We help you to help the environment!

ENVIROThERM
ZERONOX® catalysts for reducing nitrogen oxides
We help you to help the environment!

ENVIROTHERM – meet our company
ENVIROTHERM GmbH was founded in 2003 by the Allied group (www.alliedresourcecorp.com) as a medium-sized engineering company, and is an international supplier of thermal processes (gasification of solid fuels, fluidised bed combustion, and the disposal of residual materials after the destruction of chemical weapons) as well as of equipment/systems for treating flue gas (dedusting/denitrification). In this brochure we will be dealing specifically with the use of honeycomb catalysts for the catalytic treatment of flue gases.

The catalysts are produced by a joint venture in Chengdu, China, and are delivered worldwide. The important fields of customer advice, customer services and distribution are the responsibility of your contact in Essen, North Rhine Westphalia in Germany. This location is also the point of contact for more information and personal meetings.

The predecessor of ENVIROTHERM GmbH was KWH Katalysatorwerke Hüls GmbH, which was founded in 1960 as a joint German-American company for the development of catalysts and catalytic processes. The main field of business was defined very early on as the reduction of pollutants in flue gases. In 1984, the move was successfully made to selective catalytic reduction (SCR) technology. Just two years later, the first honeycomb catalysts for the conversion of nitrogen oxides were supplied. In 1993, KWH focused entirely on the field of SCR and catalytic dioxin reduction. Over 40,000 m³ of the ZERONOX® and ZERONOX® D catalysts have since been supplied. On 1 July 2001, KWH was taken over by the Allied group, and has been operating since 2005 as ENVIROTHERM GmbH. For the SCR catalysts, ENVIROTHERM continues the long tradition of KWH.

The production of catalysts was transferred to a joint venture in Chengdu, Sichuan Province in the People’s Republic of China, where since November 2006 high quality SCR catalysts are being produced. The production facilities were expanded in 2010 by the construction of a second plant with twice the capacity.
Our products

**ZERONOX®**
SCR catalysts for breaking down nitrogen oxides selectively remove the pollutant NO\textsubscript{x} and minimise undesired secondary reactions. Compared to the non-catalytic process, the slip of NH\textsubscript{3} is considerably lower, and thus imposes less of a burden on the environment.

**ZERONOX® D**
Used in a great number of waste incineration plants in Europe, Asia and North America since 1994 for the destruction of dioxins, furanes and nitrogen oxides. ZERONOX® D catalysts are predominantly used for dioxin reduction in association with denitrification.

Our range of services
Comprehensive customer service and our other services make us your competent partner for SCR technology and dioxin reduction. ENVIROTERM is oriented towards developing customer specific problem solutions.

Our management systems
ENVIROTERM has a certified quality management system in conformity with EN ISO 9001. In addition, the production facility in Chengdu uses a certified environmental management system in conformity with EN ISO 14001.
Effects of nitrogen oxides as air pollutants

During the combustion of fossil fuels and regenerative energy sources such as coal, oil, gas, biomass, peat and waste, and during other thermal processes, nitrogen oxides are generated generally referred to as NO\textsubscript{X}. These predominantly consist of nitrogen monoxide (NO) and to a lesser extent of nitrogen dioxide (NO\textsubscript{2}). As these gases are proven to cause harm to the environment and to health, the reduction of the NO\textsubscript{X} content is a significant component of any environmentally friendly flue gas treatment for combustion processes.

Environmental programmes across the world include measures to reduce levels of nitrogen oxides. There are various methods and processes available to achieve this, of which the SCR process has proven to be the most effective. Conversion rates of up to 98 % can be achieved on an industrial scale by new systems.

**ZERONOX\textsuperscript{®} catalysts:**

No chance for nitrogen oxides

Nitrogen oxides are amongst other things responsible for what is known as „summer smog“, the increased levels of ozone in the lower layers of the atmosphere, for the death of forests, and for the pollution of waterways by acid rain and over-fertilisation.
The SCR process for reducing nitrogen oxides

The use of ammonia or urea as a means of reducing nitrogen oxide allows the stoichiometric conversion of nitrogen oxides into products that occur naturally in the atmosphere, nitrogen (N₂) and water vapour (H₂O).

The vast majority of the nitrogen oxides, which are generally present as NO, can be converted according to the following reaction equation:

\[4 \text{ NO} + 4 \text{ NH}_3 + \text{ O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}\]

These reactions could also, in principle, be conducted without a catalyst in a narrow temperature window at approx. 900°C. This causes a considerable proportion of the ammonia to combust and form nitrogen oxides, however, which has a significant negative impact on the efficiency of the ammonia utilisation and the achievable NOₓ conversion rates.

The SCR process permits the reduction of nitrogen oxides, dependent on flue gas conditions and catalyst type, in a broad temperature window between approx. 160°C and just under 500°C. This allows a high level of selectiveness of almost 100% as regards ammonia conversion, and NOₓ conversion rates of up to 95% can be achieved throughout the entire guarantee period. The SCR process is furthermore extremely flexible in terms of fuel utilisation and the loading condition of the upstream combustion system.

