European Catalysts Manufacturers Association

A sector group of Cefic

GUIDELINES FOR THE MANAGEMENT OF SPENT CATALYSTS

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Responsible Care

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FOREWORD

Founded in 1983, the ***European Catalysts Manufacturers Association***, ECMA (under the aegis of CEFIC, European Chemical Industry Council) addresses the health, safety and environmental issues surrounding the manufacture, distribution and use of catalysts and the management of spent catalysts.

To help promote Responsible Care and Product Stewardship, and aware of the concerns the public and regulators have over waste disposal, the members of ECMA have produced this guide to promote the responsible management of spent catalysts. It is primarily aimed at users of catalysts and at all those who have responsibility for the management of catalysts after their use. It is however, implicit that each catalyst user has a unique obligation to determine their regulatory obligations in accordance with their local requirements.

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INTRODUCTION

The world of catalysts is diverse, including homogeneous and heterogeneous catalysts, catalyst precursors as well as final catalysts, catalysts which may be treated with chemical activators and reagents, involving permanent and non-permanent transformations. These guidelines for the management of spent catalysts are typically applicable to heterogeneous catalysts used in the chemicals or oil industries.

These catalysts gradually lose their catalytic activity, usually through structural changes, poisoning, or the deposition of extraneous material. A catalyst charge is spent when it no longer exhibits the necessary activity and/or specificity required by the user. Similarly, absorbents and other materials used for the purification of fluid streams are spent when they are no longer able to remove the particular impurities from the fluid stream to the specified concentration.

A catalyst, or absorbent, which can no longer perform its original duty, is referred to as “spent catalyst”. Depending primarily upon the chemical and structural changes in the catalyst during use, the user is faced with a number of options for dealing with the spent material. These may include:

- Regeneration and reuse of the material.

- Use of the material in another process.

- Recovery of some or all of the components in the material.

- Disposal of the material.

If structural changes or severe poisoning effects have occurred within the catalyst during use such changes are likely to be irreversible and it is unlikely that the catalyst can be regenerated for reuse. If however the catalyst has been deactivated by surface contamination it may be possible to regenerate the catalyst. Spent catalyst that cannot be regenerated for reuse may be able to be used for a different catalytic or chemical process, or processed by the metals recovery industry, or have to be disposed of.

Regeneration and Reuse of the Material

If a catalyst, or absorbent, has been deactivated by the surface deposition of extraneous matter or by the incorporation of a removable poison it may be possible to regenerate the catalyst and restore catalytic activity. Regeneration is carried out by removing, usually by burning off, surface coatings and/or absorbed species.

Regeneration, if technically feasible, is the environmentally and economically preferred option for dealing with spent catalysts as it facilitates extended use of the catalyst, minimises the use of new raw materials, and reduces the need for ultimate recovery or disposal.

Use of the Spent Material in another Process

Once a catalyst or an absorbent is spent it no longer exhibits the necessary activity and/or specificity required for use in the original process, but it may have properties or characteristics that enable it to be used for some other chemical or catalytic reaction. While this is a relatively rare method of reusing spent catalysts such a possibility should be borne in mind when considering the composition and properties of a spent catalyst or absorbent.

Recovery of Components in the Material

Significant structural changes or severe poisoning effects that occur within the catalyst during use are normally irreversible and prevent the catalyst from being regenerated for reuse. In this situation the catalyst must be discharged from the operating unit and may be sent for recovery (reclamation) of some or all of its constituents, or used in some other processes, such as cement manufacture in the case of fluid cracking catalysts.

Recycling of spent catalysts in this way, with subsequent recovery of constituent components, is a widespread method of dealing with spent catalysts. Many catalysts contain significant amounts of metal-based constituents which can be recovered by a variety of different treatment methods. Recovery offers an environmentally sound alternative to other disposal methods, since the recovery of metals not only reduces the amount of waste for disposal but also conserves natural resources. There may also be an economic benefit to the user in ensuring that metallic components in the catalyst are recovered.

