

# Recycling Technology for Metallic Substrates: a Closed Cycle

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## ABSTRACT

Emissions during the use phase of vehicles are of increasing interest in environmental protection, and consequently, there is considerable interest in exhaust systems. The automotive exhaust system including the catalytic converter is, because of the precious metals in the catalyst, of particular interest for the recycling of automotive parts. The paper will describe the recycling technology of ceramic and metal catalyst substrates. The process will be analyzed in detail with the example of metal supports. As a result the complete life cycle and the recycling efficiency are presented.

## INTRODUCTION

As early as the sixties, the first attempts were made to reduce the harmful substances in car exhaust gases by means of catalytic converters. As a result, converters were first employed in the USA in the seventies and were introduced to Europe in the eighties. While the emphasis at first was on the oxidation of carbon monoxide (CO) and hydrocarbons (HC), nitrogen oxides (NO<sub>x</sub>) are also reduced in today's three-way converters.

The chemical reaction is achieved in a stoichiometric equilibrium with precious metal catalysts, platinum, rhodium and palladium. In the reduction processes, this chemical equilibrium ensures that precisely enough oxygen is released for oxidation. As its name indicates, the catalyst is not a collector (filter) but a converter of exhaust gases.

A large reactive surface of the catalyst is necessary to convert the exhaust gases which are led through the exhaust train at high speed. This is ensured by the structure of the substrate and by the surface-enlarging wash coat.

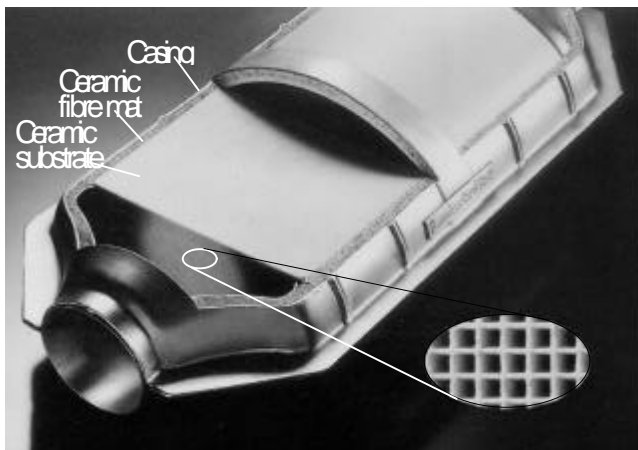
The surface of a conventional substrate is approx. 3 m<sup>2</sup> at 1 liter of volume and is increased to several thousand m<sup>2</sup> by the wash coat. Efforts to increase catalyst efficiency tends to bring about further increases in specific geometrical surface area.

The first catalysts for motor vehicles were manufactured from coated loose material (pellets). However, the relative movements of the parts led to wear and tear due to friction. Ceramic monoliths therefore displaced them almost completely. Increasingly stricter exhaust gas legislation made it necessary for the efficiency of converters to be continually increased. The metal converters developed at the end of the eighties which are manufactured from thin brazed metal foil offer some advantages in this respect. One advantage is the increased specific geometric surface area compared to that of the ceramic substrate. As efficiency is dependent first and foremost on the area of the geometric surface (where the parameters are otherwise identical), the metal catalyst can be reduced in volume while remaining equally effective. This means that the quantity of precious metals required is likewise reduced. In addition, the employment of especially thin metal foil reduces the thermal mass of the substrate so that it reaches its working temperature far more quickly. Metal substrates are therefore employed to an increasing degree. The recycling procedure used for ceramic substrates is only partly suitable for metal substrates. For this reason, a new process, described in the following, was developed.

## 2. DIFFERENCES IN THE STRUCTURE OF CATALYSTS

### 2.1 STRUCTURE OF A CERAMIC MONOLITH CATALYST

The ceramic substrate has a honeycomb structure. The exhaust gas flows through the coated channels and contacts the precious metals. The monolith is surrounded by an insulating element (ceramic fibre mat) whose purpose is not just to insulate the catalyst thermally but also to secure it mechanically. As with a silencer, the steel case is the outer "packaging" of the converter (Fig. 1).

