Reduction of PCDD/F Emissions From Iron Ore Sintering Plants - The First Full-Scale SCR Installation

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Abstract

From the many dioxin/furan measurements and research activities conducted during the last decade, it has been concluded that not only waste combustion plants, but in principle all process categories, in which chlorine is a component in the process in combination with a carbon source and metal oxides at a temperature above 180 °C, are potential sources of dioxins and furans. Therefore, in some European countries such as Germany, the Netherlands and Great Britain processes with these conditions precedent were examined in order to gain a more detailed knowledge regarding their individual relevance and contribution to the overall release to the environment.

The above mentioned conditions are also present in iron ore sintering plants. It has been found that these facilities emit a significant quantity of dioxins/furans. Consequently, suitable control technologies must be identified, which on the one hand demonstrate excellent dioxin/furan control performance and on the other hand avoid extensive additional cost burdens for the sinter material. This latter requirement is especially important due to the worldwide competition on the steel market and its significance for national employment. The catalytic dioxin/furan control technology is a very promising approach in meeting both targets. Within this paper, the technology is described in detail. Also, the worldwide first full scale DeDiox-reactor for the thermal destruction of dioxins/furans downstream a sinter plants is presented.

Introduction

As shown in **Table 1**, municipal solid waste incineration (MSWI) was one of the most important sources of dioxins/furans in Germany until emission limits were first promulgated in the early 1990´s. Since then, existing facilities were retrofitted and equipped with extensive flue gas cleaning systems and dioxin/furan emissions have been significantly reduced. Others were shut down completely or replaced, even though the total number increased by over 20%.

Nowadays, one significant source of dioxin/furan in Germany are sintering processes in the primary metal industry and similar processes in the secondary non ferrous industry. Within sintering processes, a mixture of various substances is coalesced at high temperature (1000 – 1200 °C). The material is mixed with coke, which provides the source for the carbon as well as the chlorine, and transported on a chain grate. Burners above this grate heat the top of the material to the required temperature causing the coke to ignite. By sucking air through the mixture, the flame front is moved through the sintering bed. Consequently, ideal conditions for the formation of dioxins/furans, which can not be avoided, exist locally regarding temperature and material composition. Sintering plants are normally equipped with electrostatic precipitators (ESPs) as gas cleaning devices. Stack measurements at such plants show average dioxin/furan concentrations in a range from 1 to 5 ng I-TEQ/Nm^3 at volumetric dry flow rates ranging from 250,000 to 1,000,000 Nm^3/h. The current regulations for these processes do not require dioxin/furan emission control equipment.

Table 1: Emission Sources of Dioxins/Furans in Germany [1]

	1989/90	*1994/95*	*Prognosis 1999/2000*
	g I-TEQ/a	g I-TEQ/a	g I-TEQ/a
Waste Incineration	400	30	< 4
Metal Industry	740	240	< 40
Power Stations (Fossil Fuel)	5	3	< 3
Industrial Combustion	20	15	< 15
Other Thermal Industrial Processes	1	< 1	< 1
Domestic Coal and Wood Combustion	20	15	10
Crematoria	4	2	< 1
Traffic	10	4	< 1

Therefore, the German-based sintering plant operators joined forces to set up a demonstration project for the development of a method to reduce dioxin/furan emissions from sintering plants. In August 1996, the companies EKO Stahl GmbH, Hüttenwerke Krupp Mannesmann GmbH, Krupp Hoesch Stahl AG, Preussag Stahl AG, Rogesa Roheisengesellschaft Saar mbH and Thyssen Krupp Stahl AG formed a project consortium named “Reduction of Dioxin/Furan Emissions from Sintering Plants”. In the meantime, Sidmar N.V. (Belgium) and Sollac S.A. (France) have also joined the consortium.

The consortium has submitted applications for funding of the project to

- the European Union’s Life program
- the program for financing of investments for demonstration purposes run by the German Federal Minister for the Environment, Nature Conservation and Reactor Safety, as well as
- the state government of North Rhine-Westphalia.

Getting these applications approved was not easy, since they were submitted at a time when the EU Commission was in the process of deliberation fundamental issues. The situation was further complicated, because public funds were scarce due to the high demands for public funding. The European Union and the German Environment Ministry have now approved the applications, while the North Rhine-Westphalian state government declined the application.

In the meantime the project has been fully acknowledged by German federal and state authorities, who have agreed to refrain from passing any new regulations until the final results of the studies become available. During last year, the selected demonstration technologies were installed downstream the sintering strand SB 2 of the Thyssen Krupp Stahl AG in Duisburg and the full scale demonstration project was started up in late 1998.