Disposal of the Material

Disposal of a spent catalyst or absorbent by such a method as landfill is always the environmentally least preferred option, and is an option that is subject to specific, stringent controls. Landfill does not remove or destroy any hazardous materials which, if risks are not properly managed, may pose long-term health and environmental hazards, and be affected by future regulatory changes.

The generator of spent catalyst will need to make a choice from the above general methods when considering how to deal with a spent catalyst; and there are many factors to consider in making such a choice.

CHARACTERISATION OF THE SPENT CATALYST

The catalyst user should, while the catalyst is still in operation, consider how the spent catalyst will be dealt with; paying particular attention to the precautions that will need to be taken and the prior arrangements that will need to be made. While the catalyst is still in operation, or remains in the plant, it may not be possible to take samples but the user will still be able to collect essential information and define the discharge procedures to be used.

The discharge procedures might be designed, for example, to purge hydrocarbons or other process materials, or obtain the spent catalyst in an oxidised or reduced form, or in a wet or dry state, etc. In this way it can be ensured that the spent catalyst is obtained in the necessary form for further processing.

Catalyst Composition

The composition of the spent catalyst determines to a large extent the type of recovery process that may be used; and which companies may be able to process the spent catalyst.

Information on the composition of the original, new catalyst is usually available from the catalyst supplier. This information, combined with information on contaminants arising from the process feedstock, and plant data on the likely physical and chemical changes experienced by the catalyst during loading, commissioning, operation and discharge, will enable the catalyst user to prepare a preliminary description of the spent catalyst. Those companies capable of processing the catalyst may also be able to provide analysis and advice on composition.

Hazardous Properties

Information about any hazardous properties of the original, new catalyst is available from the catalyst supplier's Safety Data Sheet. It is important to note however that that Safety Data Sheet applies only to the new, unused catalyst; and does not cover the spent catalyst, which may have substantially different properties or hazards from the new catalyst.

The catalyst user must therefore be aware of the potentially changed properties or composition of the spent catalyst in order to give an accurate description of the material. Safety documentation should be prepared for the spent catalysts; and that documentation should contain the information necessary to determine how the spent catalyst is to be safely and correctly handled, classified, packaged, labeled, stored, transported and treated/processed.

Some considerations that can be resolved before the spent catalyst is discharged might include:

- What were the composition and properties of the original catalyst?
- How will it be treated prior to and during discharge? What are the options at both of these stages to ensure that the discharged, spent catalyst is obtained in the best state for further handling or processing?
- Has the catalyst been contaminated in use? If so, by what and to what degree?
- What are the expected chemical and physical characteristics of the discharged spent catalyst?
- Will the spent catalyst have any potentially hazardous properties?
- How will the spent catalyst be classified, packaged, labeled, stored and transported after discharge?

Once the spent catalyst has been discharged it should be analysed and tested to provide the definitive information for safety documentation, for the regulatory authorities and for the companies involved in the transport and processing of the spent catalyst.

IDENTIFICATION OF PROCESSING OPTIONS

Once the spent catalyst has been discharged from the operating plant and characterised then processing options can be confirmed.

Reuse

When considering the possibility of off-site regeneration of spent catalysts, such as for spent hydrotreating catalysts from refineries, it is usual to first to check the technical feasibility of regeneration. This is usually carried out by a potential regeneration company using a combination of a laboratory-scale trial regeneration of the material together with appropriate chemical and physical analyses. This evaluation is likely to provide the basis of how the catalyst may, or may not, be regenerated and to which specifications.

Catalysts that can be regenerated are usually capable of use through several operation/regeneration cycles. It is important to note that in the case of regeneration of spent catalyst, the product often does not change ownership, and that its original economic value is fully recovered and exploitable.

