DIOXIN EMISSION MONITORING PROGRAM FROM A LARGE SINTER PLANT

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Abstract
The production and processing of metals, in particular the sintering of iron ore, is blamed for being a major industrial emission source of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) in the European Union (EU). This evidence were discovered in 1992, long after dioxins were first identified in incineration effluents (1977). In the framework of the implementation of the Stockholm Convention on Persistent Organic Pollutants (POPs), the fine ores sintering process has been selected for detailed investigation.
In the EU the lack of measured data of PCDD/F from sintering plants, in particular from steel plants in Italy, is currently a serious gap to design appropriate strategies, and mandatory or voluntary monitoring programs are an important step on the way of manage the issue. [1, 2, 3]
Consequently the Regional Government of Apulia, hosting the second largest integrated iron and steel plant in EU, have launched an extensive investigation for monitoring PCDD/F emissions from stack gas of Taranto's sintering unit (identified as AGL-2). The activity involves the Regional Environmental Prevention and Protection Agency of Apulia (ARPA - Puglia), the company, and the Institute of Atmospheric Pollution of Italian National Research Center (CNR-IIA). The monitoring will be carried out since June 11th. Some preliminary results will be reported in this paper.

Introduction

PCDD/F from sintering plant e European strategies

At the EU Council Conference in June 1993, the German Delegation presented a memorandum with the objective of reviewing the knowledge available on dioxin emissions from industrial sources in the Member States, and demonstrating the possibilities of limiting the emissions of PCDDs/PCDFs into the environment and into the human food chain as a precautionary measure.
The European Commission in 1995 implemented the project ''Identification of Relevant Industrial Sources of Dioxins and Furans; Quantification of their Emissions and Evaluation of Abatement Technologies''.
In the last twenty years, as dioxin emissions from municipal solid waste incinerators (MSWIs) decreased, the relevance of emissions from other sources, in particular from sintering plants, has grown in proportion. [4]
At present, there are still insufficient field measurement data to fully assess the extent of dioxin pollution caused by sintering process, the influence of feed and plant operating parameters, and the primary measures to be taken to reduce emissions at the source. Furthermore, studies about mechanisms of dioxin formation in thermal metallurgical processes and possible techniques for dioxin reduction are scarce.
Several researches have highlighted that the PCDD/F are emitted intensively from sintering process. Due to process optimization, especially by input control, actual emission concentrations/factors referring to emissions after abatement, which is normally carried out using an electrostatic precipitator with three to four fields, normally are in the range of 0.5 - 5 $ng_{I\text{-}TEQ}/Nm^3$ which is (with 2.100 Nm^3/t_{sinter}) 1 - 10 $\mu g_{I\text{-}TEQ}/t_{sinter}$. In some case, emission concentrations of up to 43 $ng_{I\text{-}TEQ}/Nm^3$ (replicate analysis) have been determined.[5]
PCDFs are dominant in the stack flue gases of sinter plants and PCDFs/PCDDs ratio exceeds 1 extremely. [6]
The mechanism of formation of dioxins, which is well investigated in the incineration process, is poorly understood in the context of sintering.
There are three reasons for the presence of PCDD/Fs during combustion:

1. the raw materials contain these molecules, and they are incompletely destroyed during combustion;
2. these molecules are formed from chlorinated precursors such as PCBs, chlorinated phenols and chlorinated benzene in combustion chambers, or via reactions with fly ash;
3. dioxins/furans are formed via de novo synthesis.

It can be assumed that the same three possibilities apply to the formation of PCDD/Fs during sintering processes.

[7, 8]

