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Options and processes for spent catalyst handling and utilization

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Abstract

The quantity of spent hydroprocessing catalysts discarded as solid wastes in the petroleum refining industries has increased remarkably in recent years due to a rapid growth in the hydroprocessing capacity to meet the rising demand for low-sulfur fuels. Due to their toxic nature, spent hydroprocessing catalysts have been branded as hazardous wastes, and the refiners are experiencing pressure from environmental authorities to handle them safely. Several alternative methods such as reclamation of metals, rejuvenation and reuse, disposal in landfills and preparation of useful materials using spent catalysts as raw materials are available to deal with the spent catalyst problem. The technical feasibility as well as the environmental and economic aspects of these options are reviewed. In addition, details of two bench-scale processes, one for rejuvenation of spent hydroprocessing catalysts, and the other for producing non-leachable synthetic aggregate materials that were developed in this laboratory, are presented in this paper.
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Keywords: Spent hydroprocessing catalysts; Hazardous wastes; Safe disposal; Rejuvenation; Synthetic aggregates

1. Introduction

Large quantities of catalysts are used in the refining industry for the purification and upgrading of various petroleum streams and residues [1]. The catalysts deactivate with time and the spent catalysts are usually discarded as solid wastes. The quantity of spent catalysts discharged from different processing units depends largely on the amount of fresh catalysts used, their life and the deposits formed on them during use in the reactors. In most refineries, a major portion of the spent catalyst wastes come from the hydroprocessing units.

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The volume of spent hydroprocessing catalysts discarded as solid wastes has increased significantly due to a steady increase in the processing of heavier feedstocks containing higher sulfur, nitrogen and metal contents, together with a rapid growth in the distillates hydroprocessing capacity to meet the increasing demand for low-sulfur fuels [2]. In Kuwait alone, around 7000 t of spent catalysts are generated every year as solid wastes from the hydrotreating and hydrocracking units.

Environmental laws concerning spent catalyst disposal have become increasingly more severe in recent years. Spent hydroprocessing catalysts have been classified as hazardous wastes by the Environmental Protection Agency in the USA [3]. The most important hazardous characteristic of spent hydroprocessing catalysts is their toxic nature. Chemicals such as V, Ni, Mo and Co present in the catalyst can be leached by water after disposal and pollute the environment [4]. Besides the formation of leachates, the spent hydroprocessing catalysts, when in contact with water, can liberate toxic gases. The formation of the dangerous HCN gas from the coke deposited on hydroprocessing catalysts that contains a substantial amount of nitrogen has been reported.

The hazardous nature of the spent catalysts is attracting the attention of environmental authorities in many countries and the refiners are experiencing pressures from environmental authorities for safe handling of spent catalysts. Several alternative methods such as disposal in landfills, reclamation of metals, regeneration/rejuvenation and reuse, and utilization as raw materials to produce other useful products are available to the refiners to deal with the spent catalyst problem [5,6]. The choice between these options depends on technical feasibility and economic considerations. In this paper, the various options available for handling the spent catalysts problem are reviewed. In addition, details of two processes, one for rejuvenation of spent residue hydrotreating catalysts, and the other for producing non-leachable synthetic aggregate materials from spent catalysts, that were developed in this laboratory as part of a research program on spent catalyst handling and utilization, are presented.

2. Spent catalyst handling options

2.1. Disposal as landfill

Historically, spent catalysts have been disposed off as landfill in approved dump-sites. Catalyst, or any other waste, could be disposed off into a landfill only if it could be proven with certainty that the landfill met non-hazardous criteria. In the USA, the disposal and treatment of spent refinery catalysts is governed by the Resource Conservation and Recovery Act (RCRA), which holds not only the approved dump-site owner liable, but the owner of the buried waste as well. This environmental responsibility continues for the life of the dump-site. The current RCRA regulations require landfills to be built with double liners as well as with leachate collection and groundwater monitoring facilities. Thus, the landfill option is becoming expensive today. In addition, it carries with it a continuing environmental liability. The potential future liability of landfills is estimated at about US$ 200 t^{-1} [7]. Treatment prior to landfilling may be necessary in some cases increasing the cost. However, when the other alternatives such as regeneration and reclamation are not viable

economically, disposal as landfill is the only option available. Some refiners store spent catalysts on specially designed sites, awaiting the time when better treatment techniques will be available. However, this kind of storage is only a temporary solution.

