TREATMENT OF USED CATALYZERS

CASE STUDY OF NIS REFINERY BELGRADE

Jovanić Predrag[1], Milica Vlahović[1], Sanja Martinović1,Goran Jakšić[2]

1. Institute for Technology of Nuclear and other Raw Mineral Materials, 86 Franchet d'Esperey St. Belgrade Serbia and Montenegro, e-mail: p.jovanic@itnms.ac.yu
2. NIS Refinery Belgrade, Pancevacki put bb, Belgrade, Serbia and Montenegro

ABSTRACT

Extensive environmental protection measures have been undertaken in all segments of Oil Industry Serbia. By introducing "waste" as a category of processing industry practically ceased to exist and all products of particular process must be processed to the environmentally acceptable level. The first phase of the project is the review of technologies used in the processing of spent catalysts as well as the balance of obtained products based on literature data and experience of other refineries. Until now, the emphasis in a spent catalyst processing was on metal extraction, while the other possibly useful products, first of all catalysts support, were considered as waste product of these technologies. Three-phase separation technology has been proposed as a treatment of spent catalysts: Oil phase is returned to refinery to be processed again, wastewater and extracted fluid are sent to recycling plant, while the solid ceramic residue is further processed. The aim of this research was to present the solutions based on the study of recycling solid waste derived from spent catalysts in respect to regulations and experiences of the countries with developed industry and experimentally obtained results. As a result of experimental research, technology of spent catalyst revalorization has been proposed.

INTRODUCTION

Spent catalysts present complex system composed of support, metal and elements of reactive system such as carbon, hydrocarbons, sulphur and hard metals. As the process progresses, catalysis become less efficient and have to be replaced with the fresh ones, which leads to the issue of spent catalysts treatment. Only small part of the catalysts could be regenerated *in-situ*, while the catalysts are still in the reactor, by oxidation of hydrocarbons, carbon and sulphur. There are five options for the spent catalyst treatment:

- Usage in the less demanding applications (processes)
- Regeneration *ex-situ* and their reusage
- Separation of metal and ceramic support
- Combustion in the cement kiln
- Landfill solution

The above sequence has been made from the aspect of ecological impact of spent catalysts manipulation; certainly, the most desirable application is their permanent usage in various processes, while the worst is their deposition in the land. The current technologies do not recommend regeneration of the catalysts with pores filled with metals. This kind of catalysts must be recycled.

In Serbia &Montenegro, as well as worldwide, government agencies for environmental protection are in charge of the spent catalysts problems. In the USA, regulations set by EPA (Environmental Protection Agency) in 1999, significantly reduce possibility of environmental accidents during the treatment and regeneration of spent catalysts from oil industry. According to the EPA, the spent catalysts are considered as "hazardous waste". Regenerated catalysts with precious metals and spent catalysts originating in processing of used oil or water-oil system and similar systems are not considered as hazardous wastes. Spent catalysts, which could be regenerated, are hazardous until the regeneration has been completed. EPA recommends this kind of spent catalysts treatment that includes recycling and regeneration, while there is a trend of prohibition of their land deposition. Recent analysis of EPA does not recommend usage of the cement kiln for spent catalysts combustion.

The of spent catalysts treatments in use in Europe are studied in the "Recommendation for management of spent catalysts", published by ESMA-Association of European Catalysts Producers. Regulations concerning transport of spent catalysts are crucial because no matter what will be done with the catalysts, they must be transported outside the plant as the hazardous wastes.

On the basis of available data, it is possible to generate several recommendations for protection of health and environment during the spent catalysts treatment. In order to secure the proper spent catalysts treatment, the facilities (technologies) production, storage, treatment, regeneration, inertion or dumping should: fully comply with relevant regulations,possess all necessary licenses, satisfy all existing technical standards of protection,manage materials according to the recommendations for hazardous waste, comply with ISO 14000.

SPENT CATALYSTS TREATMENT METHODOLOGY

Figure 1 shows the block-diagram of used oil treatment and the place of the spent catalyzers genereting during the process.