Taranto's sintering unit

With about 200,000 inhabitants Taranto, second most populated town of Apulia Region (Southern Italy), hosts a heavy industrial district unfavourably positioned toward nearby residential areas and upstream prevailing winds.
The industrial district includes over the large iron and steel integrated complex, one of the largest oil refinery in S. Italy, a large kiln factory and several SMEs, making actually Taranto one of the most industrialized city of S. Italy, officially listed among "*Italy's 15 areas at high risk of environmental crisis*" according to laws No. 349/86 and 305/89.
A scheme of the sintering installations at the Taranto's iron and steel plant (15 km^2, a potential production of about 10-12 million t of steel per year and about 13.000 workers) under our investigation is shown in Fig. 1.
The heart of the process is a slowly moving, horizontal belt that supports the feed during drying, preheating, ignition, and ore sintering. The process is initiated by a gas/oil start-up burner that ignites the coke in the feed layer on top. As the feed proceeds with the belt, ambient air is aspired downwards through the charge, so that the combustion and sintering zone slowly descend through the layer until breakthrough, signaling the end of the process. The resulting sinter is then cooled and calibrated; the off spec. fractions are recycled, either as a bedding for the sintering layer (coarse), or in the feed (fine). The off-gases are generally led through a first system of a multiple-field electrostatic precipitator (ESP) for cleaning before passing through a second system of a moder Moving Electrode Electrostatic Precipitator (MEEP). In the MEEP, several groups of electrode plates move on caterpillar tracks. They are continuously cleaned by rotating brushes. Thus, the strongly adhesive dust is easily removed from the plates and the insulating effect of the dust layer is avoided after that off-gas (3.400.000 Nm^3/h) are discharged via a tall stack (named E312) 210 m long with an external diameter of 13 m.

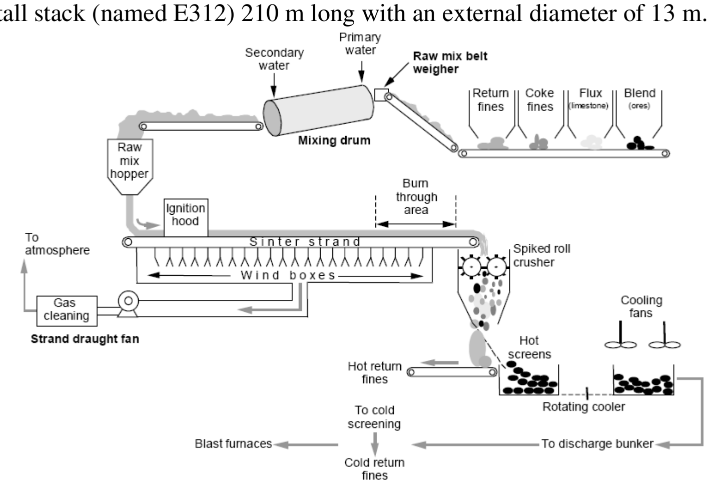

Fig. 1 Schematic diagram of the Taranto's sinter plant

In most cases, the cooling takes place in separate equipment peripheral to the belt, which may be an important factor for total generation of dioxins. The temperature and oxygen field, the air distribution and flow patterns through the sintering belt all are complex, because of the cross-flow arrangement of feed and air, the hot sintering front, gradually moving downward through the burden, its variable porosity, temperature and composition (coke is depleted, lime converted into complex oxides, hematite is partly reduced, salts and volatile heavy metals are volatilized). In a cross and downward flow, ambient air is aspired through the burden by the large underpressure under the belt, rapidly preheated while cooling the hot sinter, then used for coke combustion in a thin seam, and the resulting hot off-gas is used to preheat, then dry the underlying feed. Then there are a series of windboxes/dividers and gas collectors with subjacent dust hoppers below the sinter belt.

Estimated data emission from Taranto's iron and steel plant

The European Pollutant Emission Register (EPER) – the first European-wide register of industrial emissions into air and water – indicates in the last revision (2004) that the 40 % of PCDD/F emissions in EU25 comes from metal industries, followed from cement, lime and ceramic production with 27 %, and only after from waste incinerator with 12 % of the total emitted. Share in determination methodology for emission of PCDD/F to air is based on data calculated (20.2 %), estimated (24.7 %) and measured (55.1 %). The Taranto iron and steel plant contributed to about 8.8 % of total European emission to air of PCDD/F with 76.2 $g_{I\text{-}TEQ}$ estimated in the 2004.

