PCDD/F PROFILES OF AN IRON ORE SINTERING PLANT

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Introduction

Dioxin is formed as an unintentional by-product of many industrial processes involving chlorine such as waste incineration[1,2,3], chemical and pesticide, pulp and paper bleaching and sintering plants.

Regarding the European dioxin air emissions[4], in 1985 the most important emission source was the municipal waste incineration: in 20 years there was a dramatic decrease of these emissions by about 90% from the 4000 g I-TEQ/year initial value to 200 g I-TEQ/year. In the same years, the iron ore sintering emissions decreased by about 50% from 1500 g I-TEQ/year to 400 g I-TEQ/year. So at the moment the iron sintering process is the principal PCDD/F source[5].

Iron sintering plants are associated with the manufacture of iron and steel, often in integrated steel mills. The sintering process is a pre-treatment step in the production of iron, where fine particles of iron ores are agglomerated by combustion. Agglomeration of the fines is necessary to enable the passage of hot gases during the subsequent blast furnace operation[6].

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. Moistened feed is delivered as a layer onto a continuously moving grate or "strand." The surface is ignited with gas burners at the start of the strand, and air is drawn through the moving bed causing the fuel to burn. Strand velocity and gas flow are controlled to ensure that "burn through" (i.e. the point at which the burning fuel layer reaches the base of the strand) occurs just prior to the sinter being discharged. The solidified sinter is then broken into pieces in a crusher and is air-cooled.

Combustion gases are cleaned in electrostatic precipitators (ESPs), which significantly reduce dust emissions. Water scrubbers (Wetfine) is then used for its high collection efficiency for gaseous emissions[7].

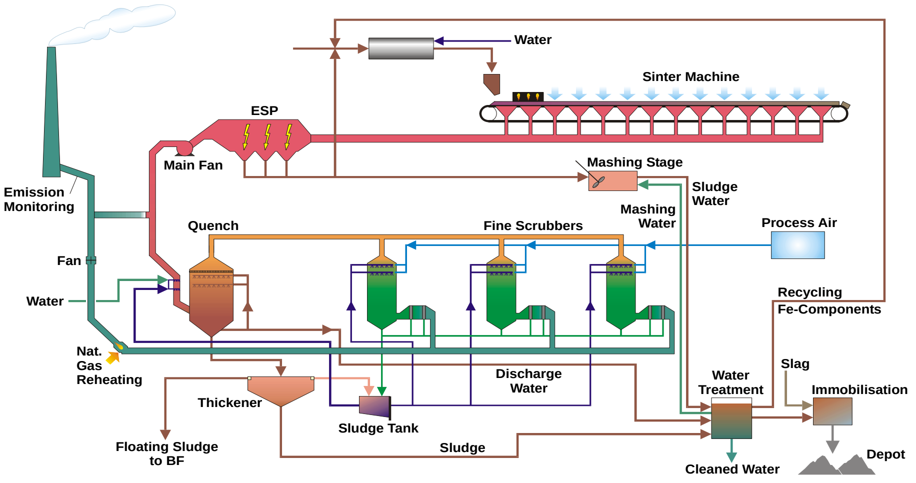

Fig.1 Plant layout

Materials and Methods

Sampling
Three campaigns were carried out: three PCDD/F samplings lasting 8 hours were performed in each campaign.
A glass probe was used and isokinetic conditions were maintained along the whole sampling period. The temperature of the probe was mantained at 125°C before and during filtration. After the thermostatic filtration, the gas was cooled down to 4°C to condense water and other condensable and adsorbed into a PUF. The thimbles were previously spiked by labelled ^{13}C sampling standards according to the EN1948 methods part1.

Analysis methods
The PCDD/F were monitored according to the EN1948 methods part 2 and 3. The analysis were carried out recovering the pollutants by liquid-liquid extraction from the condensed water and by solid-liquid (i.e. toluene) extraction with Soxhlet from particulate and PUF and collecting all together. After a two-stage clean-up involving a multi-layer silica and an allumina column, the extract was finally analyzed by HRGC/HRMS. A gas chromatograph Fisons 8000 coupled with a selective mass detector VG Autospec was used, operating in SIM mode. The concentrations were calculated considering half of the detection limit for those compounds not detected. The concentrations were reported with reference to normal conditions and 11% of oxygen.

Results and Discussion

In a sintering plant many factors condition the PCDD/F formation, the sintering process can be unstable and the operative variables are hard to check: many authors suggest carrying out a continuous monitoring to minimize the variables due to the process fluctuations[8].
Therefore we carried out a 10 days monitoring, splitted in three campaigns of three samplings each one.
The Tab.1 shows the three samplings concentration for each campaign and the average value.
The PCDD/F concentration ranges from 0.07 to 0.53 ng I-TEQ/Nm^3.

PCDD/PCDF I-TEQ (ng/Nm^3)

Campaign / Sampling	C1	C2	C3
R1	0,51	0,45	0,16
R2	0,35	0,07	0,34
R3	0,22	0,53	0,18
Average	**0,36**	**0,35**	**0,22**

Tab.1 PCDD/F concentration (ng I-TEQ/Nm^3) at the stack

Fingerprint of PCDD/Fs congeneres
The analysis of a congeneres profile is difficult because it is a result of formation, accumulation and mixing of dioxins at different positions and time during the process.
The iron sintering is of course one of combustion processes; therefore its congeneres profile has the characteristics of the combustion pattern in an incineration process[9]. Common features can be pointed out for these profiles:

- the total concentration of PCDFs is larger than PCDDs by more than 10 times [5,9,10] (expressed in ng/Nm^3 and not corrected by TEF) (Tab.2)

Campaign	Concentration [ng/Nm^3]	
	PCDD	PCDF
C1	0,23	3,38
C2	0,17	3,34
C3	0,08	2,16

Tab.2 Comparison PCDD-PCDF (ng/Nm^3)

- comparing PCDDs (Tab.3) and PCDFs (Tab.4) profiles[9], in PCDDs the highly chlorinated congeneres have definitely a larger concentrations compared with the other ones

Congeners / %	C1	C2	C3
2,3,7,8-TetraCDD	2	3	6
1,2,3,7,8-PentaCDD	3	5	5
1,2,3,4,7,8-HexaCDD	4	4	7
1,2,3,6,7,8-HexaCDD	7	6	11
1,2,3,7,8,9-Hexa-CDD	5	7	7
1,2,3,4,6,7,8-HeptaCDD	32	33	26
OctaCDD	46	43	39

Tab. 3 PCDD fingerprint (% = [ng/Nm^{3}congener]/[ng/Nm^3 PCDD total])

Congeners / %	C1	C2	C3
2,3,7,8-Tetra CDF	12	12	29
1,2,3,7,8-PentaCDF	9	11	11
2,3,4,7,8Penta CDF	12	17	18
1,2,3,4,7,8-HexaCDF	12	12	10
1,2,3,6,7,8-HexaCDF	11	9	8
2,3,4,6,7,8-HexaCDF	9	8	7
1,2,3,7,8,9-HexaCDF	5	4	2
1,2,3,4,6,7,8-HeptaCDF	18	17	10
1,2,3,4,7,8,9-HeptaCDF	3	3	1
OctaCDF	10	8	4

Tab.4 PCDF fingerprint (% = [ng/Nm^{3}congener]/[ng/Nm^3 PCDF total])

Clearly, multiplying the concentrations by TEFs, the profiles change with the prevalence of PentaCDF over all the congeners of PCDDs and PCDFs, and of TetraCDD among the PCDDs.

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