As a result of intensive pre-studies and numerous pilot-plant trials, the two most promising control technologies were identified. These are the installation of:

- Carbon based additive injection upstream the existing ESP
- Oxidation catalyst between the existing I.D. fan and the stack (tail-end arrangement)

The additive injection will be the first control step [2]. Former pilot-plant results showed that this technology would be able to reduce the dioxin/furan content to concentrations between 0.3 – 0.8 ng I-TEQ/Nm3 using pulverised open Hearth Oven Coke (HOC), a lignite based activated carbon. The adsorption efficiency of HOC, pulverised activated carbon (PAC) or other adsorbents will be investigated in the later research program. The oxidation catalyst serves as a final polishing step to meet a target value of 0.1 ng I-TEQ/Nm3 in combination with the upstream injection. Both processes will also be tested independently from each other.

This paper will concentrate on the catalytic dioxin/furan control process installed under a general contract awarded to the L.&C. Steinmüller GmbH (LCS).

Catalytic Dioxin/Furan Control

As known from flue gas cleaning plants downstream waste incinerators, the principle of catalytic dioxin/furan control is applied downstream of adsorption processes. CO_2 and HCl are formed as destruction products. The oxidation reactions of polychlorinated dioxins and furans occur on the catalyst surface in the presence of oxygen. Usually, ceramic honeycomb catalysts are used similar to those known from the SCR (selective catalytic reaction) process for the decomposition of nitrous oxides (NO_x). The dioxin/furan reduction efficiency depends on the installed catalyst volume. Therefore, the process can be designed to meet specific requirements. Dioxin/furan measurements downstream municipal solid waste incineration plants showed that emission values below 0.05 ng I-TEQ/Nm^3 (dry basis, 11 % O_2) can be achieved [3]. The main advantages of the catalytic process are:

- dioxin/furan destruction without the formation of toxic products,
- no chemicals/adsorbents are required,
- low pressure drop,
- easy operation,
- low maintenance requirement,
- no additional staff required,
- combination with NO_x removal is possible,
- no residues apart from spent catalyst (after several years),
- the spent catalyst will be taken back by the catalyst manufacturer for recycling.

Typically, in MSWI catalytic dioxin removal is combined with NO_x removal. In that cases, the SO_2 and SO_3 concentration downstream the flue gas pre-cleaning plant determine the minimum operating temperature of the SCR-system which usually is above 170°C to avoid catalyst fouling due to ammonia-bisulfate deposition.

The ceramic honeycomb catalyst was chosen primarily because of its relatively low pressure drop and – despite of the low operating temperature - very promising control performance in pilot tests. Therefore, no additional I.D. fan had to be installed.

Catalyst

The catalyst consists of ceramic elements with a honeycomb structure. These elements are combined to modules in a separate casing with dimensions of approximately 940 x 1885 mm. Other dimensions are also possible. In this case, each module is equipped with 6 x 12 elements. The cross sectional dimensions of each element are 150 x 150 mm. The length of each element and the number of levels are chosen depending on the required total catalyst volume. Due to fabrication restrictions, the maximum length of an element is limited to 1000-1300 mm (depending on the element's pitch, which corresponds to the opening dimensions of the catalyst). The modules are installed on the supporting structure of each level of the reactor.

The catalyst material is a homogenous ceramic mass. Thus, in the event of erosion, the catalyst activity is not reduced, but may even be increased. The principal constituents are TiO_2 (titanium dioxide) as a porous base material diffused with active substances, usually V_2O_5 (vanadium pentoxide) and WO_3 (tungsten trioxide). The catalyst installed in this plant is a proprietary catalyst, which was solely developed for these kinds of applications by Katalysatorenwerke Hüls GmbH (KWH).

Pilot-Plant Experience

Before selecting the described catalytic approach, intensive trials on a test reactor with a volumetric flow rate of 150 m^3/h have been performed in order to be able to determine the adequate dimensioning of the demonstration plant. During the testing phase of more than a year, the steel manufactures research institute as well as KWH determined that even at flue gas temperatures as low as 130 – 200 °C dioxin/furan degradation took place. Neither absorption nor adsorption effects of dioxins/furans on the catalyst surface have been detected even at the low end of the temperature range. Deactivation of the catalyst was constantly monitored and determined to be in the range of permissible measuring tolerances.

First Full-Scale Dediox-Reactor Downstream an Iron Ore Sintering Plant

On October 14th, 1997, LCS was awarded the contract for the installation of the full-scale catalytic oxidation reactor as the first application of this kind. KWH was awarded the oxidation catalyst supply contract. The reactor is arranged downstream the existing ESP and I.D. fan. The flue gas enters the reactor from the top and leaves at the bottom to the existing stack (**Figure 1**). This tail end solution was selected due to its high availability, low pressure drop and the lack of additional residue treatment. The maximum permissible pressure drop for the total retrofit was restricted to 10 mbar. Other dioxin/furan control technologies [3] such as activated carbon reactors (ACR) or fabric filters with upstream adsorbent injection would have led to a much higher pressure drop (15 to 20 mbar) resulting not only in the corresponding increased electricity cost and additive cost but also in the requirement of an additional I.D. fan.