Catalysts sent to landfills must be properly treated for stability. Efforts have been made to develop processes for the treatment of the spent catalyst by suitable procedures that can reduce leachability. For example, the Maectite process, patented by Sevenson Environmental Services Inc. [8], is capable of converting reactive metals contained in solid wastes into non-leachable minerals in the apatite and barite group. These minerals are resistant to acidity and degradation by geological and chemical conditions such as those found in landfills and natural settings. A similar method known as Sealosafe has been developed by Stablex Corporation for the treatment of hazardous wastes to make them non-leachable [9]. The process involves adding a mixture of calcium containing cement powder and an aluminosilicate powder to the waste material dispersed in water and converting them to an impermeable solid. It is believed that these processes can also be applicable to the spent solid refinery catalysts, although, so far, there is no published information to confirm it.

Another approach that can decrease the leachability is the encapsulation and chemical fixation/stabilization of the waste material. Radioactive wastes are usually treated by these methods and could be adopted for spent catalysts also [10]. In the case of encapsulation, the waste material is treated with substances such as bitumen, concrete or polymers and they are well sealed in the thermoplastic agent. Encapsulation with vitreous silicates has also been reported. It is important that the encapsulant has to be stable over long periods of time. However, long-term effects of this method are not known. In the stabilization process, the toxic metals in the hazardous wastes are converted to environmentally safe products by thermal treatment until the solid becomes a molten bath. After solidification, the molten bath has a spinel structure that can bond harmful species and convert them into a non-leachable form.

These treatment methods are, however, highly energy intensive and very expensive. They do not offer profitable solution to the waste disposal problem. No organization will undertake the treatment procedures for waste catalysis unless the costs associated with the disposal methods are acceptably low. The cost of land filling is expected to become prohibitive in the future. For a hazardous waste like the spent hydroprocessing catalyst, land filling and other treatment methods are not preferable when all costs and liabilities are taken into account. Alternative beneficial outlets are, therefore, considered by the refiners to minimize the cost of handling, storage and disposal.

3. Recovery of metals

Recovery of metals and other components from the spent catalysts is possible, and the technology for metals reclamation is well established. For catalysts containing precious metals such as platinum and palladium, metals recovery processes are highly profitable. For spent hydroprocessing catalysts which contain Mo, Ni, Co, V and Al_2O_3, process economics for recovery of the metals are influenced by metals prices, metals content, transportation costs and purity of the recovered metals.

Worldwide several companies such as Gulf Chemical & Metallurgical Corporation (USA), Cri-met (USA), Taiyo Koko Co. (Japan), Eurecat (France), Spent Catalyst Recycling

(Germany), ACI-Industries (USA), Taiyo Mining and Industrial Co. (Japan), Aura Metallurgic (Germany), Sadaci (Belgium), Full Yield Industries (Taiwan), etc. are involved in metals reclamation from spent hydroprocessing catalysts. 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 to 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.

In recent years, high costs of shipping and low metals concentrations have increased the processing costs. These factors together with fluctuation in the market prices of recovered metals and their purity significantly influence the commercial viability of processes used for metal reclamation from spent hydroprocessing catalysts. This option is further complicated by the Basel Convention on the transport of spent hydroprocessing catalysts that are branded as hazardous wastes.

