PCDD/F EMISSIONS IN HOT-DIP GALVANISING FACILITIES. EVALUATION IN THE FRAME OF SPANISH DIOXIN INVENTORY

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Introduction

Galvanising is a corrosion protection process for steel in with it is coated with zinc to protect it from rust. Protection from corrosion and long life is essential to use steel in construction, transport, agriculture and power transmissions. Galvanising will protect steel structures for decades and minimises maintenance, saving energy and resources.

Nevertheless, because of physicochemical characteristics of the process, the formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) is favoured. Therefore, the "Hot Galvanising Sector" was considered as a possible PCDD/F source in the European Inventory[1,2]. PCDD/F presence in this sector, classified in CORINAIR as code n. 040307, are included in the national inventories of Germany and Switzerland[3], and from the Danish Environment Protection Agency[4], corresponding emission factors were indicated.

In the frame of the Spanish Dioxin Inventory, the evaluation of this sector was established. During the 2002 survey, ten installations were considered to be a sufficient representation of the Spanish sector and were sampled. Solid matrices: ashes from the surfaces of Zn bath, dust from gas cleaning systems and air emissions were measured to quantify and characterise their PCDD/Fs content.

We present here the data obtained in this survey for ashes, filter dust and flue gases and the preliminary emission factors for facilities equipped with gas cleaning systems.

Materials and Methods

1. Process Description

The “hot dip galvanising” process consists on immersing clean, oxide-free iron or steel into molten zinc to form a zinc coating, which is metallically bonded to the iron or steel's surface. Thus, this zinc coating protects the ion or steel surfaces against corrosion[5]

All galvanising consists on four fundamental steps: surface preparation, prefluxing, galvanising and finishing. The preparation steps consist in cleaning and pickling operations that free the surface from dirt, grease, rust and scale. The preflux step serves to dissolve any oxide that may have been formed on the iron or steel surface after pickling and prevents formation of rust. Clean, oxide-free work is galvanised by immersion into molten zinc. Finishing operations include quenching, removing excess zinc and inspection. The galvanising reaction only occurs on a chemically clean surface. It is essential that this is free from grease, dirt and scale before galvanising. Contamination is removed by a variety of processes. Common practice is to degrease with an *alkaline or acidic* degreasing solution into which the component is dipped. The article is then rinsed and finally dipped in *hydrochloric acid* at ambient temperature to remove rust and mill scale. After further rinsing, the components undergo a fluxing procedure. This is usually a solution of about *30% zinc ammonium chloride at around 65-80°C.*. The clean iron or steel component is dipped into the molten zinc (which is commonly about 450°C). A typical immersion time is four or five minutes but it can be longer for heavy articles having high thermal inertia or when the zinc is required to penetrate internal spaces. Post galvanising treatment can include quenching into water or air-cooling.

Hot dip galvanising process was shown to be a source of PCDD/Fs emission. This is due to the presence of factors favouring the generation of these pollutants during the different steps: 450ºC bath temperature, chlorine presence (Cl_2Zn-$ClNH_4$ in the fluxing step), presence of particulates, organic matter (grease remaining in works and/or bath composition) and presence of metallic catalyse (zinc, iron chloride and metallic impurities from baths).

2. Sector Description in Spain

In Spain forty plants compose discontinuous hot deep galvanising sector. Presently, twenty six of them (65 %) already use bath enclosures capture and gas cleaning equipment (bag filters) and are related to a 72,7% of 502 kTm of annual production galvanising steel during 2002. The others fourteen (35 %), will implement gas treatment in the near future to fulfil the 96/61 IPPC European Directive and are responsible of 27.3% of the total galvanising steel production. From the 26 installations working with gas cleaning systems we have selected ten of them, following indications of the Galvanising Spanish Technical Sector (ATEG). They consider these plants constitute a good preliminary representation on this type of installations.

Table 1 summarises installations reference and the sample types The samples included filter dust, flue gas and ashes placed on the molten zinc surface bath. Although such ashes are constituted mainly of zinc oxide, the present investigation attempted to probe the organic matter traces that may contain dioxins and furans[4].

Table 1. Spanish Galvanising Plants references and sample types during 2002 survey

REFERENCE	SAMPLE TYPE		
DA-8	Ash	Filter dust	Flue gas
DA-9	Ash	Filter dust	Flue gas
DA-10		Filter dust	Flue gas
DA-11	Ash	Filter dust	
DB-4	Ash	Filter dust	Flue gas
DB-5	Ash	Filter dust	
DB-6	Ash	Filter dust	
DB-7	Ash	Filter dust	Flue gas
SD-1	Ash	Filter dust	Flue gas
SD-2	Ash	Filter dust	Flue gas

3. Sampling and Analysis Method.

The samples and PCDD/Fs analysis were carried out according to the EN–1948-1,2,3 method. We measured PCDD/Fs air emissions in seven installations because in that moment, only these facilities had platforms to incorporate the air sampling train. Considering that these installations work in the non-continuos mode, the samplings were restricted to the dipping in the bath. The sampling time ranges, for each plant, as a function of the dipping number per time unit and suction flow of ventilation system. Sampling temperature was about room temperature and oxygen percentage was similar to the atmospheric one, owing both to the sampling zone and flow induced by the ventilation system.