Table 2 shows the most important dates concerning the retrofit time schedule. One very important criterion for selecting LCS was the guaranteed tie-in time of the new reactor of only 54 hours, which was met. This resulted in a minimum downtime of the sintering plant.

Table 2: Time Schedule of Dediox-Reactor Retrofit, Thyssen SB 2

• 14.10.1997	Award of Contract
• 25.05.1998	Start of erection
• 02. – 06.11.1998	Installation of catalyst modules
• 10.11.1998, 22.00h	Start of dismantling for tie-in
• 13.11.1998, 4.00h	Tie-in finished after 54 h
• 16.11.1998	Start of trial run
• 15.12.1998	End of trial run, preliminary acceptance by Thyssen Krupp AG

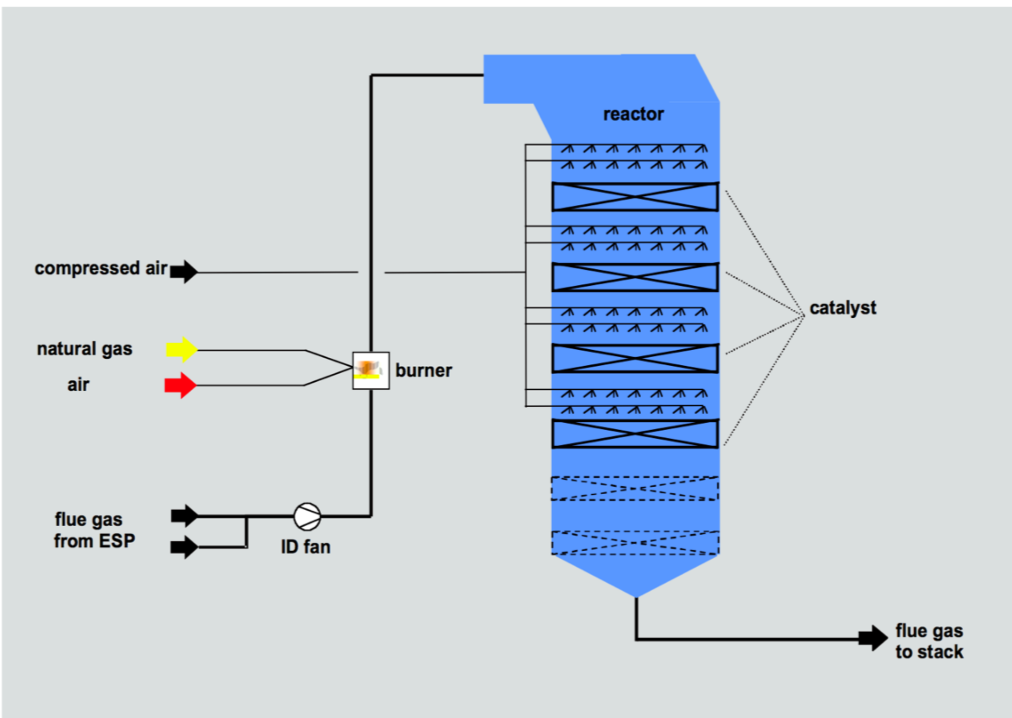

Figure 1: Oxidation Reactor for Dioxin Control Thyssen SB 2 STEINMÜLLER

The reactor is designed for an operating temperature of 100 - 140°C and a flue gas volumetric flow rate of 400,000 m^3/h (wet @ STP). The catalyst was designed for a dioxin/furan reduction efficiency of 75 %. Due to the residual dust content of approximately 50 mg/Nm^3 and the lack of experience concerning the dust properties, a large pitch of 6.5 mm was chosen.

The reactor accommodates six catalyst layers. Four of them are equipped with catalyst while two of them are spare layers, which can be equipped later to enhance the overall catalyst life time. In addition, soot blowers are arranged upstream of each catalyst layer. Supplied with compressed air, they are operated on a discontinuous basis.

Upstream the catalyst, a natural gas burner is installed which fulfils two purposes:

- Preheating of the catalyst to temperatures above the water dew point during start-up of the sinter plant,
- adjusting the SCR temperature to investigate the temperature influence on dioxin/furan control efficiency.

Due to the longer preheating process of the sintering belt itself, the start-up time of the catalyst is completely integrated in the overall start-up process. Consequently, no loss of time and production of sinter occurs.

First Operational Experience

Up to this point in time, the reactor has been in continuous operation without problems. It fully complies with the operational requirements of the sintering plant without imposing any restrictions on sinter production. The actual pressure drop is well below the limit of 10 mbar. After six months of good operating experience, the soot blowers of the 3^{rd} and 4^{th} layer had been switched off without observing an increase in pressure drop. Since the plant operates automatically, no additional operating staff is required.

Outlook

A very comprehensive dioxin/furan sampling and measuring program has been started by the consortium, which will continue, to the middle of next year. It is at present not foreseeable whether the target value of 0.1 ng/Nm^3 can be reached with the combined process.

References:

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