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Innovative lines of SCR catalysis: NO_x reduction for stationary diesel engine exhaust gas and dioxin abatement for waste incineration facilities

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Abstract

As shown by the NO_x emission control for stationary diesel engines and the dioxin abatement for waste incineration facilities, SCR catalysts have been optimized for certain applications by modifying specific material properties.

Keywords: SCR catalysis; Nitrogen oxides; Diesel engine exhaust gas; Dioxin abatement; Waste incineration facilities

1. Introduction

Selective catalytic reduction (SCR) is a proven technique for NO_x removal from powerplant flue gases. Since 1986 more than 80 coal-fired boilers have been equipped with Siemens catalytic reactors in Europe and the USA (Table 1).

With regard to the catalytic reactors for NO_x reduction, efforts have been made to find innovative application lines for this technique (Table 2). Among other emission sources such as wood incineration and treatment of waste gases from chemical process facilities, two major fields of activity have been developed. The first one is the development of specific SCR catalysts and the corresponding SCR system for diesel engine exhaust gas treatment. Furthermore the decomposition of dioxins promoted by optimized cata-

Table 1
Experience in NO_x removal from coal-fired power plant flue gases

		Honeycomb-type catalysts	Plate-type catalysts
Boilers equipped	Initial charge	31	27
	Reloading	7	18
m^3 of catalysts		7800	10100

Table 2
Field of applications

	Ref.
Coal-Fired Power Plants	89
Wood Incineration Boilers	4
Heavy Fuel Oil Boilers	4
Chemical Industry	6
Stationary Diesel Engines	18
Waste Incineration Facilities	16

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lytic reactors is a very interesting and successful application.

In the following, particular aspects of these two new types of catalytic reactors will be illustrated more closely and documented with results from performing tests.

2. Siemens diesel catalyst

To meet NO_x emission control limits for stationary diesel engines installed in small cogeneration plants or peaking units, for example, special requirements have to be taken into consideration [1]. The requirements differ from those well known from NO_x reduction of coal-fired power plants (Table 3).

A new SCR system, called SINOx (SIemens NO_x system), has been developed especially for these applications. The system flow diagram shows that the SINOx-system contains all components necessary for safe operation such as a standardized catalytic reactor, a dosing and mixing unit for the reducing agent, measurement and control equipment, etc. (Fig. 1). The Siemens diesel catalyst as the 'heart' of this system links compact design with high performance and reliability (see Table 4). It is not a carrier-based system but a catalyst entirely consisting of active material. Compared with conventionally fabricated catalysts the high active surface area of the SINOx diesel catalyst allows the reduction of the required volume and therefore of the cost of the plant.

Since presentation of the system in 1994 diesel engines with a total output of nearly 25 MW have been equipped with SINOx catalysts. It was demonstrated that in spite of the small channel structure of the monolith neither blocking nor deactivation was caused by soot.

Table 3
Typical operating conditions of coal-fired power plants and stationary diesel engines

	Coal-fired power plants	Stationary diesel engine exhaust gas
Typical temperature range	300–400°C	250–550°C
Load changes	Slow, if at all	Rapid
Typical NO_x content	< 500 ppm	ca. 1500 ppm
Required NO_x conversion rate	60%–80%	80%–90%
Space required for installation	In most cases compact design not required	Compact design required very often

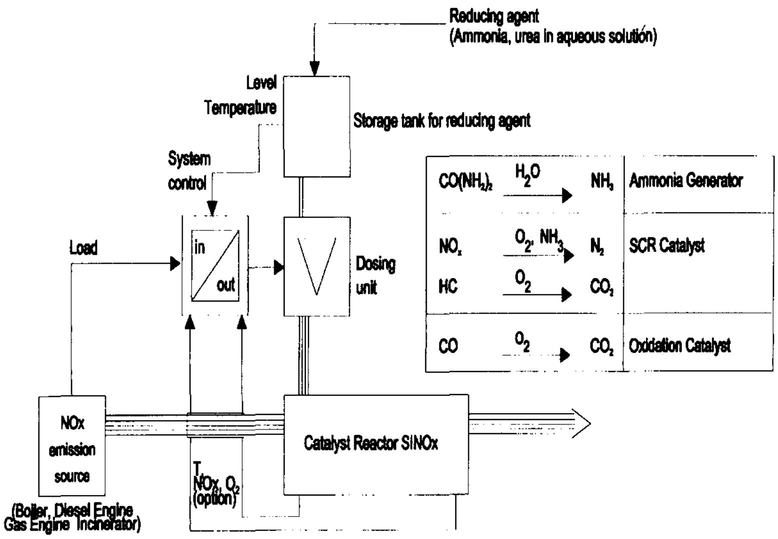

Fig. 1. Flow sheet of a SINOx system.