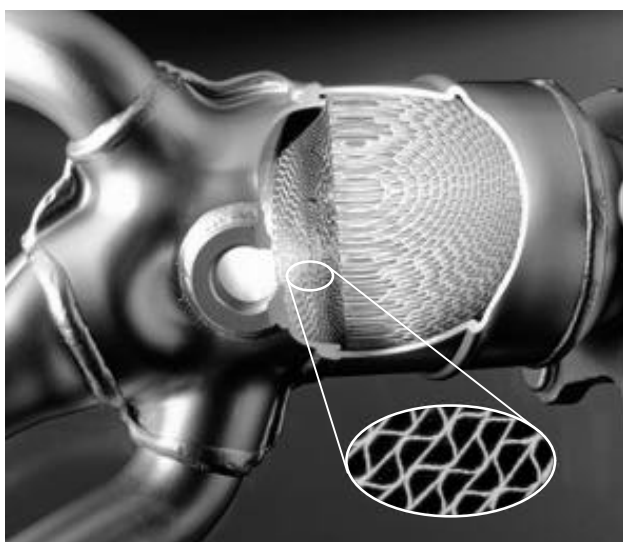


**Fig. 1: Ceramic catalyst incl. ceramic fibre mat and casing**  
[1]

## 2.2 STRUCTURE OF A CATALYTIC CONVERTER WITH METAL SUBSTRATE

The metal substrate is made of flat and corrugated metal foils. These are stacked in layers and are wound into a cylindrical or elliptical body. This body is then pressed into a metal casing and is joined by a high-temperature brazing process. The alternating flat and corrugated layers produce a channeled structure which can then be coated in order to increase its surface area - just like the ceramic substrate. Due to the integrated casing, no further measures are required to secure the substrate. If need be, additional heat insulating sheets can be applied for purposes of thermal shielding.

These two types of monoliths differ in form, size, weight and precious metal loadings as a result of different designs for the exploitation of specific advantages of the two techniques. These differences in structure bring about different requirements with regard to the recycling of these components.



## Fig. 2 : Structure of a catalyst with metal substrate

### 3. RECYCLING PROCEDURES

#### 3.1 REQUIREMENTS FOR RECYCLING

As the precious metals are applied only to certain parts of the converter (in the wash coat), the first step to be taken in the technical process of recycling is a relatively simple one: mechanically separate the washcoat and precious metals from the substrate. The next step is then to homogenize the precious metal fraction.

This is crucial for determining the value of recycling batches, i.e. statistically representative samples to acquire an analytical specimen which is analyzed for its precious metal content. The results of this analysis form the basis for the settlement of accounts with the supplier.

As described earlier, the ceramic monolith is only laid into the casing, surrounded by the ceramic fibre mat. Since the mechanical properties of the monolith are extremely different from those of the outer steel mantle, the monolith can be separated relatively easily. The ceramic material obtained by breaking down the catalyst can be easily ground to a homogeneous powder which is highly suitable for sampling.

Initially, the first recycling procedures used for metal substrates had to do without this sort of separation. Instead, the entire catalyst was processed in a melting procedure. Apart from the high costs of melting, this has a further disadvantage in that instead of concentrating the precious metals, the precious metals are diluted throughout the whole melt (including the case). Such a process is less effective; in addition, it is difficult to obtain a representative sample from the homogeneous material.

In the procedure described below, these disadvantages can be eliminated.

#### 3.2 NEWLY DEVELOPED SEPARATION PROCESS FOR THE RECYCLING OF METAL CATALYSTS

##### 3.2.1 GENERAL CONSIDERATIONS, PATENT

Special emphasis was placed in development to find a useful sampling procedure for metal catalysts. Melting a few complete components is costly and not sufficiently representative. An obvious approach was to process all of the components into a "homogeneous mass" - and to do this by mechanical rather than pyrometallurgical means. According to this approach, a specimen could then be taken from this "homogeneous mass".