Discarding of the Material

Many spent catalysts contain sufficient concentrations of metals, or other materials, for those components to be economically worth recovering; and the recovery of metals from spent catalysts has been well established for many years. Typically, the catalyst user may work either with a trader or directly with a reclaimer to facilitate this operation.

The supplier of the new catalyst or a catalyst service provider may be able to provide a list of such companies, or offer such a service as part of a package.

The choice of the catalyst user, either to deal directly with the reclaimer, or work through a trader, will depend on a number of factors relating to the actual situation.

Once a possible recovery facility has been identified, it is recommended that the spent catalyst generator considers such matters as:

- Regulatory position, including any consent/notification requirements for any transfrontier movements.
- Location of recovery facility.
- Permit situation for catalyst storage and processing.
- Processor’s previous experience with the specific catalyst type to be processed.
- Acceptance limits for critical impurities or properties.
- Description of treatment method, including identification of products and waste disposal methods.
- Point at which ownership transfers from the user to the processor or trader.
- Packaging requirements.
- Documentation requirements.
- Transport arrangements.
- Form of Certificate of Recycling/Recovery.

It may be advisable, before undertaking such processing of spent catalyst, for the generator/owner of the spent catalyst to visit the processing company in order to make an inspection or audit of the facility, verify the above information, and to obtain a firsthand impression of the facility.

REGULATORY CONSIDERATIONS

Introduction

The regeneration (off-site), recovery, or disposal of spent catalysts are subject to national and international regulations. These regulations and their interpretation evolve regularly, and particularly so at the current time. The guidance provided by the members of ECMA is intended to draw attention to the many different factors which should be considered, and list the major European and international regulations. Each catalyst user has a unique obligation to determine their regulatory obligations in accordance with their local requirements at the time.

Before consigning a spent catalyst to a reprocessing facility it is likely to be necessary for the generator/owner to have resolved a number of issues including:

- Which regulations apply from the point of discharging the spent catalyst from the operating plant to the transport of the material to the processor, regenerator, reclaimer or disposer of the spent catalyst?
- Which permits, licenses or documents are required to cover the packaging, labeling, transport and treatment of the spent catalyst?
- What is the chain of ownership and responsibility from the discharge of the spent catalyst to its ultimate treatment, destruction or disposal?
- What information has to be supplied to regulatory authorities and by whom?

If spent catalyst is being sent for regeneration and the ownership of the catalyst does not change then some national authorities do not consider the material as a waste. In such a situation the regulations pertaining to the transport/transfer of wastes do not apply. If, however, the generator of the spent catalyst consigns a spent catalyst to a recovery or disposal facility then the spent catalyst will be classified as a waste (Waste Framework Directive EC/2008/98: Art. 3.1 *"any substance or object which the holder discards or intends or is required to discard"*).

Since the definition of "waste" and "hazardous waste" can give rise to considerable discussion and different interpretations or understandings between different authorities, it may be necessary for the owner of a spent catalyst to obtain a clear understanding of the requirements of the various national or international authorities who may have jurisdiction over the spent catalyst while it is in transit through or being received in any particular country. In this case, there should also be a general understanding of which documents and permits will be required, within which timeframe, when the spent catalyst is sent for processing.

Within the European Union, the national regulations, implementing the EU Waste Framework Directive, will apply and must be observed.

Transboundary movement of waste

Treatment or disposal of spent catalysts will often involve a transboundary (international) movement, and in this context it is important to be aware of any further regulations covering the movement of waste materials between countries.

The Basel Convention (22 March 1989) describes procedures which must be followed in making transboundary movements of hazardous waste destined for reuse, recycling or recovery operations or disposal. The Basel Convention applies in many countries inside and outside Europe.

Movement between countries where only one country has ratified the Basel Convention is prohibited without the existence of special bilateral or multilateral agreements.

The OECD Decision of 14 June 2001, N° C(2001)107 final as amended, which is in accordance with the provisions of the Basel Convention, applies to transboundary movements of waste within the OECD area. It covers both hazardous and non-hazardous wastes, but only when they are destined for recovery operations.