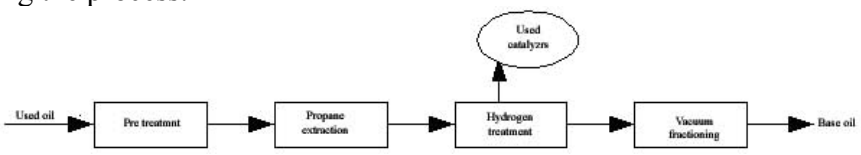

Figure 2. Schematic diagram of the NIS Refinery Belgrade used oil treatment proces

The refinery that generates the spent catalysts can provide the information's which are the basic data that can help users chose appropriate technology for spent catalyst treatment. The block-diagram, Figure 3, shows small decision making system [1] helpful in making decisions during

the analysis of spent catalysts treatment. The answer to each question has defined procedure for the spent catalyst treatment.

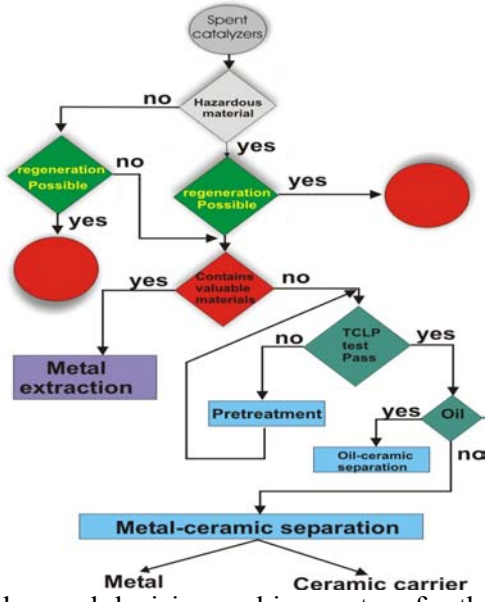

Figure 3 Block diagram of the saml decision making system for the spent catalyzers treatment

As already mentioned, catalyst lose their activity with the filling of the existing pores with metal, sulphur and carbon. When the catalyst pores are not filled with metal particles, the most part of its activity can be recovered through the controlled combustion of sulphur and carbon by the flow of air and oxygen. Regeneration could be performed *in-situ* in the refinery reactor or *ex-situ* in the commercial regeneration facilities. The main task of regeneration is burning of contaminants and recovery of catalysts as close as possible to the primary level of activity and performance. Regeneration can change physical characteristics of catalysts; for example, pores could become smaller or completely closed, active area could become smaller to, metals could migrate, while catalyst could become unacceptable. Due to increasing environmental protection requirements and stricter legislation, the treatment of spent catalyst becomes more and more important. There are two methods for solving of the problem: hydrometallurgical and pyrometallurgical. They can be distinguished as two options: separation of less valuable metals and separation of more valuable metals.

Table 2. Constituents absorbed by catalyst from the crude oil or from the processing equipment

5 - 30 %	hydrocarbons, C i H_2O
0 - 4 %	S
0 - 2 %	Fe, usually as FeS
0 - 8 %	V, usually as Vanadium sulphide

These constituents refer to catalysts contamination that is hard to remove from the system.

RESULTS

The basic assumption of the ITNMS project is that there is no waste but only more or less reusable secondary materials. Spent catalysts belong to the group of potential ceramic raw materials. This point of view is based on the level of utilization of the metal, which has been the

only way of spent catalyst treatment for years. The level of the technology efficiency was the amount of extracted metal. All technological processes in use today could yield successful results only if the content of metal is not less than 5 vol.% of metal. The smaller amounts of metal are not worth of treating so the storage is still the only feasible solution in those cases. The existing legislation treats storage of any hazardous material as an ecological treat and prohibits its landfill deposition without previous conversion into the acceptable ecological form. Also, it was the starting point in analyzing possibilities of treatments of spent catalysts originating from NIS Refinery Belgrade. Figure 1 shows the scheme of the process.

Waste materials are treated as raw materials for appropriate processes with regard to energetical feasibility and impact on environment. Recycled raw materials or products are obtained; even if there is need for storage of such materials, there will be no pollution involved. According to the above scheme, investigation of three technological treatments have been carried out with the aim to convert the spent catalyst from Oil Industry Belgrade into the acceptable ecological form.