All these factors make processing of spent hydroprocessing catalysts for metal reclamation less attractive. However, as the cost of catalyst storage and disposal continues to rise, the utilization of spent refinery catalysts for metals recovery is becoming a viable solution. As the environmental pressures increase, in many cases, the refiners are ready to supply spent hydroprocessing catalysts free of charge in order to reduce their costs for storage and disposal. If the market value of the recovered materials is high enough, then it will offset, the processing cost yielding a net profit to the reclaimer. The metal reclamation option can provide a complete solution to the environmental problem of spent hydroprocessing catalysts in a profitable way. This option, however, does not provide a complete solution for all types of catalysts. In some cases only partial recovery is possible which leaves the remaining portion to be treated or disposed by other methods.

4. Reactivation/rejuvenation and reuse of spent catalysts

This is a preferred option for minimizing the spent catalyst environmental problem, but this is not always possible. The application of this option to spent catalyst treatment depends largely on the cause of deactivation of the catalysts. Catalysts deactivated by simple coke deposition are usually regenerated by combustion of coke under controlled temperature conditions and reused. This can be repeated a few times until loss of surface area by sintering decreases the catalytic activity. Catalysts deactivated by sintering and loss of surface area of the support cannot be reactivated and reused. In general, catalysts deactivated by thermal degradation, phase separation or phase transformations cannot be reactivated easily and replacement is necessary.

Reactivation by rejuvenation process is possible in the case of spent catalysts from residual oil hydroprocessing operations. These catalysts are deactivated by fouling of the active

surface by coke and metal (V and Ni) deposits originating from the heavy feedstock [11,12]. 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 remain on the catalysts. The foulant metals are usually concentrated near the outer surface of the pellet, blocking pore mouths and reducing markedly the active surface area available within the inner pores of the catalysts. If the contaminant metals can be removed selectively by chemical treatment without affecting significantly the chemical and physical characteristics of the original catalyst, then the spent catalyst could be rejuvenated and reactivated.

A survey of literature revealed that the technology for rejuvenating spent residue hydroprocessing catalysts by selective removal of metal contaminants is not yet well developed [13,14]. However, there is considerable interest in the rejuvenation and reuse of these catalysts, since it can substantially reduce the environmental problem. During the past decade considerable research was devoted to this issue in our laboratory and a process to rejuvenate spent residue hydroprocessing catalyst was developed [15–19]. A schematic diagram of the process is shown in Fig. 1. The process consists of several operations such as deoiling, sieving, separation of heavily fouled catalysts from the partly fouled portions by jigging, metal leaching and decoking to produce rejuvenated catalysts from partly fouled spent catalyst portions and sending the heavily fouled portion for metal recovery.

In this process, mechanical separation of the partially fouled (low density) spent catalyst materials from the heavily fouled (high density) portions was carried out using a laboratory scale jigging apparatus. Jigging is a gravity separation technique based on density differences. Rejuvenation and reactivation of the spent catalyst was achieved by removing the major fouling metal (i.e. vanadium) and coke deposits from the catalyst by leaching and combustion (decoking) processes. Leaching was done prior to decoking. A reagent containing a mixture of oxalic acid and ferric nitrate in aqueous solution was used for the leaching of vanadium. Coke was removed by combustion using a gas mixture containing 5% oxygen in nitrogen under controlled temperature conditions. Up to 70% of the spent catalyst was reclaimed in the process with activity as high as 95% of fresh catalyst. Economic assessment of the process revealed that rejuvenation and reuse of the catalyst is feasible with an internal rate of return (IRR) of 20%.

The physical and chemical characteristics of the rejuvenated catalyst are compared with that of spent and fresh catalysts in Table 1. It is seen that the spent catalyst is fouled with carbon (20 wt.%) and vanadium (6.5 wt.%) deposition and its surface area and pore volume are, respectively, 62 and 86% lower than that of the fresh catalyst. Substantial improvements in the chemical and physical characteristics have occurred in the rejuvenation process. The rejuvenated catalyst contains no coke and its vanadium content is 80% lower than that of the spent catalyst. Vanadium distribution profile measurement by electron microprobe analysis showed that the 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 [20]. The surface area is increased from 98 to 240 m^2/g. A similar increase in catalyst pore volume is also noticed. HDS activity measurements showed that over 95% of the activity of the fresh catalyst was recovered by rejuvenation.