However, the first attempts ended with an alarming result: the crushing produced a fine dust rich in precious metals, and this dust was in danger of being lost unless a costly dust col-

lection process was employed. The wash coat had become partly separated from the substrate! This counterproductive effect would have meant the end of these attempts had it not been for a further attempt to deliberately turn the negative effect to good use. Thus the idea came about to no longer produce a uniform "homogeneous mass" but to remove the entire wash coat with its precious metal content from the remaining material by means of an explicit separation procedure. This was subsequently demonstrated in testing. This procedure - since patented throughout the world (US Patent 005279464A) - enables not just the wash coat with its precious metals to be recovered, but also the steel fraction.

### 3.2.2 STAGES OF THE PROCESS

This procedure is based on the empirically acquired experience that by observing certain process parameters, the wash coat can be separated from the substrate by mechanical means. If this produces a mixture of particles differing from each other in form, size and weight, then these can be separated from each other. The end result is that different but homogeneous fractions of high purity are recovered.

#### a) Mechanical Reduction

In the first stage, the catalysts are reduced to a defined particle size by means of a shredder. Through the high degree of deformation of the substrate foil, caused by the applied mechanical energy, a large part of the wash coat already becomes detached and can be collected by means of air separation.

#### b) Magnetic Separation

In most cases (depending on the materials used), the remaining metallic fraction can be magnetically separated. The casing material - often austenitic - is not processed any further. On the other hand, a residue of wash coat still adheres to the substrate foil.

#### c) Mechanical Aftertreatment

In a further processing stage, the residue of precious metals on the substrate foil is separated from the steel parts by means of a mechanical separation unit. A hammer mill is employed to "beat" the remaining particles of the wash coat away from the foil; here too, the foil and ceramic particles can be separated from each other by means of air separation. All fractions of the wash coat are brought together for homogenization and sampling. The substrate foil and casing material can be reutilized in steel smelting.

