Recycling of precious metal catalysts

A look at the best available technologies for efficient and environmentally sound recycling of complex spent catalysts used in both oil refining and petrochemical processes

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Precious metal catalysts are crucial for many technical syntheses. The main application fields in oil refining are catalytic reforming, isomerisation and hydrocracking. Such precious metal-bearing catalysts are also used in bulk and speciality chemicals productions such as vinyl acetate monomer (VAM), purified terephtalic acid (PTA) and many hydrogenation processes. The noble metals involved are mainly platinum (Pt) and palladium (Pd), but also the other platinum group metals (PGM) ruthenium (Ru), iridium (Ir) and rhodium (Rh), as well as gold (Au) and silver (Ag), either alone or in combination. Often, other metals (for example, Sn, Pb, Ni, Co, Ge) are used as promoters. All these metals are coated on various carriers such as alumina, silica, zeolites and carbon.

Due to the high value of precious metals, the recycling of the spent catalyst at the end of its useful life is crucial for the overall economic performance of a catalytic process. Refining companies specialising in precious metals recycling have developed suitable technologies for the efficient reclaiming of these valuable metals. However, selecting the right recovery process and recycling company for a specific spent catalyst is not easy. Focus is usually on economical considerations – the total cost to be paid and the amount of metals finally returned from the recycling chain. In this context, the reliability and accuracy of the weighing and sampling preparation is crucial, since the analytical metals content obtained on the retained sample is the basis for all further calculations. Along with the economical questions, the environmental issues must not be neglected:

— What environmental, health and safety (EHS) risks arise in a certain recycling chain?

— What liabilities are the spent generator exposed to?

— How secure can the spent generator be about the technical, commercial and environmental performance of the selected refiner?

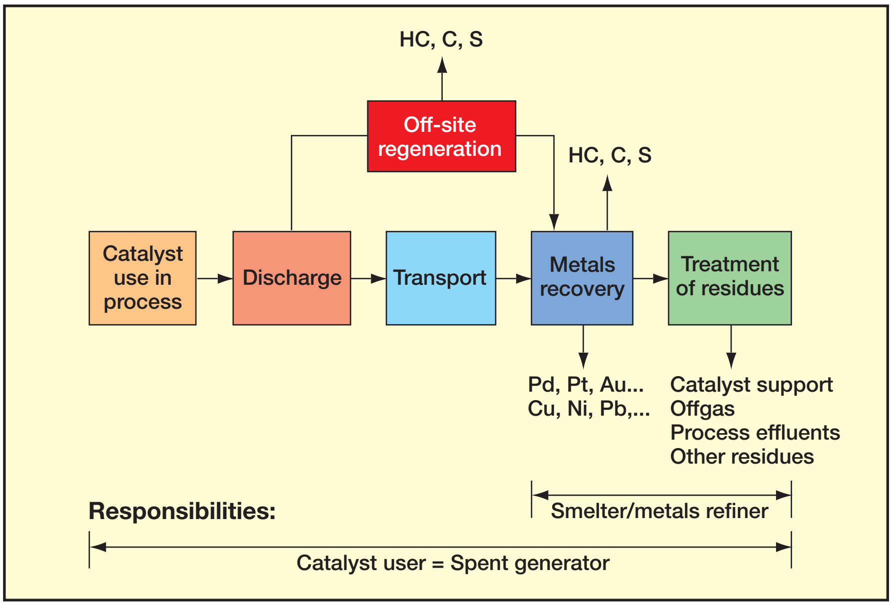

Figure 1 *Recycling chain and responsibilities – two options*

Besides their valuable content of precious metals (Pt, Pd, Au, and so on), spent catalysts also contain a complex mix of different substances, such as:

— Catalytic base metals and promoters: Sn, Pb, Ni, Co, and so forth

— Fe, Ni, Cr from process corrosion of reactor walls and tubes

— Hazardous elements by way of contamination through the feed/crude oil (As, Hg and more)

— Halogens (Cl, F, and so on) such as found in isomerisation catalysts

— Carbon (for example, high coked "heel" CCR catalysts) and hydrocarbon contamination from the catalytic process.

In one way or another, the recycling chain (Figure 1) has to cope with these complex mixtures. Just reclaiming the valuable metals is not sufficient; the whole recovery chain has to be evaluated for its environmental soundness.

The generator of a spent catalyst has to ensure that all the operators involved in the recycling chain are acting in an EHS-compliant way when treating the spent catalyst. This responsibility is related to individual regulations in specific countries, to the Basel liability protocol as well as to the principles of responsible care, to which the chemical and oil-refining industry have committed themselves.

