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DIOXINS AND FURANS AS POLLUTANT EMISSIONS FROM INTEGRATED STEEL WORKS

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ABSTRACT

In the metallurgical industry are several sources for pollutant emissions but the main source is the sintering process. In this paper are analyzed the generation process of persistent organic pollutant emissions (dioxins and furans) mainly from the sintering sector. Also, the emergent techniques that must be apply to prevent or to control emissions of persistent organic pollutants-POPs (the category of substances that includes the dioxins and furans) from iron ores sintering process are presented. These were selected in accordance with best practices that are specifically for the integrated steel works.

KEYWORDS*:* dioxins, furans, sintering process, emergent techniques

1. Introduction

Since 1920, as a result of global industrialization the global level of dioxins increases. The decreasing of dioxin level in the environment and the endeavor to control the environmental pollution phenomena began in 1970, when PCBs were recognized as highly toxic chemicals [1].

Dioxins and furans, more precisely polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are two of the twelve Persistent Organic Pollutants (POPs) covered by the Stockholm Convention on Persistent Organic Pollutants (POPs). PCDD/PCDF, together with polychlorinated biphenyls (PCB) and hexachlorobenzene (HCB) are listed in Annex C of the Stockholm Convention POPs; they are unintentionally generated and are commonly named "by-products". Polychlorinated dibenzo-p-dioxins (dioxins, PCDD) and polychlorinated dibenzofurans (furans, PCDF) are two groups of planar, tricyclic ethers which have up to eight chlorine atoms attached at carbon atoms 1 to 4 and 6 to 9, Figure 1 and 2.

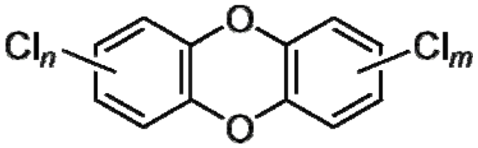

Fig.1. *General structure of PCDDs where n and m can range from 0 to 4.*

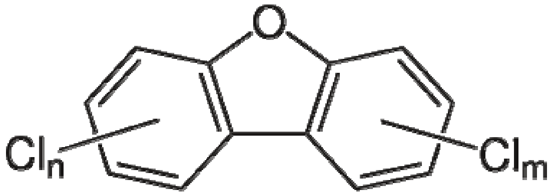

Fig.2. *General structure of PCDFs, where $2 \le n+m \le 8$.*

In total, there are 75 possible PCDD congeners and 135 possible PCDF congeners giving a total of 210 congeners. Dioxins and furans are generally very insoluble in water, are lipophilic and are persistent. PCDD and PCDF have never been produced intentionally but are unwanted by products of many chemical industrial processes and of all combustion processes.

Almost all possible 210 congeners are released from these sources and, due to chemical, physical, and biological stability and longrange transport, are ubiquitous and have been detected in all environmental compartments.

Due to the persistence of the 2, 3, 7, 8-substituted congeners and the lipophilicity of these compounds, PCDD/PCDF accumulate in fatty tissues and in carbon-rich matrices such as soils and sediments.

2. Sintering of iron ores as main source for pollutant emissions of dioxins and furans in the integrated steel works

According to statistics provided by EUROFER, for the EU countries the most important quantity of steel is produced in the blast furnace/basic oxygen furnace route (approximately 62% in 2003). In these integrated flows, sinter plants have an important role for the iron ores preparation. Sinter is produced from predesigned mixtures.

Sintering involves the heating of fine iron ore with flux and coke fines or coal to produce a semi-molten mass that solidifies into porous pieces of sinter with the size and strength characteristics necessary for feeding into the blast furnace.

At the same time, they provide the opportunity for recovery of waste that contained useful elements. In some integrated steel works the sinter process is the unique possible technological solution to be applied for recycling internal valuable wastes [3, 4].

The flexibility of the sintering process permits conversion of a variety of materials, including iron ore fines, captured dusts, ore concentrates, and other iron-bearing materials of small particle size (e.g., mill scale) into a clinker-like agglomerate.

In addition to sinter, residues or wastes result from process. In integrated steelworks applying the blast furnace/basic oxygen route, sinter plants dominate the overall emissions for atmospheric pollutants [5]. From the materials-handling operations results the airborne dust, and from the combustion reaction on the strand result products of combustion such as CO, CO_2, SO_x, NO_x, and particulate matter. As result the sintering process produces a large variety of pollutants like dust, heavy metals, SO_2, HCl, HF, Polycyclic aromatic hydrocarbons (PAHs) and also chlorinated organic compounds (polychlorinated biphenyls-PCBs; polychlorinated dibenzo-*p*-dioxins-PCDD and polychlorinated dibenzofurans-PCDF) etc. In the European Union, the following air pollutants emitted from the process of sintering iron ores are important: particulate matter, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Tl, V, Zn, HCl, HF, NO_x, SO_2, CO, CO_2, VOCs (volatile organic compounds), PAHs, PCDDs/PCDFs and PCBs. In accordance with CORINAIR standard, except gaseous ammonia all components are known to be emitted from sinter plants, Table 1 [6].