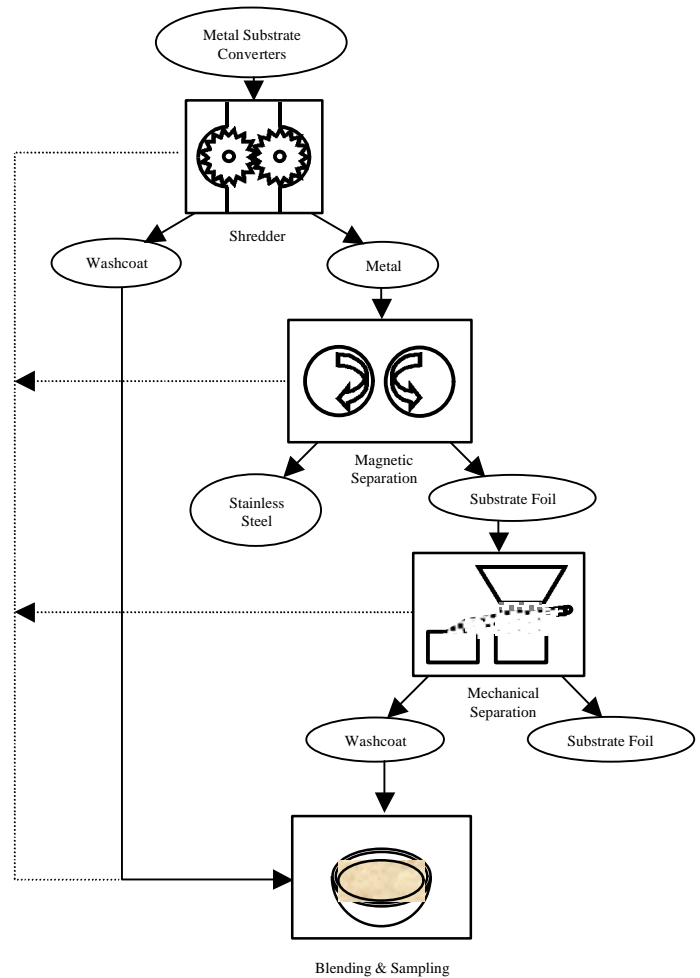


Fig. 3: Separation Process

### 3.2.3 FRACTIONS AFTER SEPARATION

After separation, the fractions of the wash coat containing the precious metals, the substrate foil, and the casing material are available individually for further processing as shown in Figure 4.



Fig. 4 : Fractions after separation

### 3.2.4 SAMPLING

All subsequent steps for the recovery of the precious metals now focus exclusively on the separated wash coat. As already mentioned, sampling is of major importance in the recycling of precious metals so that the content of the material can accurately be determined by means of an analysis. For ceramic materials, multiple-stage homogenization and separation processes are generally employed. The first step here is a synchronous milling and sieving procedure. Steel residue can thus be separated and larger parts of the wash coat can be reduced to a uniform maximum size.

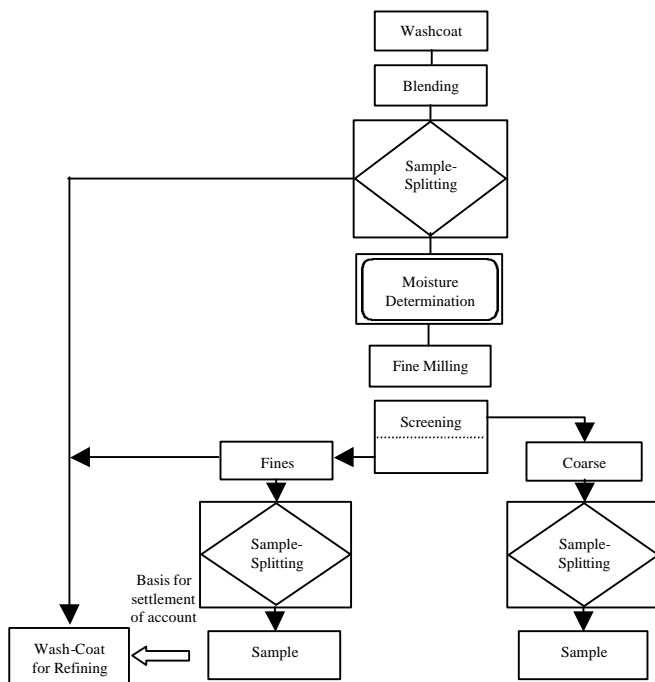


Fig. 5 : Sampling

The sample produced is also subjected to a drying process to fix its moisture content. As a ceramic material, the wash coat always contains a slight amount of moisture; this can amount to over 3% of the weight of the catalysts if these are stored under unfavorable conditions.

## 4 COMPARISON OF CATALYST TYPES IN RECYCLING

### 4.1 ADVANTAGES AND DISADVANTAGES IN SUMMARY

The decanning of ceramic catalysts can be effected with far simpler means when compared to the shredding process employed for metal catalysts.

The result in both cases is a ceramic material, which means that no costly technical procedure is required for the sampling. The only constituent requiring further processing in the case of metal catalysts is the wash coat with precious metals, with ceramic catalysts the substrate is also involved. This has a substantial effect on costs.

The subsequent recovery of the precious metals is therefore less costly because only a far smaller quantity of material needs to be refined. In addition, the substrate fraction of the metal catalyst can be used for steel smelting while the ceramic substrate is reduced to slag.

The greater expenditure on pretreatment is rewarded by lower costs in further processing. Neither of the procedures can be credited with advantages of economy. From the ecological point of view, however, it is advantageous when only a small fraction of the material which cannot be returned to the materials cycle - this is the case with metal catalysts.