Table 4
Specification of the SINOx diesel catalyst

Performance	Honeycomb-type
Surface area	882 or 1265 m^2/m^3 (46 or 100 cpsi)
Pitch	3.7 or 2.5 mm
Temperature range	250–550°C
Geometry	150 mm × 150 mm or ∅ = 380 mm

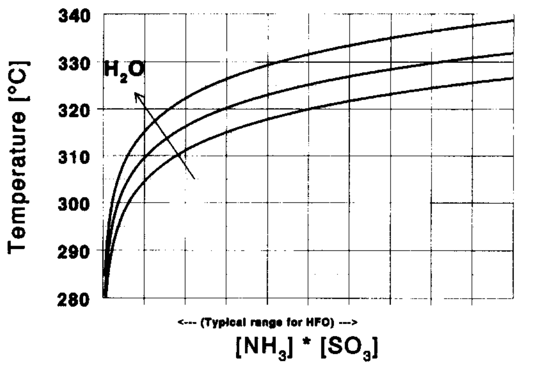

Fig. 2. Lowest allowable gas temperature for SCR process operation.

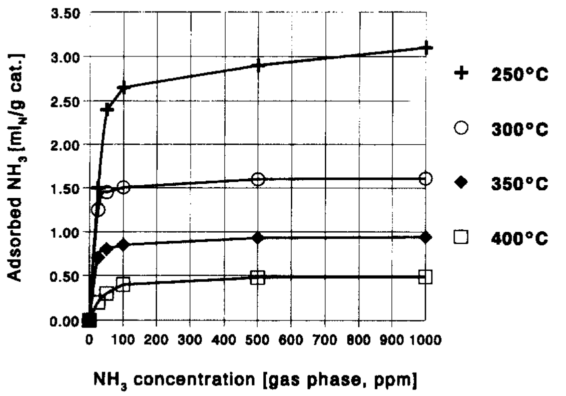

Fig. 3. NH_3 adsorption equilibrium on SCR catalyst (for one specific catalyst).

Considerable potential for improvements are evident when considering such a NO_x reduction installation and its everyday operation. The usage of heavy oil with high sulfur content, for example, imposes high demands on the catalytic reactors. It is an accepted fact that V_2O_5, brought into the exhaust gas by the heavy fuel oil, changes the activity of the catalyst relative not only to NO_x reduction but to SO_2 oxidation, too. V_2O_5 precipitating on the catalyst and the walls of the reactor causes an increase in activity for both reactions. The increase in the SO_2 oxidation rate with its undesired consequences (corrosion, precipitation of $(NH_4)HSO_4$ in equipment downstream the catalyst) has been treated in some detail. As opposed to the reduction of NO_x which takes place mostly on the surface of the catalyst, the conversion of SO_2 to SO_3 occurs within the volume. Consequently our objective is to install catalysts with a very thin layer of catalytic material. The catalysts applied to our heavy fuel oil plants are either plate-type catalysts (steel coated with active material) or special heavy fuel oil honeycomb-type catalysts. The latter are monoliths with very thin walls.

Another problem connected with heavy fuel oil is the minimum temperature required for heavy fuel oil operation. As shown in Fig. 2, the temperature should not fall below a certain value to prevent the formation of $(NH_4)HSO_4$ on the surface of the catalyst as this would cause significant deactivation. A typical heavy fuel oil application requires a minimum temperature of about 310 to 330°C.

The efficiency of an SCR installation for stationary diesel engines depends, among others, on the consumption of reducing agent, typically urea solution, which is hydrolyzed to ammonia in a special hydrolysis unit [2]. Therefore methods for precise dosing of this reagent are worth discussing. Looking at dosing algorithm, the storage capability of the catalytic material for ammonia has to be taken into consideration. Fig. 3 shows the NH_3 adsorption equilibrium on SCR catalyst depending on temperature and ammonia concentration in the gas phase. This behavior of the catalyst has far-reaching consequences for the dosing algorithm. Especially looking at engines running with rapid load changes, the distinct buffer potential for ammonia requires ingenious dosing strategies. To observe the limits concerning NO_x and NH_3 the control action has to be very quick. By contrasts oscillations of the concentration of the two compounds has to be minimized. Normally the load of the diesel engine determines the amount of reducing agent needed. During commissioning the dependencies between load on the one hand and gas flow, NO_x, etc. on the other hand is determined and programmed into the control unit. But it goes without saying that measuring relevant exhaust gas compounds during operation is necessary for controlling the limits especially in the case of high demands for NO_x conversion rates.