Results and Discussion

1. PCDD/Fs emissions

PCDD/Fs data obtained from the matrices studied in the monitored facilities during the 2002-year are shown in Table 2. As can be seen, PCDD/Fs concentrations associated to the ashes, 0.7-107 pg I-TEQ/g, are negligible. Also, emission ranges in the flue gases are very low, 0.003-0.014 ng I-TEQ/Nm^3, in comparison with the values related to German[2] hot-dip galvanising plants, which gave air emission concentrations intervals between 0.007 and 0.132 ng I-TEQ/Nm^3. This demonstrates the high efficiency of the filter systems that prevent the pollutants´ exit to the atmosphere.

With respect to the PCDD/Fs in the filter dusts, it is important to point out that the possible reutilization of such dusts could involve the mobilisation or incorporation of these pollutants to other industrial processes. This fact could increase and/or incorporate the PCDD/F contents in final products or other wastes.

Table 2. PCDD/Fs emissions from ten Spanish hot dip galvanizing plants evaluated during survey 2002

	Ash	Filter dust	Flew gas
	I-TEQ pg/g	I-TEQ pg/g	I-TEQ pg/Nm^3
DA-8	**107.2**	**1093**	**5.8**
DA-9	**0.7**	**946**	**3.0**
DA-10		**821/695**	**4.0**
DA-11	**13.2**	**1804/1601**	
DB-4	**3.8**	**1708**	**5.4**
DB-5	**15.2**	**127**	
DB-6	**2.3**	**755**	
DB-7	**16.3**	**1766**	**7.9**
SD-1	**10.9**	**8075**	**13.7**
SD-2	**0.7**	**487**	**4.8**

2. Typical Patterns

Each matrix resulting from the ten samplings has been analysed to obtain a comparative study of the different installations. Figure 1 shows the mean patterns related to the solid matrices: ten ashes and twelve filter dust samples and Figure 2 plots the results of the gas matrix: seven air emissions. From these Figures it can be concluded that in flue gas and filter dusts have a toxic PCDD/Fs content mainly due to the furan contribution (>85% in filter dusts and >70% in air emissions), where 2,3,7,8-PCDF is the most relevant congener.

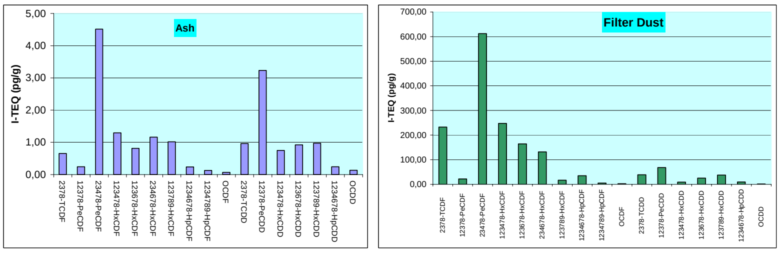

Figure 1. Average Toxic Pattern of ashes and filter dusts

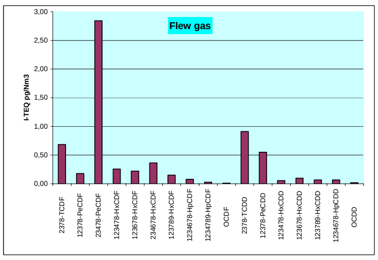

Figure 2. Average Toxic Pattern of air emissions

On the other hand, for ash samples, the PCDD/F toxic content is in the same order for PCDDs than for PCDFs, pointing out that the dioxin generation responds to other formation mechanisms.

3. Emission Factor

Preliminary emission factors have been estimated from data supplied by four plants (Table 3).

Table 3. Emission factors corresponding with four different Spanish galvanising plants.

μg I-TEQ/t galvanised steel in referenced facilities							
DA-10	**0.027**	**DA-9**	**0.019**	**DB-4**	**0.024**	**SD-1**	**0.061**

From available data, the average emission factor has been calculated to 33 ng I-TEQ/t galvanised steel. It is very important to note that this average emission factor is representative for 72.7% of the total production, related to plants with adequate air pollution control systems. The emission factors for the rest of the installations that do not have filter systems, presumably will be higher and thus increase the emission of the galvanising sector. Information from other countries is not available. For the German case, it is not known whether the air emission factors include installations working without gas cleaning treatment systems.

Conclusions

These experimental results from hot dip galvanising sector corroborate the formation of PCDD/Fs in the evaluated processes. Nevertheless, the use of air filter devices assures very low PCDD/Fs air emissions. The data evidence the concentration of PCDD/Fs in dusts and solid particulate. Taking into account IPPC96/61 European Directive related to the Galvanising Sector, recommends to capture more than 95% (SS limit < 150 mgN/m3) of particulate emissions from air, it is especially recommendable for PCDD/Fs emission prevention the use of bath enclosures together with filters. Total contribution of this sector in the Spanish inventory will not be able to be evaluated suitability without additional research considering more experimental measurements to confirm data existing and the knowledge of emission pathways in facilities without air cleaning devices.

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