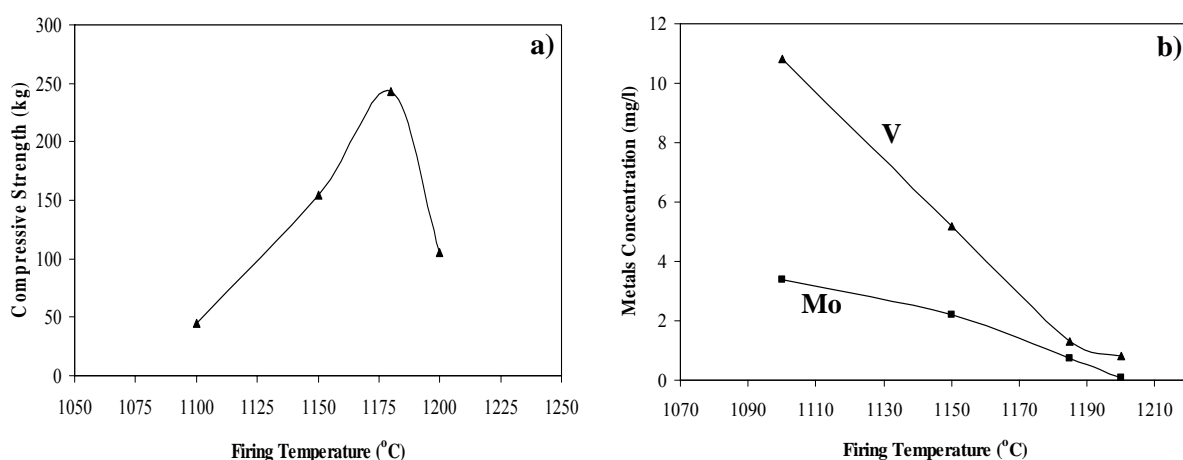


Figure 2. Effect of firing temperature on a) Comprehensive Strength b) Metal leaching.

Since the synthetic aggregates produced by this process were stable and non-leachable and had high compressive strength, they could be used in the construction industry for concrete production by incorporating in a cement matrix. Cement concrete prepared from the spent catalyst-based synthetic aggregate had a compressive strength of 461 kg/cm, while that of natural aggregate was 485 kg/cm<sup>2</sup>.

The sequence of operational steps used for the preparation of active HDM catalysts from spent catalysts is shown in Figure. 3. The spent catalysts was first deoiled and then grounded to a fine powder. The powdered spent catalyst material was mixed with boehmite (40% spent cat and 60% boehmite), peptized with an acid (2% HNO<sub>3</sub>), kneaded and then extruded. The catalyst extrudates were dried at 110°C for 24h and calcined at 450 – 500°C. The catalyst extrudates contained V, Mo and Ni on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, had high surface area, pore volume and crushing strength and were substantially more active for promoting HDM (V and Ni removal) and HDS reactions than a reference commercial HDM catalysts (Figure. 4).

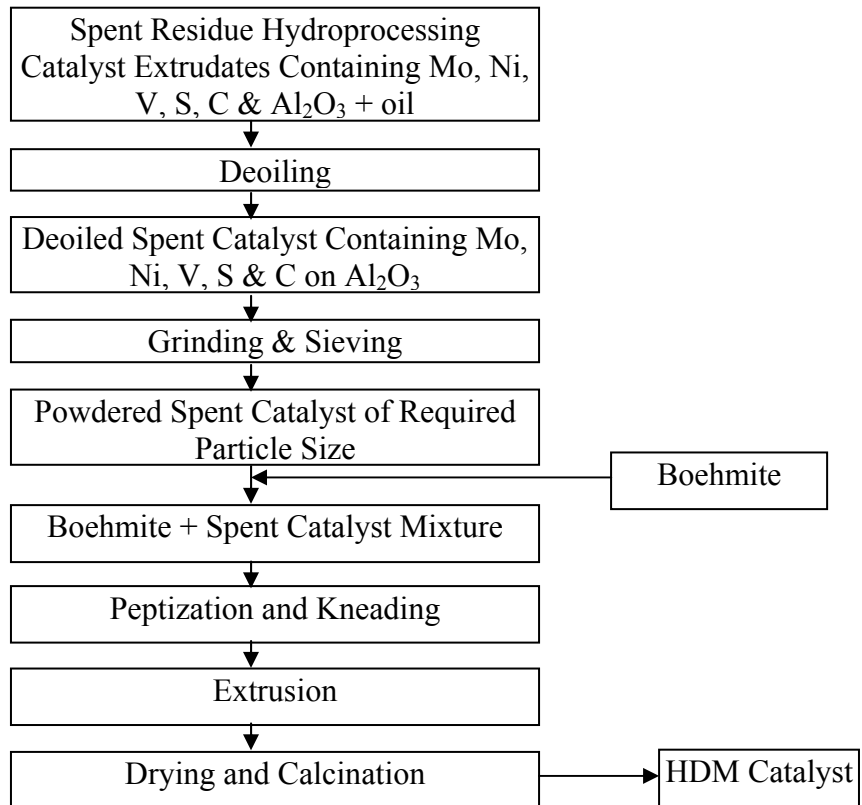


Figure 3. Operational steps in the preparation of catalyst extrudates from spent catalyst.

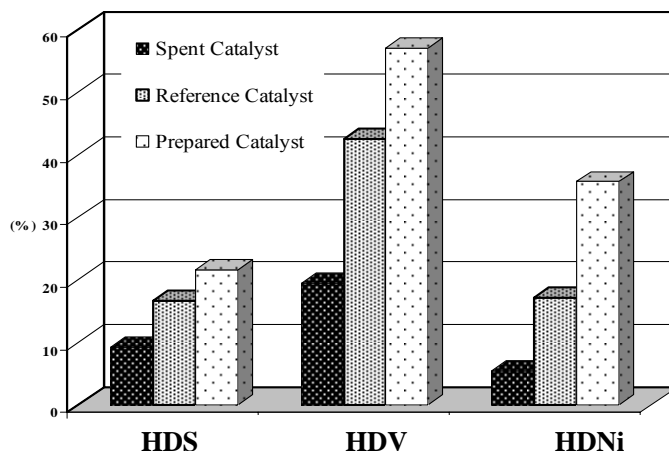


Figure 4. Comparison of the HDS, HDV and HDNi activities of spent, prepared and reference catalysts.

## 5. CONCLUSIONS

Research on the development of processes for minimization and recycling of spent hydrotreating catalyst wastes has received increasing attention in recent years because of their hazardous nature and stringent environmental regulations on their disposal. In this paper, various methods used for spent catalyst waste reduction at source and the processed available for their recycling and reutilizations are reviewed. In addition, details of three process, one for rejuvenation and reactivation of metal-fouled spent hydroprocessing catalysts for reuse, the other for producing

non-leachable synthetic aggregate materials with high compressive strength for use in the construction industry, and the third for the preparation of active new hydrodemetallization catalysts from spent catalysts that were developed at Kuwait Institute for Scientific Research are presented and discussed. The spent catalyst wastes can be recycled and their environmental problem can be minimized by these processes.

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