Several factors may contribute to the remarkable activity improvement achieved in the rejuvenation process. These include substantial increase in catalyst surface area and pore

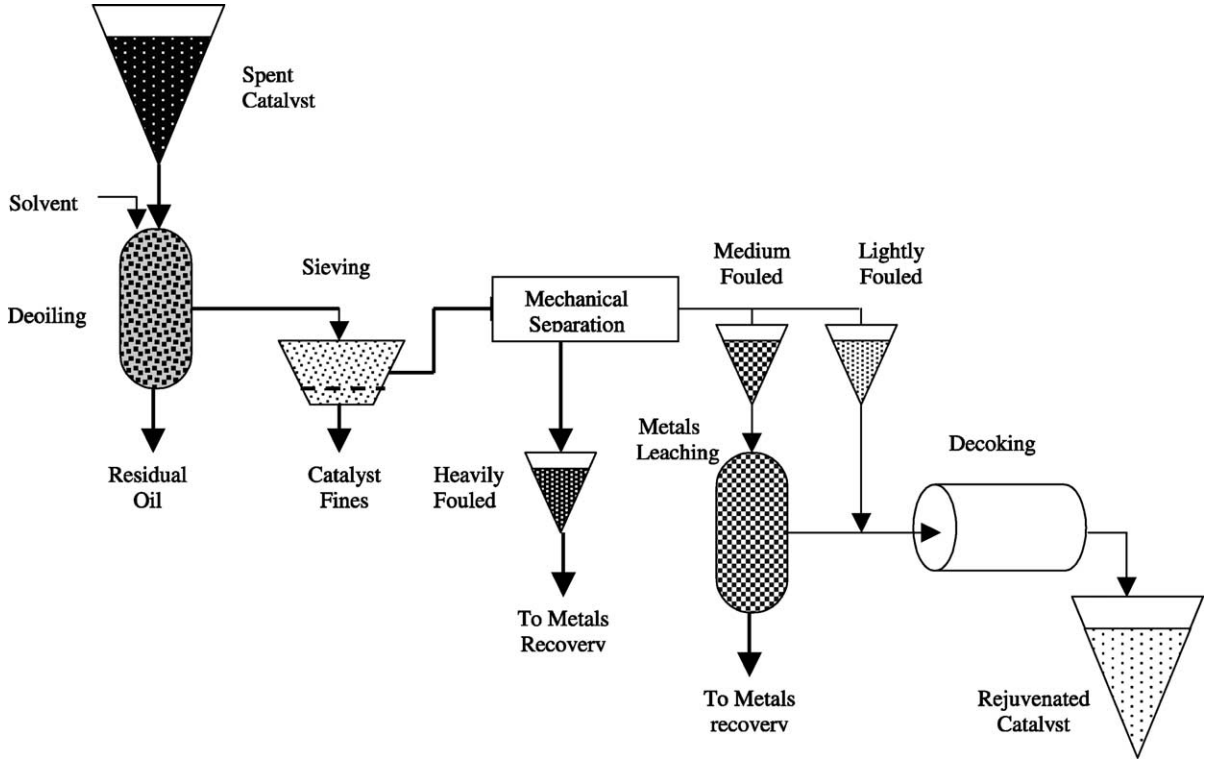

Fig. 1. Rejuvenation process flow diagram.

Table 1
Characteristics of fresh, spent and rejuvenated catalysts

Catalyst characteristics	Spent	Fresh	Rejuvenated
Chemical composition (wt.%)			
MoO_3	11.2	12.0	10.1
CoO	3.2	4.2	3.05
Ni	2.8	0.0	0.94
V	6.5	0.0	1.3
C	20.0	0.0	–
S	6.3	0.0	–
Fe	0.19	0.1	0.06
Na	0.50	0.2	0.35
Physical properties			
Surface area (m^2/g)	98	257	240
Bulk density (g/ml)	1.03	0.7	0.79
Side crushing strength (N/mm)	7.3	7.5	7.1
Pore volume (ml/g)	0.048	0.55	0.48
Pore size distribution (Å)			
<50	0.022	0.00	0.0
50–100	0.013	0.012	0.10
100–250	0.001	0.52	0.37
250–500	0.003	0.01	0.002
500–1000	0.001	0.0	0.000
1000–10000	0.008	0.01	0.008