Table 1. *Contribution of the pollutant emissions from iron ore sintering plant reported to global emissions of inventory CORINAIR 90 (Made for the EU Member States)*

Source / Sinter process	Contribution to the global emissions [%] (including those issued in nature)										
	SO_2	**NO_x**	**NMVOC**	**CH_4**	**CO**	**CO_2**	**N_2O**	**NH_3**	**TSP***	**PM_{10}***	**$PM_{2.5}$***
Typical contribution	1.3	1.0	0.1	0.1	4.9	0.4	-	-	1.82	1.96	2.97
Maximum value									5.13	5.37	9.09
Minimum value									0.245	0.234	0.321

* EU $PM_{2.5}$ Inventory project for EU25 for year 2000 (TNO 2006) (contribution to total emissions, excluding those related to agricultural soils)
0 – emission reported but the exact value is lower as rounded limit (0.1 %)
- missions were not reported

Most of the SO_2 emission has its origins in sulphur of the coke combustion. For the nitrogen oxides, NOx emission is the predominant as a result of rapid cooling gas. The main source of the NOx emissions is the nitrogen content of coke (approximately 80%) and the iron ores (approximately 20%). Raw materials are responsible to heavy metal emissions.

In generally, the dust released is associated to the heavy metals emission. During sintering process, some heavy metals are volatilized from the raw materials used and pass in the flue gas as volatile compounds (eg. chlorides).

We refer mainly to Zn, Pb and Cd. Arsenic is emitted in the gas as As_2O_3. In the presence of carbon and chlorine or its precursor such oily components, polycyclic organic compounds (PAHs, PCDD/PCDF) are formed.

Some wastes, such as mill scale may be contaminated with oil residues that are the precursors for the formation of polycyclic aromatic hydrocarbons, dioxins and furans respectively. In the same time, chlorine compounds can be brought into the process of sintering iron ores or coke. The chlorine content of the input material deposed as strand on the sintering bed increases from the recycled materials as dust/sludge from the cleaning off-gas system and as mill scale or sewage sludge. This is reflected in the nature and concentration of the inorganic gaseous chlorine compounds involved in waste gas emissions or on fine dust particles generated in the sintering process. Therefore, for the iron ores sintering process the raw materials are the main source of dioxins and furans emissions, Figure 3. The majority of these emissions are found distributed in the air and solid waste, Table 2.