To determine the financial expense involved in the recycling of metal and ceramic catalysts, two different systems employed in a modern 2 liter engine are examined. The two systems are equally effective and have similar geometric surface areas. The characteristics of the metal substrate are such that the metal catalyst system has less volume.

Comparison is made by setting the values to 100% for ceramic catalysts as the basis. The differences then are shown by calculating the ratio, giving the percentage of Metalits.

### Geometrical Data of Catalysts

	Metalit™	Ceramic substrate
Size	Ø118x174 mm	Ø143x152 mm
Cell density and foil thickness	400 cps / 50 µm	400 cps / 6.5 mil
Catalyst volume	1.9 l	2.44 l
Geometric surface area	6.1 m²	6.2 m²

With the same volume-specific quantity of wash coat, this likewise means a smaller quantity of precious metals.

### Data of Catalytic Coating

	Metalit™	Ceramic substrate
Washcoat mass	150 g/l --- 332.5 g	150 g/l --- 427.0 g

Precious metal loading	50 g/ft <sup>3</sup> , Pt/Rh 5:1 --- 3.39 g	50 g/ft <sup>3</sup> , Pt/Rh 5:1 --- 4.357
Value of precious metals	77.9 %	100 %

There are considerable differences in the methods employed in the recycling process, especially in the way the materials are broken down. With the ceramic catalyst, the substrate including the coating is ground into a homogeneous powder. With the metal catalyst, the metallic substances and the wash coat powder have been separated in the mechanical shredding and separation processes. It is somewhat more expensive to break down the metal catalyst with the separation of the coating powder but it results in a higher concentration of precious metals.

### Downsizing of Substrates

	Metalit <sup>TM</sup>	Ceramic substrate
Costs of Shredder Process	568 %	
Costs for Dismantling and milling		100 %

This means less powder is subsequently processed in order to recover the precious metals, which leads to substantial cost savings in this stage of the process.

### Precious Metal Recycling Costs

	Metalit <sup>TM</sup>	Ceramic substrate
Value of precious metal content	77.9 %	100 %
Metal fees	77.9 %	100 %
Processing costs powder	21.3 %	100 %
Value of recycled PM	77.9 %	100 %
Overall Loss	78.9 %	100 %

A further advantage over processes formerly employed is the possibility of recovering the materials of the converter separated into fractions.

### Value of Steel recycled

	Metalit <sup>TM</sup>	Ceramic substrate
Mantle + matrix	292 %	
Mantle		100 %

As a result of these cost savings, the absolute costs for the recycling of catalyst systems are somewhat less for the metal catalyst and the value of the material recovered in relation to the costs of recycling is comparable for both types of catalyst substrates.

### Overall Recycling Costs

	Metalit <sup>TM</sup>	Ceramic substrate
Costs / substrate	79.5 %	100 %
Recovered value / costs	2.58 DM/DM	2.58 DM/DM

It has been demonstrated that compared to the traditional melt process, a more efficient alternative is mechanical pretreatment.

- **Sampling**

The original development objective of producing a material capable of being sampled was attained despite the change in research plan. The wash coat powder recovered is ideal for sampling as it is a conventional ceramic material.

- **Recycling of steel**

In contrast to the fusion procedure, mechanical separation allows the steel fractions to also be reutilized. This is advantageous not only economically but also - and especially - ecologically.

- **Costs**

From today's point of view, the recycling of both designs is to be categorized as equally expensive even if the respective cost-intensive factors are in different stages of the processing.

In conclusion, it can be stated that with the mechanical pretreatment of catalytic converters having metal substrates, a further step has been taken that contributes both economically and ecologically towards the improved recycling of automobiles.

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## REFERENCES

1. Abgasanlagen für Kraftfahrzeuge, Band 47, Verlag moderne Technik AG&Co. KG

## 5. SUMMARY