volume as a result of the removal of foulant metals and coke from the pores and redistribution and dispersion of metals (Mo, Co, Ni and V) on the catalyst surface during the leaching process. In addition, part of the inactive cobalt and nickel atoms present in the tetrahedral sites of the alumina support as cobalt aluminate and nickel aluminate may be leached by the reagents and redistributed over the molybdate layer. Such close proximity of the Co and Ni promoters with molybdenum species would allow a better interaction between them and lead to the formation of precursors for active Co–Mo–S and Ni–MO–S phase structures in the final catalyst [21]. In addition, the redistributed and well-dispersed vanadium remaining in the catalyst can also promote HDS reaction.

5. Utilization of spent catalysts as raw materials to produce other valuable products

Utilization of spent catalysis as raw materials in the production of other valuable products is an attractive option from environmental and economical points of view. Spent fluid catalytic cracking (FCC) catalysts have been successfully utilized in cement production. In the USA, cement kilns process about 60,000 t per year of spent FCC catalysts [7]. No information is available on a similar application of spent hydroprocessing catalysts. The reuse of spent catalysts to form new catalyst compositions has been reported in a few studies. Gardner and Kidd [22] investigated the possibility of preparation of an active

hydrodesulfurization (HDS) catalyst composition from a spent hydrotreating catalysts by mixing them with alumina containing materials and shaping the mixture into compacted extrudates. In another study on the subject [23], decoked spent catalyst was ground and mixed with an unspecified additive and the resulting mixture was shaped to form particles of new hydroprocessing catalyst. High temperature sintering was used for pore enlargement.

Although the utilization of the spent catalysts in the preparation of fresh or new active catalyst composition will help to reduce the spent catalyst problem to some extent, it will not be able to solve the problem completely. All catalysts deactivate eventually to a point where further regeneration and recycling becomes uneconomical and they are discarded as wastes. Processes currently available for making spent catalysts non-leachable for safe disposal are very expensive and not cost-effective. The cost involved in the treatment of spent catalysts to make them non-leachable could be offset if the non-leachable material produced in the process were used in some other applications. Recently, a process for making highly stabilized non-leachable anorthite glass ceramic materials from spent hydrotreating catalysts has been reported by Sun et al. [24].

In our laboratory, we focused our attention on the development of a process to produce non-leachable materials of high compressive strength such as synthetic aggregates from spent hydroprocessing catalysts. The potential for the use of such synthetic aggregates in cement concrete production was also evaluated as part of the study. The chemical composition of spent catalyst and other raw materials used in the process are presented in Table 2.

The process involved mixing the spent catalyst in the form of a fine powder (particle size less than 180 μm) with clay, gatch, sand and water, shaping the wet mix into small balls of about 20 mm diameter, drying the balls at 110 °C for 12 h and then heating them at high temperature in the range 1150–1300 °C.

The compressive strength of the produced aggregate material was determined using an Instron Machine. The leaching behavior of the material was tested by the standard EPA procedure. Both the compressive strength and leachability of harmful metals (e.g. V and Mo) from the prepared aggregate materials showed a strong dependence on the firing tem-

Table 2
Chemical composition (wt.%) of spent catalyst and other raw materials

Chemical composition	Spent catalyst	Sand	Gatch	Clay
V_2O_5	13.0	–	–	–
MoO_3	5.4	–	–	–
NiO	5.5	–	–	–
SiO_2	–	90.6	79.8	33.8
Al_2O_3	37.6	4.8	6.6	7.9
Fe_2O_3	0.07	0.07	2.91	4.1
CaO	0.03	0.5	2.02	21
MgO	–	–	0.65	5.6
SO_4	1.5	0.35	1.72	0.6
K_2O	0.08	1.33	1.10	1.04
Na_2O	1.3	1.08	0.45	1.7
Loss on ignition	35.6	1.6	3.83	24