With the SCR process, the highest reduction rates of any denitrification process can be achieved in an economical manner. It is currently the technology with the best availability, and is therefore future-proof.

Traditional application areas for SCR technology include power plants, gas turbines, waste incineration plants, chemical plants, cogeneration power plants and glass factories. SCR catalysts are also increasingly being used at facilities burning wood and other biomass, at cement works, and on mobile as well as stationary combustion engines, including diesel motors on ships. The wide variety of application opportunities and new developments demands flexibility and customised technology.

**ENVIROTHERM** solves flue gas problems

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**ENVIRO**

**ZERONOX®** catalysts for reducing nitrogen oxides
The basis of our ZERONOX® catalysts is titanium dioxide (TiO₂) in the catalytically active form of anatase. The ceramic honeycomb with its defined porous structure consists of approx. 80 % TiO₂. This mounting material is acid resistant and is therefore particularly suitable in the case of acidic flue gases.

With the most catalytically active components, vanadium pentoxide (V₂O₅) and tungsten oxide (WO₃), the catalytic properties can be customised for specific applications.

ZERONOX® catalysts are so-called monolithic catalysts, i.e. they are made 100 % from catalytically active material. Combined with the honeycomb structure, this makes them ideal for use in dust-laden flue gases. The catalyst can be customised to the specific dust load of the flue gases by the selection of the opening width (“pitch”) of the channels. Blocking of the catalyst channels is thus avoided.

Designing it as a monolithic catalyst furthermore reduces losses of activity, as the minimal abrasion continues to expose fresh active material to the catalyst surface, making it available for reducing NOₓ. Our ZERONOX® catalysts have a quadratic cross section of 150 x 150 mm and can be supplied up to lengths of 1300 mm. Their variable honeycomb structure is produced by quadratic channels that run lengthwise through the catalyst elements.

Our many years of experience in the application-specific selection of formulations and geometries guarantees you get the optimum benefit from our products.

**Pollutants have no chance against ZERONOX® catalysts!**
Manufacturing begins with the production of titanium dioxide powder using our own process. This powder is then placed in mixing systems, which knead the structure compound based on chemical formulations and feed it into the extrusion process. This is where the individual honeycombs, the catalyst elements, are manufactured. This is followed by drying and firing. The finished catalyst elements are installed in steel frames, the catalyst modules.

The modular structure of the catalyst system with ZERONOX®

A standard catalyst module contains 72 catalyst elements, however this can be adapted to customer specific requirements. The modules have a base area of approx. 1 x 2 m. This ensures the catalysts can be transported safely and installed quickly. The modules are assembled into catalyst layers inside the SCR reactor. Each catalyst layer generally has individual catalyst elements that can be removed for test purposes. These sample elements can be removed from the reactors during stoppages in order to determine their current catalytic and mechanical condition. In the case of flue gases containing dust, a vertical gas flow from top to bottom has proven effective. In the case of flue gases with low dust loads, a horizontal arrangement of the modules is also common.
The system variants of ZERONOX® catalysts

**High dust system**
The high dust system is most widely used in coal fired power plants for breaking down nitrogen oxides. The SCR reactor is installed directly downstream of the boiler. This is where the optimum operational temperatures of 320 – 430° C for the SCR process can be found. Dust loads of up to 15 g/m³ are typically found in the flue gas. In the case of fluidised bed combustion of low grade coal, dust content can be as high as 50 g/m³ or more.

**Low dust raw gas system**
For the low dust raw gas system, the catalysts are installed directly downstream of the dust collector. The flue gas temperatures are generally sufficient for the catalytic reaction without the need for additional heating. The remaining flue gas treatment elements, e. g. gas scrubbers, are installed downstream of the SCR reactor.

**Low dust clean gas system**
The low dust clean gas system, also familiar under the name „tail-end system“, is particularly used when retrofitting existing waste incineration plants. It was initially used predominantly in coal fired power plants with slagtap furnaces and ash recirculation systems. In the case of low dust clean gas systems, the SCR reactor is located at the end of the flue gas treatment system, meaning that there are no further catalyst poisons present in the flue gas, hence significantly increasing the service life of the catalysts. It is however necessary to heat the flue gas, the cost implications of which mean that this arrangement plays only a minor role, especially at large facilities.

**Combi-catalyst technology**
One of the special application variations of our catalysts is the combi-catalyst technology. It offers the ability to simultaneously reduce nitrogen oxides, dioxins, furanes and hydrocarbons from flue gases that contain multiple pollutants.
ZERONOX® catalysts – selection and design

First an appropriate system variant is selected. This is dependent on the temperature and composition of the flue gas. In addition, the potential presence of catalyst poisons plays a role. The selection of the catalyst geometry is specific to the installation. The dust content and the maximum tolerable pressure loss in the flue gas are decisive here, as the aperture size influences the total pressure loss of the flue gas treatment system, and hence affects the investment and operating costs for the compressor.