3. Siemens dioxin catalyst

In the early 1980s pollution control regulations focussed on controlling power plant SO_2 and NO_x emissions. Attention has now been directed to the emissions of waste incineration facilities. These plants unavoidably emit NO_x in addition to the desired combustion products CO_2 and H_2O and, depending on the reaction conditions and waste composition, also halogenated organic compounds in the event that complete oxidation is suppressed. Because of their toxicity, polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), which are formed under such conditions, are of great interest when creating new emissions control legislation [3]. It has been recognized that fly ash acting as a heterogeneous catalyst plays a crucial role in the formation of PCDD and PCDF in the afterburning zone of waste incineration facilities [4]. One simple way to destroy chlorinated volatile organic compounds relies on antagonistic materials to support a catalytic oxidation process.

As a rule, dioxin abatement catalytic reactors are operated together with $DeNO_x$ reactors. Specified requirements for the two reactor systems are essentially determined by the operating conditions of $DeNO_x$ catalysis. Since both process steps are oxidation reactions, it comes as no surprise that $DeNO_x$ material exhibits a certain inherent propensity for oxidation of dioxins. In the SCR process working typically in the temperature range of 200 to 500°C, NH_3 is oxidized in the presence of NO via

$$4NO + O_2 + 4NH_3 \rightarrow 4N_2 + 6H_2O$$

Catalytic material for decomposition of dioxins must be tailored to these operating conditions. Therefore, it is advantageous not only from a process engineering standpoint to implement both of these processes simultaneously (Fig. 4).

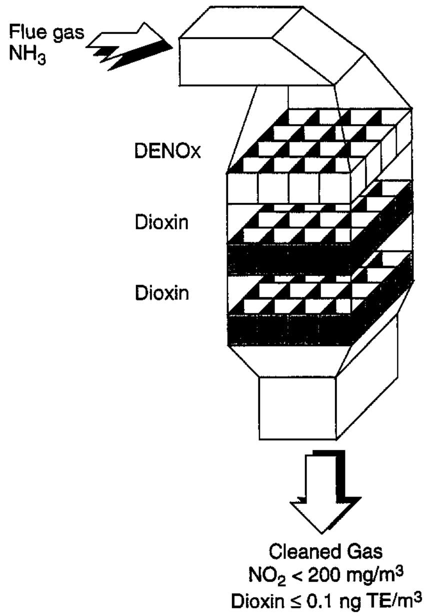

Fig. 4. SCR/dioxin reactor.

It has been discovered that the oxidation of unsaturated chlorinated compounds is more difficult than the oxidation of saturated chlorinated compounds, which is in direct contrast to the oxidation of non-halogenated hydrocarbons. It was additionally learned that the presence of water, the concentration of oxygen in the gaseous stream and operating conditions have significant effects on the activity of the catalyst [5]. The influence of ammonia has also been discussed in the literature [6]. Of necessity, Siemens has developed a suitable catalytic material based on TiO_2 which offers the advantages of the catalyst geometry required for this application and employs fabrication technology similar to that used for honeycomb-type $DeNO_x$ catalysts.

In 1987 catalyst material development was first focussed on industrial gas cleaning systems to achieve the oxidation of waste gases such as hydrocarbons, aromatics and the halogenated derivatives [7]. Screening investigations of dioxin tracers conveniently confirmed that there is indeed a mechanistic correlation between PCDD/PCDF and the precursor compounds such as chlorophenols, polychlorinated biphenyls and

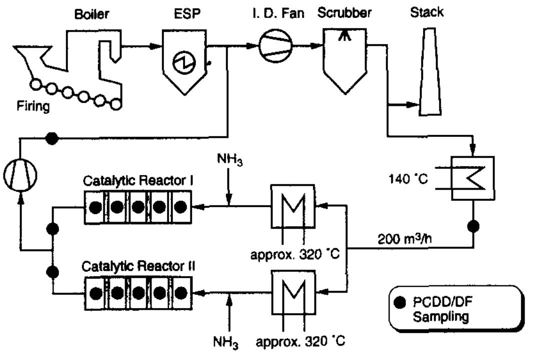

Fig. 5. Arrangement and operating conditions of the RWE pilot plant.