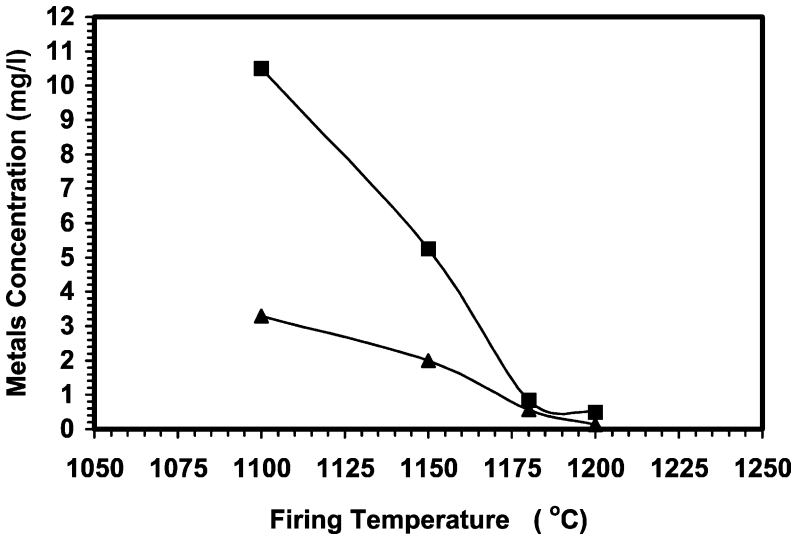

Fig. 2. Effect of firing temperature on metals leaching from the synthetic aggregate materials.

perature (Figs. 2 and 3). Synthetic aggregate materials with minimum leaching (<1 mg/l) and maximum compressive strength were produced when the firing temperature was around 1175 °C.

In order to test the possibility of using the synthetic aggregate materials produced in the process from spent catalysts, about 2 kg of the material was mixed with cement and sand and concrete cubes were prepared. The compressive strength of the concrete was tested

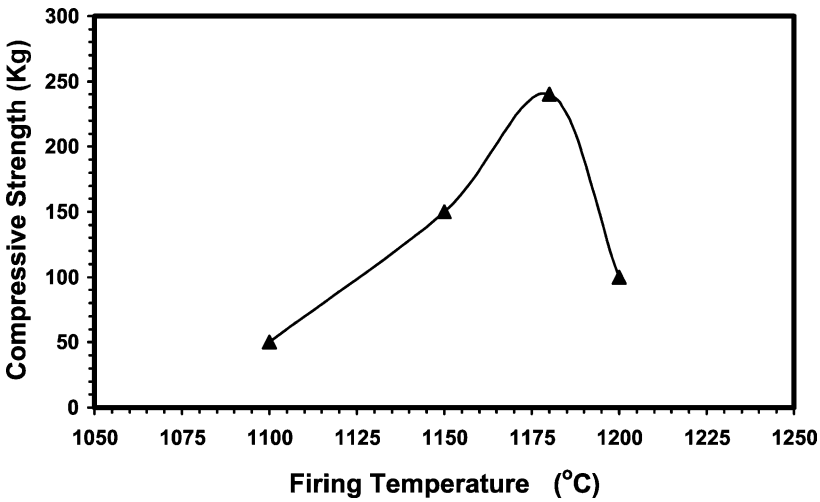

Fig. 3. Effect of firing temperature on compressive strength of the synthetic aggregate materials.

Table 3
Compressive strength of concrete cubes prepared from synthetic and natural aggregates

Aggregate source	Concrete density (g/cm^3)	Compressive strength (kg/cm^2)
Spent catalyst-based synthetic aggregate	2.52	461
Natural aggregate	2.79	485

after 7 days. For comparison, concrete cubes from a traditional natural aggregates were also prepared and tested.