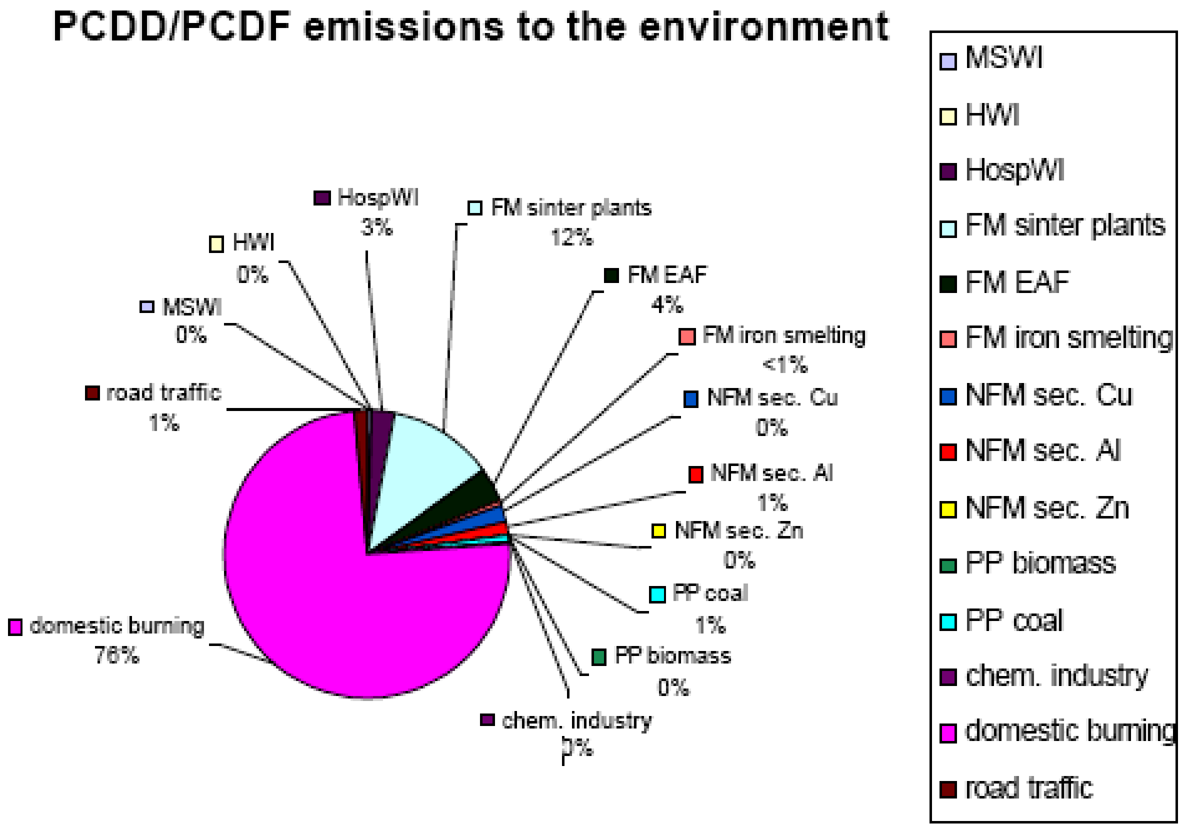

Fig. 3. *Share of dioxins and furans emissions from iron ores sintering process reported to relative distribution of air emissions from investigated sectors in EU 25 [7].*

Table 2. *UNEP* matrix for the dioxins sources contained in Category 2 and the emission factors for the iron ores sintering [μg I-TEQ/t product] [7].*

Subcategory UNEP	Cod SNAP	Dioxins/Furans contained in:				
		air	water	soil	product	residues
2a	30301/40	0.3				0.003

*UNEP – United Nations Environment Programme

According to material balance, together with ferrous sinter, sewage sludge from wastewater treatment, dust from flue gas treatment and de-dusted gases discharged into the atmosphere or recirculated in the sinter strand are significant outputs of the sintering process.

Reported to the liquid steel production of an integrated steelworks, can be appreciate that from the treatments for cleaning gas the amount of dust resulted ranging from 0.9 to 15 kg/t. According to European steel production, the majority of facilities used the recycling of sinter off-gas (waste-gas).

Recirculation of part of the off-gas from the entire sinter strand, or sectional recirculation of off-gas, can minimize formation and release of pollutants.

The dust arises from dry cleaning of the wastes gases contain alkali and metal chlorides. These emissions can be reduced if the waste gas dedusting operations are developed in several steps (by using the bag filters and scrubbing system).

The dust amount and sludge resulted from these treatment steps is higher, i.e. approximately 0.2...0.5 kg dust/t, respectively ~0.3 kg sludge/t for which it was considered a contamination with dioxins and furans in the range <0.01 to 20 ppb (mean value approx. 1.1 ng TEQ/g). The annual amount of the off gas released from sinter strands was estimated at approx. 2300 Nm^3, with a contamination level reported for EU states in the range 0.1...5 ng TEQ/Nm^3 (for the off-gases the medium value of PCDD/PCDF contamination is 1.2 ng TEQ/Nm^3, taking into account the optimization measures implemented to the sintering processes). At a European scale the estimated emissions amount are ~ 595 g TEQ/y. Thereof ~525g are emitted to air and ~70g are emitted to waste. Dioxins emissions and furans released to the sinter production for the UE states are presented in Table 3 [7, 8].

Table 3. *Country specific estimation on emitted amounts of dioxins and furans in the year 2003*

Country	**Production of crude steel (oxygen)** [kt/y]	**Emission to air** [g TEQ/y]	**Discharge to flue gas treatment as residues** [g TEQ/y]
AT	3.700	10.2	2.0
BE	15.300	42.0	8.4
CY		0.0	0.0
CZ	6.330	126.6	3.5
DE	28.950	79.5	15.9
DK		0.0	0.0
EE		0.0	0.0
ES	5.400	14.8	3.0
FI	2.700	7.4	1.5
FR	21.550	59.2	11.9
GR		0.0	0.0
HU	900	4.5	0.5
IE		0.0	0.0
IT	11.500	31.6	6.3
LT		0.0	0.0
LU		0.0	0.0
LV		0.0	0.0
MT		0.0	0.0
NL	4.400	12.1	2.4
PL	9.000	13.5	5.0
PT		0.0	0.0
SE		0.0	0.0
SI	250	5.0	0.1
SK	4.000	80.0	2.2
UK	13.800	37.9	7.6
EU-25	127.780	524.4	70.3
EU-15	107.300	294.8	59.0
EU-10	20.480	229.6	11.3

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3. New and emergent techniques to reduce emissions of dioxins/furans generated in the iron ores sintering sectors

There are several factors to prevent or control emissions of persistent organic pollutants-POPs (the category of substances that includes the dioxins and furans) from stationary sources. Also there are the available measures that can be applied separately or together.