Epidemiological data in Taranto area

The metropolitan area of Taranto has been labeled by WHO area at high environmental risk because of the above cited presence of several large industries and elevated rates for all-causes mortality and all cancer mortality, higher than regional mortality rates, especially for lung cancer. [10] Also standardized incidence rates, provided by the local Cancer Registry, show a critical epidemiological situation in the at-risk area: in the period 1999-2001, excesses have been found in males for all cancers, lung cancer, pleural mesothelioma, bladder cancer and non-Hodgkin lymphoma and these figures are more evident when comparing the rates of the city of Taranto with the whole province. The observed excesses strongly suggest the presence of occupational and environmental risk factors: a case-control study, recently conducted with the aim at evaluating the relationship between the distance from industrial sites and cancer occurrence, has shown a significant association between lung cancer risk and the residence near the steel plant. [11]

Materials and Methods

In order to characterize the PCDD/F loads in the sinter material and to understand the possible PCDD/F formation processes, solid samples of process solid material will be collected from the sinter feed as well as dusts discharged from the subsequent primary ESP and secondary MEEP fields.
For sampling, extraction, clean-up, identification and quantification of PCDD/F will be followed the European Standard (EN 1948-1-2-3:2006) prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN. This European Standard has been developed to measure PCDD/PCDF concentrations at about 0,1 ng I-TEQ/m^3 in stationary source emissions and specifies both method validation and a framework of quality control requirements which shall be fulfilled by any PCDD/PCDF sampling.
The procedure described in the three parts of EN 1948 specifies requirements which shall be met in order to measure the 17 congeners necessary to calculate the total I-TEQ. [12, 8]

Results and Discussion

The results of monitoring activities will be provided. The Italian Inventory of Emissions and Sources (INES) includes data since 2002 to 2005, provided by large industries. [13] For the Taranto plant, for which only estimated data are available, an increased trend for all air pollutants is reported. PCDD/F levels rose from 71.4 g/year in 2002 to 90.3 in 2005, and similar figures are registered for particulate matter (PM) as shown in above graphic, for SO_x (ranging from 37958.7 Mg/year in 2002 to 41840.5 Mg/year in 2005), NO_x (25185.9 Mg/year to 41840.5 Mg/year), PAHs (25913.9 kg/year to 31124.3 kg/year). On the other side, Italian emissions of PCDD/F decreased in this period from 222.5 g/year to 103.0 g/year in 2005, so the contribution of Taranto plant to total national PCDD/F emissions grew from 32% to 90%.

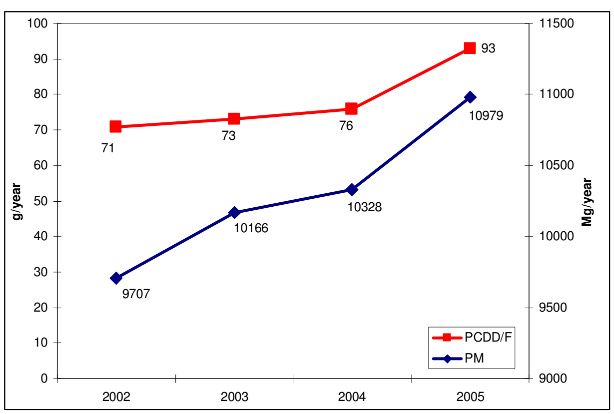

Fig. 2 Trend of PCDD/F and PM emissions from Taranto Plant. 2002-2005 (Estimated data)

The reported data largely justify the peculiar attention paid to the on-going monitoring campaign, both for the Institutions involved and for population living in the area. A critical point is also the Italian legislation about threshold values established for PCDD/F.

PCDD/F emission limit values (ELVs), applying to metal industry, have been introduced only in a few countries, e.g. AU, BE, CZ, DE, SE. In Italy a general emission limit for dioxins has been in force since 1990 (confirmed by the last Law 152/06) which all industrial installations must comply with. That ELV refers to total dioxin concentration instead of I-TEQ, while threshold for soil and water are defined as I-TEQ.

ELV for existing installations in Italy is being set to 0.01 $mg_{total\ dioxins}/Nm^3$. Depending on the profile of emitted dioxin congeners, it can be estimated that this ELV converts to a range of 100-500 $ng_{I\text{-}TEQ}/Nm^3$ which is orders of magnitude higher than all other currently applied ELVs in EU.

The value is quite high thus it is unlikely it could be exceeded by any plant even under the worst conditions. It is noteworthy that for incinerators a national Law 133/05 establishes a threshold of 0.1 $ng_{I\text{-}TEQ}/Nm^3$. More recently, in the north-eastern Italian region of Friuli Venezia-Giulia a regional law required a sinter plant located in Trieste not to exceed a limit value of 0.4 $ng_{I\text{-}TEQ}/Nm^3$.

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