It categorises waste in two different lists; green and amber.

- The green list covers wastes that present low risk for human health and the environment, and therefore are subject only to the controls normally applied in commercial transactions.
- The amber list covers wastes presenting sufficient risk to justify their control, and for which prior notification of the proposed movement is required to authorities in all concerned countries (those of export, transit and import). A tracking document is also required for the movements of the waste. The transport can take place as soon as written consent is given, or after an objection period has passed, if no objections have been raised (tacit consent).

Within the EU, the international transport of waste is covered by Regulation (EEC) N° 1013/2006 of 14 June 2006 on shipments of waste. This EU regulation implements the above mentioned international agreements.

Most types of spent catalyst are listed on the OECD green list, some on the amber list. However, a green list spent catalyst must be treated as amber list if contaminated with other materials which increase the risks sufficiently to meet the criteria for the amber list, or which prevent recovery in an environmentally sound manner. Also OECD member countries may classify wastes differently from the OECD lists if required by their national legislation or according to their national testing procedures.

Important annexes (lists) to the EC Regulations are regularly revised by the EC Commission.

In the event of doubt on the correct categorisation or classification of “wastes” it is recommended that the local regulatory authorities are consulted with respect to their requirements.

MAKING THE CHOICE OF TREATMENT AND FINALISING ARRANGEMENTS

The final selection of a regeneration, recovery or disposal partner should only be taken after consideration of the aspects discussed above.

The geographical location of the facility may need consideration with respect to OECD and related international legislation to control transfrontier shipments of wastes.

Clearly state in the contract who is responsible during the different stages of the movement of the spent catalyst, from the catalyst user's plant through to the regeneration, recovery or disposal of the material at the processing facility.

On discharge of the spent catalyst from the user's plant and prior to shipment for processing, check that the preliminary characterisation of the spent catalyst is accurate or whether it needs to be modified. In the event of modification, does that modification have any effect on the proposed regeneration or recovery arrangements?

The contractual parties should also agree the course of action to be followed in the event that the catalyst cannot be regenerated, recovered or disposed of in the intended manner, e.g. due to regulatory authority objections or to the material not conforming to the original description or specification.

It should also be clear which party is responsible for the production and submission of the various documents and notifications required by the regulatory authorities.

If pre-shipment samples of the spent catalyst are required, then this should be specified from the start of the considerations on how to process the spent catalyst.

After the regeneration, recovery or disposal of the spent catalyst is complete, the catalyst user should check that processing was carried out as planned and that appropriate documentary evidence of this is obtained.

WASTE REGULATORY REFERENCES

UNEP ***Basel Convention*** on the Control of Transboundary Movements of Hazardous Wastes and their Disposal - UNEP/IG.80.3 - 22 March 1989
http://www.basel.int/TheConvention/Overview/tabid/1271/Default.aspx

OECD - Decision of the Council concerning the ***Control of Transboundary Movements of Wastes*** Destined for Recovery Operations, No. C(2001)107 final as amended (Amended on 28 February 2002 - C(2001)107/ADD1, 9 March 2004 - C(2004)20, 2 December 2005 - C(2005)141, 4 December 2008 - C(2008)156)
14 June 2001
http://www.oecd.org/document/52/0,3746,en_2649_34395_2674996_1_1_1_1,00.html

DIRECTIVE 2008/98/EC on waste and repealing certain Directives (***Waste Framework Directive***)
19 November 2008
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:312:0003:0030:EN:PDF

REGULATION (EC) No 1013/2006 on ***shipments of waste***
14 June 2006
http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:190:0001:0098:EN:PDF

DECISION 2000/532/EC establishing a ***list of wastes***
3 May 2000
http://eur-lex.europa.eu/LexUriServ/site/en/consleg/2000/D/02000D0532-20020101-en.pdf