One of these measures is to replace raw materials that have POPs content, if any direct relationship exists between POPs emissions and input materials. Although not determined a precise relationship between chlorine content of raw materials and emissions of dioxins/furans, should be eliminated or reduced the oil impurities from the wastes recycled, prior to their use of sinter strands.

Halogenated compounds can be a source of dioxins/furans in the sintering process if these are present in the input materials subjected to the thermal agglomeration (coke dust, salts from the ores) and in the recyclable materials added (blast furnace dust, steelmaking dusts, sludge from wastewater treatment, mill scale etc.) [9, 10].

The avoid use of the contaminated material (associated with the helplessness to recycling by other ways the wastes with high iron content as a substitute for iron ores) leads to accumulation of considerable quantities of landfilled wastes with negative effects especially on the environment. These are determined by the storage on large areas, and potential risks of air, soil and water pollution in case of uncontrolled storage and long times. Other methods relate to the application of best environmental practices, such as sound internal flow, preventive maintenance programs; the control of the processes to ensure complete combustion and to minimize the formation and release of PCDD, PCDF and other pollutants by the control parameters (temperature of combustion, strand speed, bed composition, optimum flue gas treatment by post-combustion, thermal or catalytic oxidation, adsorption or cleaning), treatment applied to sewage, residues or sludge from cleaning systems etc [11, 12].

Most effective solution to reduce the dioxins and furans emissions is to combine different secondary measures, the so-called measure "end-of-pipe", as follows [13-15]:

- recirculation of off-gases (recycling of sinter off-gas) which significantly reducing of the dioxins/furans emissions and more significantly which reducing of the gaseous effluents flow. On this way, the cost of the devices installing for the anti-emissions on the discharge is diminished;

- utilisation as removal techniques the following: the textile filters/filter bags; the adsorption/absorption that involves sorption of PCDD and PCDF to a material such as activated carbon together with effective particulate matter (de-dusting) control; the regenerative activated carbon technology (the electrostatic precipitator is used to reduce dust concentration in the off-gases prior to entry to the activated carbon unit); the sorption technique that use of lignite or activated carbon injection, together with a fabric filter; the fine wet scrubbing system

4. Conclusions

The PCDD/PCDF emissions of the sintering sectors from the ferrous metallurgy are quite significant, they are typically in range of 0.4 to 4 ngET/m^3.

To prevention and control of these emissions must be applied the solutions adapted from Best Available Techniques (BAT). In the European Union are known and implemented a series of process integration techniques, specific emerging technologies for sinter plants are following: the optimizing of the processes to minimize the dioxins and furans emissions; the recycling into sinter process of the wastes containing iron content; decreasing of the oil content in materials feed to the sinter strand, reducing the sulphur content in feed for sintering; heat recovery from sintering and cooling sinter process; off-gases recirculation.

However, for sinter plants of the European Union states is necessary to use the following "end-of-pipe" techniques like the using of the dry electrostatic precipitation, dust filters, cyclone, with fine wet scrubbing systems, gas desulphurization of gases wastes, selective catalytic reduction etc.

Environmental concerns and also the high operating costs led to declining use of traditional sinter plants. In return, were developed other techniques which allow increasing the amount of wastes recycled in the feed mixtures (as an alternative to sintering process). Some of these are tested in the pilot-scale plants. These methods (rotary hearth processes-Inmetco, fluidized bed process, smelting plasma processes-Siromelt, Plasmelt, Daido Special Method, CONTOP, RADUST) [13].

For these recycling solutions, the main objective is to apply special treatment before recycling wastes. These involve decomposition, vaporisation and separation of heavy hydrocarbons and also zinc and other heavy metals (if they are present in remarkable amounts of iron-containing wastes).

From a technical standpoint it is possible to solve these problems. The following solutions are available: the selective leaching of zinc, lead and other heavy metals by hydrometallurgical treatment; processing at high temperature to vaporize the zinc and lead and to decompose of the heavy hydrocarbons and cyanides. The aims of pirometallurgical methods are the reducing of the iron oxides. The product resulted from process is a molten alloy (similar to blast furnace product) or an oxides melts with high iron content. In the first case, the product is loaded directly into the basic oxygen furnace as a substitute for ferrous scraps. In the latter case, iron-rich slag can be recycled into sinter plants or into blast furnace.

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