When operating an SCR reactor, it is imperative that the temperature does not fall below the working minimum. The minimum working temperature here is the temperature below which ammonium salts can be expected to form on the catalyst. This process is dependent on the SO₃ and NH₃ concentrations in the presence of water, and occurs between 160°C and 320°C.

The ammonium salts are ammonium hydrosulfate NH₄HSO₄ and ammonium sulfate (NH₄)₂SO₄, which are formed according to the following reaction equations.

Where there is an excess of NH₃:

\[
2 \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)\text{SO}_4
\]

Where there is an excess of SO₃:

\[
\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4
\]

In order to guarantee the safe operation of the SCR reactor, the temperature must not fall below the working minimum for extended periods. The process whereby the catalysts are coated with ammonium salts is reversible, i.e. they can be regenerated. The formation of ammonium salts is not the only effect of sulphur oxides, however.

Pressure loss comparison for various catalyst geometries dependent on the gas velocity at the same temperature

![Pressure loss comparison graph]

Temperature and concentration-dependent formation of ammonium sulfate (NH₄)₂SO₄ and ammonium hydrosulfate NH₄HSO₄ from SO₃ and NH₃ at normal pressure

![Temperature and concentration graph]
The combustion of fuels containing sulphur initially leads to the formation of SO₂. A proportion of SO₃ is then also formed in the combustion chamber according to the following reaction:

\[
2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3
\]

This reaction is also described as “boiler conversion”. In combination with water, SO₃ is transformed into sulphuric acid, H₂SO₄. For this reason, the formation of SO₃ should be minimised due to the possibility of corrosion if the temperature falls below the acid dew point in the downstream system components. The formation of SO₃ must therefore be particularly taken into consideration.

The conversion of SO₂ to SO₃ also occurs to a small extent as a secondary reaction in the SCR process. It is dependent on the type of catalyst selected and on the operating temperature. ZERONOX® catalysts are distinguished by a high degree of selectivity, i.e. a high NOₓ conversion rate with low levels of SO₂/SO₃ conversion.

Another key figure for the design of the catalyst is the „ammonia slip“. This refers to the volume of ammonia that leaves the SCR via the gas phase without any reaction. The ammonia slip determines the volume of the catalyst exactly as does the desired degree of NOₓ conversion. At the end of the planned catalyst service life, i.e. at the retrofitting or replacement date, the ammonia slip typically must not exceed 1 – 10 vpm, depending on the type of system.

Selecting the right catalyst for the respective application is a complex optimisation task, and we will be happy to assist you in solving it. In order to design the SCR reactors to match your individual requirements, we require you to provide details about the flue gases and the boundary conditions of the plant.

A corresponding data sheet for the catalyst survey is available from our website: www.envirotherm.de/datenblatt

**ZERONOX® catalysts:**

**The right choice!**
The replacement strategy for ZERONOX® catalysts

The catalyst is subject to ageing processes while in operation. The current extent of the ageing process is determined by regular inspection and sampling. This allows the calculation of the optimum replacement or retrofitting time for the catalysts.

The residual activity that is required of the SCR reactor to comply with statutory emission limits can be found in the relevant legislation, however this may also be tightened according to the latest available technology.

In the case of an optimally designed SCR reactor, the residual activity must be sufficient to prevent the NH₃ slip from exceeding the maximum permitted level while providing the requisite NOₓ conversion rate. ENVIROTHERM uses the information from the NH₃ slip measurements, the clean gas data and the remaining residual activity of the catalyst in order to calculate the optimal and most economically effective replacement strategy for the individual catalyst layers of SCR reactors.

In order to make full use even of the residual activity of the catalyst, the possibility of retrofitting additional catalyst layers should be considered during the planning of the SCR reactor.
Experience and innovation

Our ZERONOX® catalysts have proven their reliability in continuous operation at numerous incineration and industrial facilities. ENVIROTHERM likewise ceaselessly continues to develop its catalysts further, and adapts them to new operational conditions. Alongside the evaluation of how our catalysts perform in the framework of service life monitoring, ENVIROTHERM continuously gains new insights into the operational use of the catalysts. For this purpose, ENVIROTHERM also uses catalyst test facilities, both bench-scale and micro-scale, with appropriately verified analysers.

ZERONOX® catalysts:
Continuous further development!
Customer services related to the ZERONOX® catalyst

Within the framework of our extensive range of customer services, we offer you a complete service for everything related to catalysts. Naturally our services are also available individually. Our services at a glance:

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<tr>
<th>Service Description</th>
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<tr>
<td>Recommendation of catalyst type, calculation of the catalyst volume, and calculation of the basic data for reactor optimisation</td>
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<tr>
<td>Help in optimising the fluid mechanics of the reactor</td>
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<tr>
<td>Assembly and disassembly of the catalyst modules by specialist personnel</td>
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<td>Support for commissioning</td>
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<td>Support for acceptance testing measurements</td>
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<td>Service life monitoring and replacement strategy</td>
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ENVIROtherm solves your flue gas problems
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ZERONOX® catalysts for reducing nitrogen oxides

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