Whether the spent catalyst is sent for "off-site regeneration" or not (prior to shipping to a precious metals refinery) may render the whole recycling loop more difficult to monitor. It might be more appropriate to consider a one-stop treatment at a precious metals refiner, taking care of the whole spent package in an environmentally sound way.

Metals refining

When it comes to sending out precious metal-bearing spent catalysts on a "soluble" carrier (typically a γ-Al_2O_3-carrier, which is soluble in caustic or sulphuric acid) for recovery, the

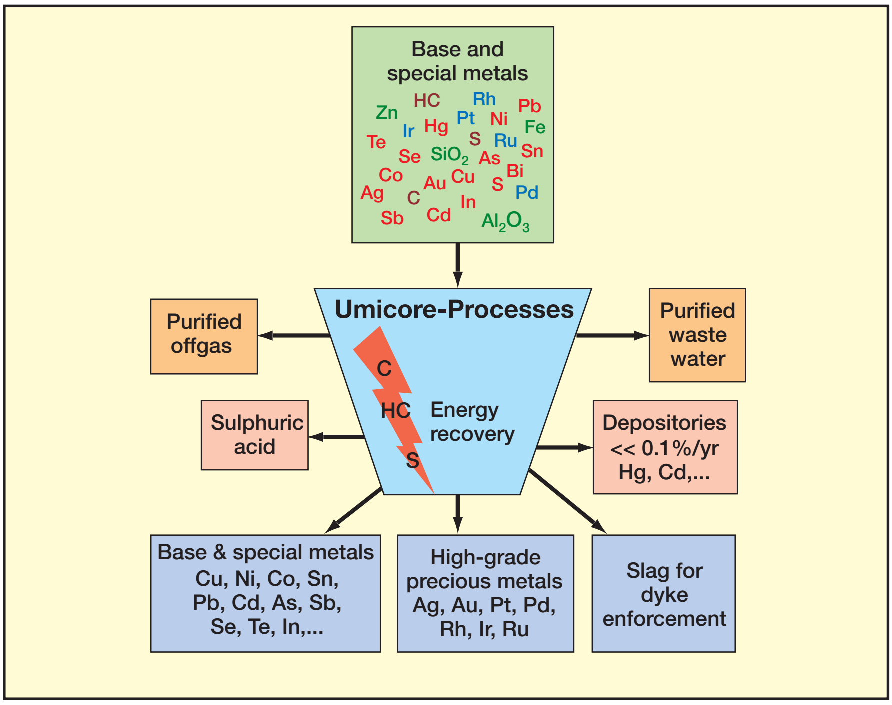

***Figure 2** Disintegration and recycling of complex metals containing wastes in a state-of-the-art precious metals smelter and refinery*

generator basically has the choice between a pyro-metallurgical or a hydro-metallurgical recovery process, the former being primarily a smelting, the latter being a wet chemical process. While a hydro-metallurgical process also offers rhenium-recovery (Re is lost with the slags in a smelter), the pyro-metallurgical process usually has a broader range of applications, such as the recovery of spent catalysts on insoluble carriers (for example, carbon or zeolites based) as well as – for certain larger, modern smelters – a high level of tolerance for contaminants (carbon, hydrocarbons, sulphur, nuisance elements, fines, and so on).

As a result, more and more soluble catalysts are finding their way into larger smelters, offering an all-in-one solution for the "untreated" spent and, equally importantly, putting all environmental stakes in the same location.

At the Umicore Hoboken plant located near Antwerp in Belgium, the untreated spent catalyst as well as numerous recycling materials (for example, spent automotive catalysts and precious metal-bearing electronic scrap) are fed into a large 250 000 MT/yr smelter, followed by separation into different process streams. When it comes to the spent precious metal catalysts, any materials are disintegrated into single elements that find their way through the process (Figure 2). Even the bulk carrier materials (alumina, silica), which are going into the slag, are turned into useful products for different applications such as dyke reinforcements or other specific construction materials.

Process gas treatment generates sulphuric acid as a by-product, the caloric value of combustibles like carbon or sulphur is used as fuel, off-gases are cleaned, process waters are sent to a water-treatment plant, making the whole plant not only a 100 per cent materials-recovery unit but also a nearly zero-waste facility when it comes to the overall environment.

The newly built smelter located at the Hoboken plant includes a state-of-the-art periphery (for example, off-gas- and water-treatment plants) and a new precious metals refinery. Figure 3 shows the principle of the flow sheet.

Environmental liabilities

Finding the right balance between economical and ecological performance is crucial when dealing with all kinds of raw materials coming from various origins. To ensure a long-term commitment towards suppliers and people, EHS should have high priority in the recycling of spent catalyst.

