POP EMISSIONS IN SPANISH STEELMAKING FACILITIES

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Introduction

Thermal processes involving organic matter and halogens have been demonstrated as halogenated aromatic compound sources[1]. For this reason, early researches focused on emissions from municipal waste incinerators. However, considerable attention is now also directed towards other industrial sources, in particular the metallurgical industry[2,3,4].

Recycling of iron and steel scrap into valuable steel is generally performed through the Electric Arc Furnace (EAF) process, where technically clean scrap is melted using electrical energy produced by striking an arc between the scrap charge and carbon electrodes. The resulting liquid is further refined, cast and finished in the same way as in the integrated process. Ferrous scrap is divided into different classes in order to optimize melting conditions and control of the metal composition, but these classes do not necessarily reflect the purity from contaminants of environmental concern. The composition and purity of the raw materials is one essential factor, another being the level of oxidation or combustion conditions in the melting process[5]. Tramp substances, such as paint, oil and coatings, which are not removed by scrap preparation, may contain precursors that can generate several persistent organic compounds, POPs, by combustion under unfavourable conditions or by de-novo synthesis[6].

Emission generating operations during the EAF steelmaking are: charging the scrap, melting and refining, removing slag, tapping steel, continuous casting and ladle metallurgical processes. These related emissions are generally collected using directed shell evacuation and supplemented with a canopy hood located above the EAF. The EAF processes produce both particle and gas-phase pollutants, with the amount and composition of the particles varying as a function of the scrap composition and types and amounts of furnace additives. In general, the captured emissions are routed to bag filters for particulate matter control[7,8].

In 1998, the Spanish Ministry of the Environment and Rural and Marine Affairs (MARM), the Energetic, Environmental and Technological Research Center (CIEMAT) and the Spanish Council for Scientific Research (CSIC) began developing the National Inventory of dioxin and furan sources. This project was designed to achieve three main objectives: (a) to evaluate PCDD/F emissions into the atmosphere, soil and water, (b) to characterize the residues from industrial activities (flue gases, fly ashes, slags, …), and (c) to compare their relative contribution and the total release of PCDD/Fs in the environment. However, in 2007 it was decided to increase the number of POPs considered from PCDD/Fs, DL-PCBs, hexachlorobenzene (HCB) and polycyclic aromatic hydrocarbons (PAHs). Consequently, several Spanish steelmaking facilities have been studied during 2009, in the frame of the Spanish POP Inventory. Data obtained in this survey correspond with the flue gas and fly ash matrices.

Materials and Methods

Seven steelmaking facilities, at different locations throughout Spain, were evaluated. All of the plants used similar technology. First, the facilities perform a preliminary separation of raw materials, before introducing them selectively into EAFs. From there, the liquid metal passes into steel refining furnaces, where some salts are added to create the different types of ferroalloys. The gas treatment systems consist mainly of: (a) gas cooling systems based on heat exchangers or air dilution, (b) particle pre-treatment systems based on particle sedimentation chambers or cyclones, and finally (c) bag filters. Their production capacities ranged between 120,000 and 1,500,000 t/a. All of the plants, except one, were sampling twice to check the repetibility of the industrial processes.

Although there is an established EU standard for the determination of PCDD/F and DL-PCB concentrations in stack gas from waste incineration (European standard EN-1948:1, 2, 3, 2007, UNE-CEN/TS 1948-4:2009)[9], these standards are not actually valid for the determination of all the compounds considered. Therefore the method used in this work was developed for sampling all POPs in a single run[10], particularly changing the amount of resin XAD-2 used. Accredited firms engaged for sampling had to adapt their systems to the new specifications. The sampling train was performed by the filter/condenser method as described in EN-1948, 2007, Part 1. In this work, gaseous and particulate POPs were withdrawn isokinetically and large volumes of flue gas were collected (average volume of 10 Nm^3, equivalent to 6-8 hours of sampling) with an amount of XAD-2 no less than 60 g. After sampling all parts of the system (nozzle, probe, filter holder, glass tube, and condenser) were rinsed with acetone and toluene.

Extraction, clean-up and analysis of flue gas samples fulfilled the minimum requirements described in the European Standard UNE-EN-1948-1,2,3:2007 for dioxins and furans, in the TS 1948 Part 4, 2007 for DL-PCBs and in the CARB 429 for PAHs[11]. HCB analysis was performed using internal procedures. Briefly, XAD-2 and glass filter were soxhlet extracted while the condensate taken from the condenser upstream the resin cartridge was liquid-liquid extracted with dichloromethane. Then, the extract from the condensate was added to the rinsing solvent and combined with the extract obtained with the soxhlet. At this point, an aliquot was taken for PAH analysis. In parallel, an Accelerated Solvent Extraction system (ASE 200, Dionex, Sunnyvale, CA, USA) was used for extracting fly ashes sampled from the bag filters. Clean-up for both flue gases and fly ashes was performed by using multilayer silica, alumina and carbon columns... Final extracts were concentrated and analysed by HRMS on a Micromass Ultima NT HRMS at 10,000 resolving power connected to an Agilent GC 6890. Identification and quantification was carried out using isotopic dilution.