The results presented in Table 3 reveal that the concrete prepared from the spent catalyst-based synthetic aggregate has a compressive strength of 461 kg/cm^2, while that of natural aggregate is 485 kg/cm^2. Both values are higher than the average compressive strength (300–400 kg/cm^2) required for reinforced concrete. These results clearly indicate that the spent catalyst-based synthetic aggregates are stable and non-leachable and they can be used in the construction industry for concrete production by incorporating in a cement matrix.

References

[1] Worldwide catalyst report: refining catalyst demand, J. Oil Gas (October) (2000) 64–66.
[2] M. Absi-Halabi, A. Stanislaus, H. Qabazard, Hydrocarbon Process. 76 (1997) 45–55.
[3] D. Rapaport, Hydrocarbon Process. 79 (2000) 11–22.
[4] E. Furimsky, Catal. Today 30 (1996) 537–668.
[5] T. Chang, J. Oil Gas (October) (1998) 79–84.
[6] D.L. Trimm, Appl. Catal. A: Gen. 212 (2001) 153–160.
[7] R.K. Clifford, Pet. Technol. Q. (Spring) (1997) 33–39.
[8] S. Shelly, Environ. Eng. World (March–April) (1995) 40.
[9] J.T. Schofield, Sealosafe process, in: Toxic and Hazardous Waste Disposal. Process for Stabilization/Solidification, vol. 1, Ann Arbor Science, Ann Arbor, MI, USA, 1979, pp. 297–319.
[10] D.L. Trimm, Stud. Surf. Sci. Catal. 53 (1990) 41–60.
[11] E. Furimsky, F.E. Massoth, Catal. Today 52 (1999) 381–495.
[12] C.H. Bartholomew, Catalyst deactivation in hydrotreating of residues. In: M. Obella, S.S. Shih (Eds.), Catalytic Hydroprocessing of Petroleum and Distillates, Marcel Dekker, New York, 1994, pp. 1–32.
[13] E. Furimsky, F.E. Massoth, Catal. Today 17 (1993) 537–668.
[14] M. Marafi, Studies on the deactivation and reactivation of spent hydroprocessing catalyst, Ph.D. thesis, The University of Aston in Birmingham, 1996.
[15] M. Marafi, A. Stanislaus, M. Absi-Halabi, Appl. Catal. B: Environ. 4 (1994) 19–27.
[16] M. Marafi, A. Stanislaus, Catal. Lett. 18 (1993) 141–151.
[17] A. Stanislaus, M. Halabi, F. Owaysi, M. Marafi, Studies on development of a process to rejuvenate spent residue hydroprocessing catalysts, Report no. 3394, Kuwait Institute for Scientific Research, Kuwait, 1990.
[18] A. Stanislaus, M. Marafi, M. Absi-Halabi, Appl. Catal. A: Gen. 105 (1993) 195–203.
[19] M. Marafi, E.K.T. Kam, A. Stanislaus, M. Absi-Halabi, Report no. 5051, Kuwait Institute for Scientific Research, Kuwait, 1997.
[20] A. Stanislaus, M. Marafi, M. Absi-Halabi, Residual oil hydrotreating catalyst rejuvenation by leaching of foulant metals: effect of metal leaching on catalyst characteristics and performance, in: M.L. Occelli, R. Chianelli (Eds.), Hydrotreating Technology for Pollution Control, Marcel Dekker, New York, 1996, pp. 327–336.
[21] H. Topsoe, B.S. Clausen, F.E. Massoth, Hydrotreating catalysis, in: J.R. Anderson, M. Boudart (Eds.), Catalysis Science and Technology, vol. 11, Springer, Berlin, 1996, pp. 1–310.
[22] L.E. Gardner, D.R. Kidd, US Patent no. 4,888,316 (1989).
[23] M. De Boer, US Patent no. 6,030,915 (2000).
[24] D.D. Sun, J.H. Tay, H.K. Cheong, D.L.K. Leung, G.R. Qian, J. Hazard. Mater. 87 (2001) 213–223.