At the Hoboken plant, an environmental management system has been implemented in accordance with ISO 14001 and in close connection with the quality system (certified against ISO 9001). The plant has also been successfully audited by several large, international oil-refining companies.

The environmental performance of the plant is continuously monitored by Umicore and by the authorities. This is reported to the Flemish authorities in detail and to the public in an annual environmental report. A whole range of measures is in place to prevent dust emission: dust-free emptying of the

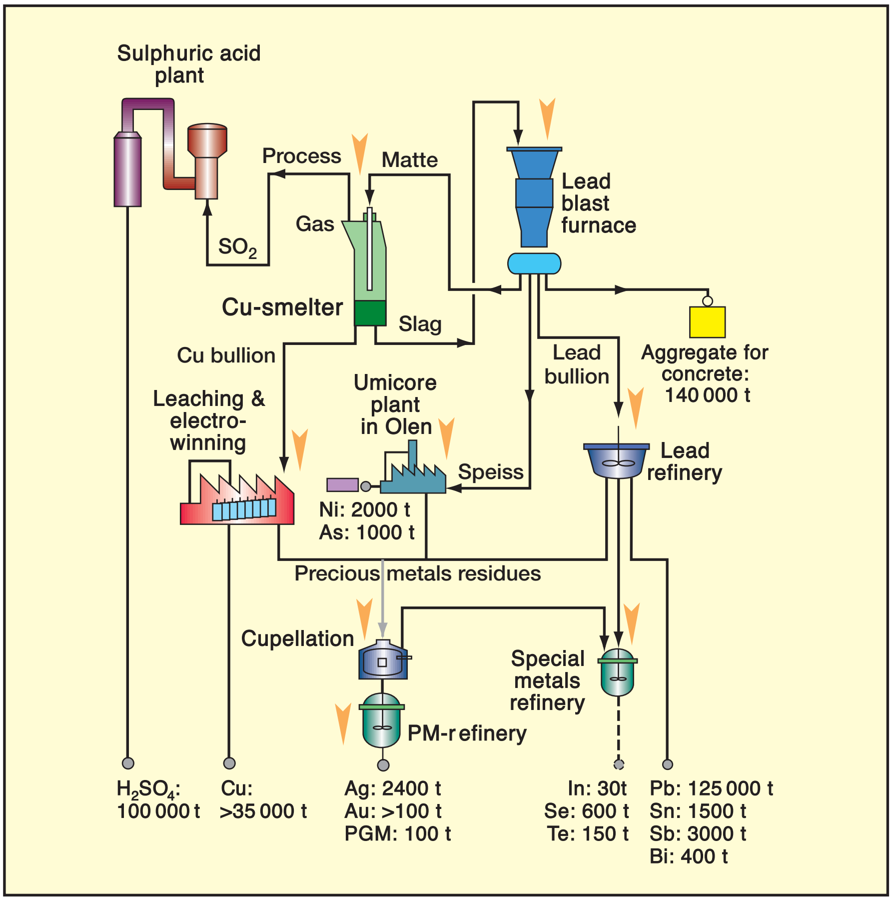

***Figure 3** Umicore's smelter and refinery*

shipped drums or big bags, dust-free sampling procedures, storage of the spent catalysts in containers inside a warehouse, emptying of the containers under aspiration, transport in covered belt systems and more. Besides their environmental importance, these installations prevent any loss of precious metals with the dust fraction, which further improves sampling accuracy and metal yields. Process gases from the smelter are cooled with energy recovery and cleaned with an electrofilter and by quenching with water injection. The SO_2 of the gases is transformed to sulphuric acid in the "contact" plant – the gas treatment and contact process act as a "perfect filter".

All process waters are collected and treated in a physico-chemical water-treatment plant. About 75 per cent of the sludge from this water-treatment plant is returned to the smelter. From the incoming water, 70 per cent is reused in the plant for sprinkling and cooling. The metal content of the effluent into the river Schelde is significantly lower than Flemish standards.