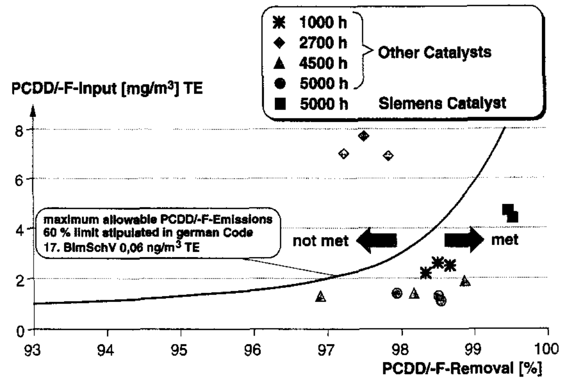

Fig. 6. Comparison of PCDD/PCDF conversion rate and service time for dioxin catalysts.

polycyclic aromatic hydrocarbons [8]. Consequently we thoroughly investigated the catalytic oxidation of chlorinated benzene derivatives. Such compounds which can act as dioxin precursors are destroyed before they form dioxin.

Dioxin conversion measurements were initially made in the RWE pilot plant Essen-Karnap in early 1992. Fig. 5 shows the arrangement and operating conditions of this plant.

Some objectives and results were first presented by Oschmann et. al. [9]. In Fig. 6a comparison of the efficiency of PCDD/PCDF decomposition over the service time is shown for various dioxin catalysts. No significant decrease in activity was detected with Siemens dioxin catalysts after 5000 operating hours. Similar positive results were obtained in a pilot plant operated by Deutsche Babcock Anlagenbau. Dioxin conversion rates ranging from 97% to 99.5% were measured in these facilities.

The first waste incineration facility in Germany was equipped with Siemens catalytic reactors for conversion of NO_x and dioxin and began operation in 1993. Plant measurements, unpublished to date, indicate that the compliance with dioxin limits of 0.1 ng TE/m^3 flue gas is reliably achieved.

The design volume calculated for combined NO_x and dioxin conversion is not of necessity the sum of the volumes V_{NO_x} and V_{dioxin} which would be required if either of these reactors were installed separately. This can be readily validated if it is considered that local conversion of NO_x decreases across the $DeNO_x$ catalyst and the residual catalytic activity of the catalyst is thus available for dioxin decomposition in this part of the catalytic reactor. The NH_3 in the flue gas is converted in this section of the catalytic reactor to such an extent that dioxin decomposition can take place without any disturbing influence. Assuming optimization of other design criteria too, combination of the two process steps downstream of the electrostatic precipitator in fact reduces the volume requirements as compared to that for either of the reactors if installed individually. This approach is attractive in that it correspondingly reduces overall investment costs, too.

4. Outlook on future trends of catalysis for NO_x- and dioxin-emission control

The following trends will influence future developments:

- *Continuous decrease of legally prescribed limits.* This development requires catalytic reactors with high activity, especially developed for high NO_x conversion rates with a NH_3 slip which decreases simultaneously.
- *Changes in engine characteristics, higher efficiency, lower temperature.* Especially at part load specific catalytic material for low temperature applications is in the center of interest.
- *Alternative reducing agents.* Some working groups deal with NO_x reduction based on hydrocarbons, for example. Furthermore SCD (selective catalytic decomposition of NO_x) can be seen as a possible technology for the future.

- *Mobile diesel applications.* Currently it is expected that fields of application will be ships, locomotives and, as a very interesting topic, trucks.
- *Decrease of the amount of catalyst required for PCDD/PCDF reduction.* Further optimizing of material properties will be made to improve the ability for usage of dioxin catalytic converters.
- *Dioxin catalysts for low temperature applications.* Similar to the conditions of the diesel market, spreading of the temperature range is necessary.
- *Decrease of deactivation by poisoning compounds contained in the flue gas.* Because of the heterogeneous distribution of the material processed in a waste incineration facility, the exact composition of the flue gases is unknown in most cases. The catalyst should be as unsensitive as possible against potential poisoning.

5. Conclusions

A new SCR system, called SINOx, developed especially for stationary diesel engines perfectly meets all requirements for exhaust gas emissions control limits. Improvements of the catalytic converter promote the use of heavy fuel oil. Furthermore, the controlling of the reducing agent required and the plant design has been optimized with respect to these applications.

Relative to dioxin abatement, extensive measurements, both in test facilities jointly performed by Siemens, operators and plant constructors, and in our own test facilities, as well as initial operating experience gathered with dioxin conversion catalysts installed in Germany's first industrial-scale reactor for combined conversion of NO_x and dioxin, have confirmed the correctness of the reactor design method used.

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