Results and Discussion
Table 1 summarises results related to the different matrices evaluated, flue gas and fly ash, coming from the gas cleaning systems of each steelmaking facility. As mentioned previously, all plants were sampled twice except that referenced as 7. Therefore, the data shown in Table 1 correspond to both samplings.

Table 1. ∑PCDD/F, ∑DL-PCB, HCB and ∑PAH emissions from seven Spanish steelmaking facilities evaluated during 2009.

REF	Flue Gas				Fly Ash			
	∑PCDD/Fs (ng I-TEQ/Nm^3)	∑DL-PCBs (ng I-TEQ/Nm^3)	HCB (ng/Nm^3)	∑PAHs (ng/nm^3)	∑PCDD/Fs (ng I-TEQ/g^3)	∑DL-PCBs (ng I-TEQ/g)	HCB (ng/g)	∑PAHs (ng/g)
1	0.45 – 3.88	0.06 – 0.13	>16.88->23.69	1442 - 3815	1.00-3.29	0.01-0.04	2.22 -9.26	4562-26486
2	0.02-0.19	0.001-0.01	2.04-42.02	227-524	0.73-2.30	0.01-0.04	3.16-13.62	4317-7387
3	0.06-0.77	n.a.-0.03	n.a.->18.24	n.a.-1073	1.48-2.68	0.05-0.10	2.35-7.20	68-5767
4	0.01-0.12	0.001-0.03	2.46-24.95	192-672	0.45-0.98	0.01-0.04	0.90-0.93	4464-9321
5	0.01-0.01	0.002-0.002	1.66-4.08	491-791	0.20-1.86	0.01-0.06	0.21-0.77	1092-132963
6	0.03-0.03	0.005-0.01	10.83-12.03	264-369	0.52-1.54	0.02-0.05	0.44-0.52	4170-4861
7	0.18	0.02	>15.13	430	0.90	0.01	0.94	1444

n.a. = not available

1. PCDD/Fs
Data related to flue gas show a wide range of PCDD/F concentrations. They varied between 0.01 and 3.88 ng I-TEQ/Nm^3, with a mean and median value of 0.43 and 0.03 ng I-TEQ/Nm^3 (n = 13), respectively. As can be observed, in most facilities data are not reproducible, probably reflecting the heterogeneity of scrap used in the steel production process. These results are comparable to those found in other European Countries such as, Italy[12], Germany, Luxembourg and Sweden[13], except the maximum result related to facility 1. It is remarkable that most plants present a PCDD/F content below 0.5 ng I-TEQ/Nm^3, which is the value associated with the use of the Best Available Techniques in the Ferrous Metal Industries [7].

PCDD/F concentrations associated to the fly ash varied between 0.20 and 3.29 ng I-TEQ/g, presenting mean and median values of 1.38 and 1.00 ng I-TEQ/g (n = 13), respectively. These data reveal that the reutilization of such

ashes in other industrial processes would involve the mobilisation or incorporation of these pollutants and could increase and/or incorporate the POP contents in final products or other wastes[14].

All facilities have presented very similar PCDD/F congener patterns, with furan groups representing the most important contribution to total mass concentration and toxicity both for flue gas and ash matrices. Figure 1. plots the distribution of 2,3,7,8 congener toxic contribution for fly ashes. As can be shown, 2,3,4,7,8-PeCDDF is the most toxic congener in all cases. Similar behaviour has been reported for metallurgical industries in other countries[12,15,16].
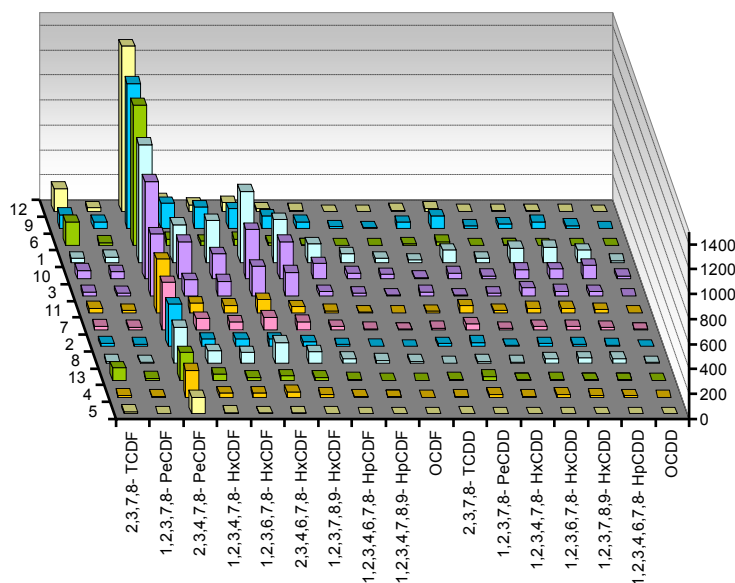