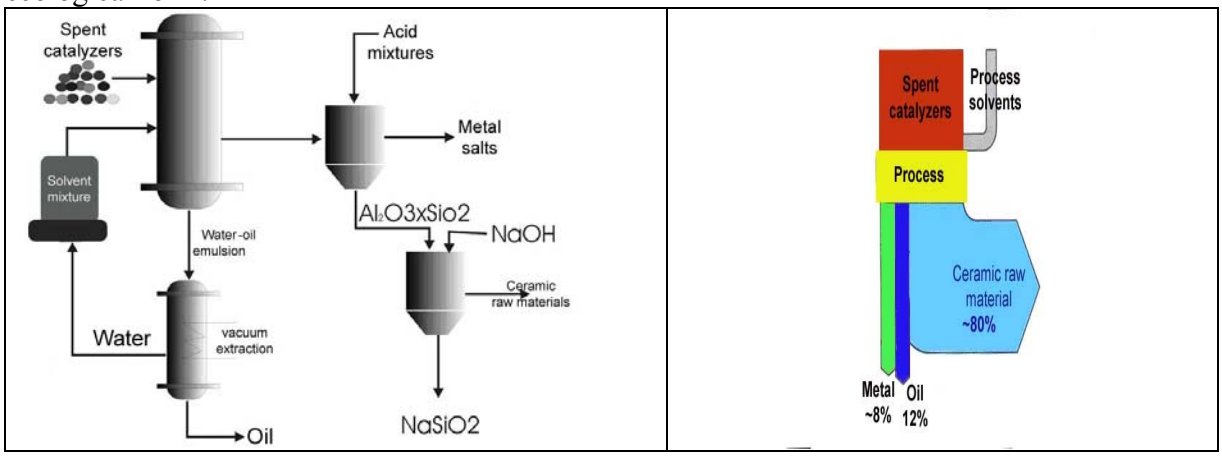

Figure 2. Scheme of oil and other organic components separation from the catalysts.

The problem could be also observed from the aspect of necessity to eliminate the adsorbed oil and present metal from the catalysis. Table 1. Shows the analysis of the spent catalysts obtaining from the NIS Refinery Belgrade.

Table 1. Basic characteristics of the catalyst

Catalysts type	Company	LOI	C (%wt)		S (%wt)		S.A.
		(%wt)	P.R	N.R	P.R.	N.R	(m2/g)
LB02	EUROCAT	23.1	23.1	0.27	5.3	0.5	165
LB02	EUROCAT	36.8	24.6	0.1	4.2	0.3	165
LB02	EUROCAT	43.6	34.9	0.3	4.1	0.4	178

Additional analysis of the present metals was done by appliance of AAS (Atomic Absorption Spectrometer) (Perkin Elmer 703), and the results are shown in the Table 2.

Table 2. Content of metal in the LB 02 catalyst

Sample	Ni	Mo	Co	Mg	V	Cu
	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
LB02	1.56	4.16	0.003	0.080	0.002	-

The content of metal is on the verge of the feasibility level, so the technologies of hydrometallurgical extraction are not justified in this case. During the research, modified technology of the metal extraction and catalyst cleaning, based on the patented technology, has been tested.

Spent catalyst is first treated with mixture of organic solvent in order to remove oil and light petroleum fractions. Thus treated catalysts are moved to the reactor where the metals from the catalysts surface are removed by the acid treatment. Removing of metal in the acid is performed at higher temperatures. After the acid treatment, cleaned support of catalyst is treated with NaOH, with the aim of SiO_2 reducing. Obtained Al_2O_3 is ecologically acceptable [2,3] and could be either stored on the land or thermally treated in order to obtain more suitable form for further processing. The solution/mixture of oil and organic solvents goes to the vacuum distillating column where the oil is separated from the other solvents, so the later can return to the process.

Oil can be further processed. The efficiency of oil separation by this technology is ~12 %, 8 % of metal and 80 % of seramic carrier.

CONCLUSION

According to the results presented in this paper an industrial plant was built for the treatmnt of the spent catalyzers from the used oil refinery plant. Capacity of this plant is 20 tons per month. According to this plant could handle all the oily materials containing the unorganic matrix, which is the first step in the land remediation process.

ACKNOWLEDGEMENTS

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LITERATURE

1. P Jovanic et all., Spent catalyzers treatment with water soluble surface active materials, Report number 012/099 MNTR, Belgrade 2002 (in Serbian)
2. K.Simonović, V.B. Mišković, D Kičević, **P.Jovanić**, Electrophoretic deposition of thin alumina films from water suspension, **Colloids and Surfaces A**, vol 209, pp.47-55 2002
3. M.Lazić, K . Simović, V.B. Mišković-Stanković , **P. Jovanić** : The inflience of bath temperature on electrophoretic deposition of alumina of steel. 2 nd internacional Conference of the Chemucal Societies of the South-Eastern European Countries on Chemical Sciences for Sustainable Development, Halkiidiki, Greece, Book of Abstract, Vol. II, 2000.