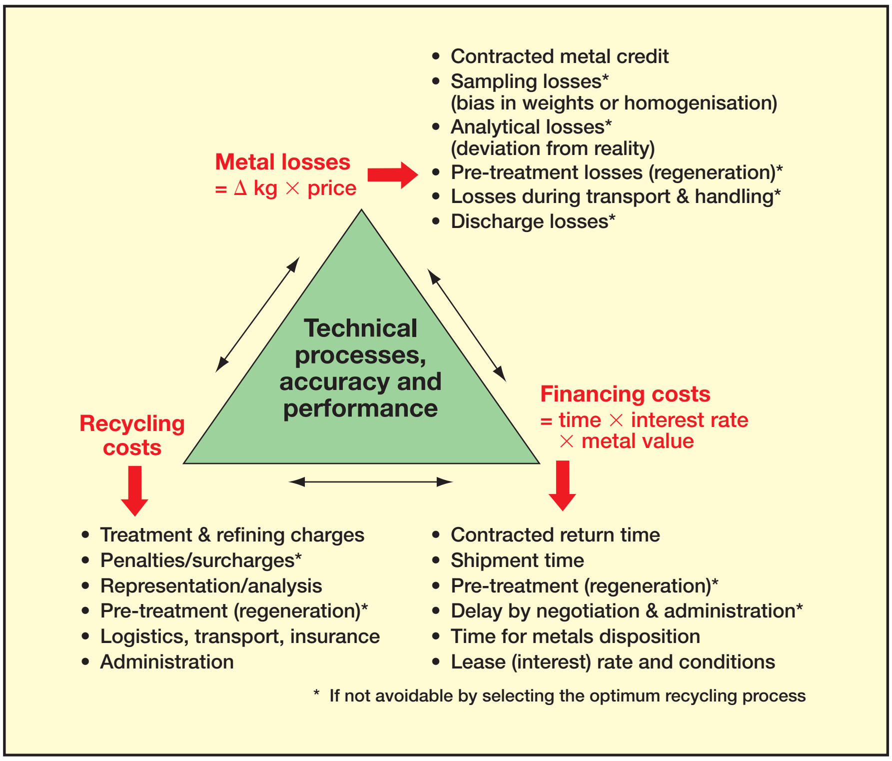

Figure 4 *Economic evaluation of a catalyst recycling job*

Economic impact

Determining the true bottom profitability of a spent catalyst-recycling job is not easy. It requires both experience and a complex calculation that has to consider not only costs but also the time of the precious metals return, as well as the total metal yield of the selected recycling chain. Figure 4 shows the main factors and interdependencies. It becomes obvious that not only the final refining step but also other parts of the selected recycling chain, such as off-site regeneration, have to be considered.

Compared to the intrinsic value of a spent precious metals catalyst, especially for Pt-spent, the reclamation costs in most cases are only a small part. Taking risks or uncertainties in the performance of the recycling chain could easily offset the recycling cost. In addition, the recycling cost could carry a hidden cost in case of inaccurate sampling. Hence, a bottom-line cost calculation is to be balanced against the general expertise, professionalism and financial soundness of the catalyst recycler as well as against the transparency and EHS compliance of the entire recycling chain.

Weighing and sampling

One of the most important economical impacts is how to determine the true precious metal content of a spent catalyst. Any 2 per cent deviation during the catalyst handling, weighing and/or sampling logically corresponds with a 2 per cent deviation in the precious metal credit! For a typical reforming or isomerisation catalyst with a Pt content of about 0.3 per cent, at current Pt prices of around US$800/troz, a 2 per cent deviation would result in a discrepancy of US$1500/Mton of spent or – for a 50 ton lot – US$75 000 in total. Hence, an accurate, transparent and reliable sampling becomes the first and most inevitable parameter for selecting your partner for precious metals reclamation.

While transparency should be imposed by the spent generator (for instance, by appointing a witness), this is in most cases not sufficient for assuring reliable and accurate sampling. Also, sampling procedures, equipment as well as skilled and dedicated workers should be part of the evaluation.

Total chain optimisation

When looking at the entire recycling chain for spent precious metal catalysts, in many cases more attention should be paid to the following aspects:

— How EHS compliant is the selected recycling chain?

— How experienced, reliable and financially sound are the partners involved in the chain?

— How transparent are the processes and how accurate are the handling and sampling of the spent?

— What costs, potential metal losses and throughput time implications could arise outside the precious metals refinery before or after the actual spent catalyst recovery?

On the other hand, other issues might be simplified ("less could be more"):

— Is it really necessary to ship a specific catalyst for off-site regeneration or could it be sent directly to an appropriate modern smelter?

— Can the number of contracting partners be reduced by making use of a total services package offered by the precious metals refiner (for example, inclusive transport arrangements and metals management)?

— Could a long-term relationship under a frame contract with a sufficiently large, flexible and reliable refining partner save costs and efforts in administration by the spent generator?

— Could an "early" technical discussion in a partnership between a generator and refiner determine any beneficial shortcuts in the handling and pre-treatment of the spent?

The best approach for a true optimisation of the recycling chain is open and comprehensive communication between the partners involved in the chain.

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