Figure 1. PCDD/F profiles in fly ashes coming from seven steelmaking facilities (ng I-TEQ/g). Samples 8, 9, 10, 11, 12 and 13 correspond to the repeated samplings in plants 1, 2, 3, 4, 5 and 6 respectively.

2. DL-PCBs

Presently there is no legislation to control the DL-PCB emission, but some countries, such as Spain, are already including them in their POP inventories. Therefore, the values measured in flue gas of the seven steelmaking plants ranged between 0.001 and 0.13 ng WHO-TEQ/Nm^3, mean: 0.02 ng WHO-TEQ/Nm^3 and median: 0.01 ng WHO-TEQ/Nm^3 (n = 12). Similarly, the results of DL-PCBs in fly ashes ranged between 0.01 and 0.10 ng WHO-TEQ/g, mean: 0.03 ng WHO-TEQ/g, median: 0.02 ng WHO-TEQ/g (n = 13). The contribution of DL-PCBs to gas emission and fly ash toxicity is lower than that related to PCDD/Fs in all cases. For PCDD/F, all facilities have presented very similar congener patterns: PCB 118 was the most abundant congener followed by PCB 105, but PCB 126 was the most toxic.

3. HCB

The values obtained for HCB ranged between 1.70 to 42.02 ng/Nm^3 in flue gas, mean: 12.51 ng/Nm^3, median: 7.45 ng/Nm^3 (n = 12), and between 0.21 and 13.62 ng/g in fly ash, mean: 3.31 ng/g, median: 0.94 ng/g (n = 13). These values are similar to those related to fly ash coming from Italian facilities and lower in the case of flue gas samples[12].

4. PAHs

The PAHs considered were the 6-Borneff ones, used by the World Health Organisation as indicators of the PAHs burden from a sample. Results ranged from 192 to 3815 ng/Nm^3, mean: 857 ng/Nm^3, median: 507 ng/Nm^3 (n = 12) in flue gas, and from 68 to 132 963 ng/g, mean: 15 915 ng/g, median: 4562 ng/g (n = 13), in fly ash. These data are in the same order as those reported for steel and iron facilities in Taiwan[4] but lower than those for other secondary metallurgical industries[17]. Regarding the distribution of the different congeners, fluoranthene was the most abundant in all flue gas samples, representing more than 75% of total PAHs. Fluoranthene was the predominant congener in 8 fly ash samples, while benzo[b]fluoranthene was in the others.

Figure 2 represents the comparison between the levels of PCDD/Fs, DL-PCBs, PAHs and HCB in flue gas. In general terms, there is a lack of reproducibility in POP levels, especially for PCDD/Fs but also in PAHs for fly ash (see Table 1). Such variability of the data could mainly be due to the differences between production processes (operation conditions of the EAFs, raw material used ...). The use of cleaner scrap, free from oil and/or paints, coatings, enamels, etc. can lead to samples with a lower content of POPs.
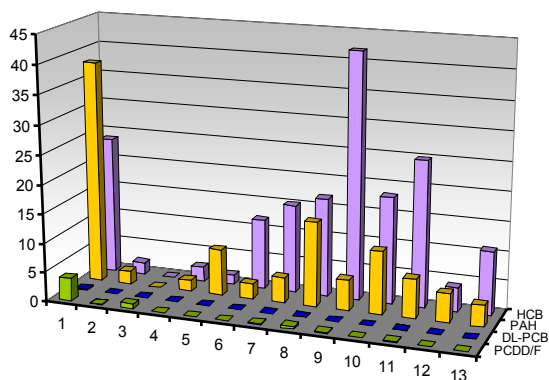

Figure 2. *Levels of PCDD/Fs, DL-PCBs, PAHs and HCB for flue gas Scale: PCDD/Fs DL-PCBs in ng I-TEQ/Nm³; PAHs in 100 x ng/Nm³ and HCB in ng/Nm³. Samples 8, 9, 10, 11, 12 and 13 correspond to the repeated samplings in plants 1, 2, 3, 4, 5 and 6 respectively.*

Results of this study revealed the presence of high outliers influencing mean POP levels. For this reason, the Working Group recommends some of these plants to install dioxin abatement systems, which could reduce these values, narrowing the data range and helping to establish accurate emission factors of this metallurgical industrial sector.

Acknowledgements

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