EXPOSURE ASSESSMENT OF WORKERS TO PCDD/Fs AND WHO-12 PCBs AT AN ELECTRIC ARC FURNACE AND A BASIC OXYGEN STEELMAKING PLANT IN THE UK

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INTRODUCTION

Steel can be produced in integrated steelworks via the blast furnace route for the primary reduction of oxide ores into liquid iron (pig iron) followed by the conversion of the pig iron into liquid steel in a basic oxygen steelmaking plant (BOS). Alternatively, steel may also be produced in an electric arc furnace (EAF) plant by recycling scrap materials recovered from the scrap metal industry. Particulate matter emitted from the BOS or the EAF steelmaking plants may contain traces of organic micro-pollutants such as PCDD/Fs and PCBs. In steelmaking, occupational exposure studies to dioxins have only been carried out in EAF and iron ore sintering plants. However, there is still a lack of information concerning the concentrations of persistent organic pollutants in the BOS process. In the UK, Sweetman et al. (2004) carried out a survey for the Health and Safety Executive (HSE) to determine PCDD/F concentrations in an EAF melting shop. The workplace concentrations found were in the range 2.4 to 4.7 pg WHO-TEQ/m^3 for fixed-position measurements[1]. More recently, Chen et al. (2006) carried out a study at an EAF plant in Taiwan, where PCDD/F workplace air concentrations of 1.55 and 1.9 pg I-TEQ/m^3 were reported in the EAF and casting departments of the plant, respectively[2]. Finally, an occupational exposure survey to dioxins was carried out at an iron ore sintering plant in Taiwan[3], indicating that workplace air concentrations ranged from 0.24 to 0.90 pg I-TEQ/m^3. In view of the toxicological importance of the cited groups of organic pollutants, it was considered important to investigate the potential exposures of Corus workers involved in the production of steel via the BOS and the EAF processes. Accordingly, surveys were carried out to determine concentrations of PCDD/Fs and WHO-12 PCBs in selected workplaces at each plant. This paper summarises the concentrations of PCDD/Fs and PCBs found in the workplace air of both steelmaking plants, provides estimation of intakes for EAF and BOS workers, and discusses the significance of the results in terms of cancer risk.

BASIC OXYGEN STEELMAKING

In the integrated steelmaking production, pig iron from the blast furnace is transported to the BOS plant, where the carbon content (approximately 4%) is lowered to less than 1%, resulting in liquid steel. After desulphurisation, the pig iron is charged into a BOS converter (vessel) to produce steel. Each vessel is able to tilt to angles up to 150^o for charging and discharging purposes. Undesirable impurities such as carbon, silicon and manganese are converted into oxides by blowing pure oxygen through a water-cooled oxygen lance directly into the hot metal. Since the oxidising reactions are exothermic, thus increasing the temperature of the pig iron, scrap metal is also added to cool down the reaction and maintain the temperature at approximately 1600 - 1650°C. At the end of the BOS process, the vessels are tilted and the steel is tapped into pre-heated ladles. Ladles are transiting via the concast plant prior being sent for further treatments in secondary steelmaking to meet the final quality requirements. Secondary metallurgy operations include alloy additions and vacuum treatment of the steel to remove gaseous hydrogen, oxygen and nitrogen. These operations are carried out at ladle arc furnaces stations. In total, Corus operates three BOS plants in the UK. In this study, surveys were carried out at Corus BOS plant A comprising a desulphurisation plant, three 1,300 tonnes BOS vessels, and three ladle arc furnace stations.

ELECTRIC ARC FURNACE STEELMAKING

In the scrap metal recycling route, the production of steel is performed in EAF plants. A typical EAF consists of a steel refractory-lined hearth with the upper shell consisting of water-cooled panels and water-cooled roof. The electrodes for input of electric power pass through the roof of the furnace. Most of the existing EAFs are powered by alternating current and have three electrodes. The roof also contains a fourth hole for direct extraction of waste gases from the steel-making reactions. The only EAF plant operated by Corus in the UK has two furnaces with a capacity per heat of about 150 tonnes of liquid steel. In the melting shop, the scrap is loaded into baskets together with lime, used as a flux for slag formation. About 60% of the scrap is charged with the first scrap basket. The roof is then closed and the electrodes lowered to within 20-30 mm above the scrap before striking an arc. After the initial charge has melted, the charging process is repeated by adding a second basket of scrap metal. To tap the furnace, the electrodes are raised, the furnace is tilted and the tap hole is opened to discharge molten steel into a refractory-lined ladle.

MATERIALS AND METHODS

Sampling

For all locations, air samples were collected using high-volume samplers equipped with a polyurethane foam plug (Supelco : 6 cm x 7.6 cm) and a glass fibre filter (Whatman GF/A 110 mm). They were operated during

12-h at a constant flow rate of 0.2 m^3/min thus enabling a sample volume of ambient air of approximately 150 m^3 to be collected. A visit inspection of all high-volume samplers was carried out every 2 hours to replace filters owing to the significant amount of dusts found in some areas of the EAF or the BOS plants. At the EAF steelmaking plant, sampling was carried out inside the melting shop area near the furnaces, inside the casting area and inside a furnace control cabin. At the BOS plant, the areas investigated included the main BOS vessel area, the desulphurisation plant, the concast area, and secondary steelmaking.

Analysis

The operation of the laboratory for PCDD/Fs and PCBs analysis has been described in more detail elsewhere [4]. Samples were analysed using a UKAS-accredited (ISO 17025) method derived from US EPA Method 23 and 1668A for PCDD/Fs and PCBs, respectively. Analysis for PCDD/Fs and PCBs was conducted by high resolution gas chromatography - high resolution mass spectrometry using an Agilent 6890 gas chromatograph coupled to a Waters Autospec Ultima high resolution mass spectrometer. A 60 m x 0.25 mm x 0.25 μm DB5-MS capillary column was used. The MS was operated at 10,000 resolution in the positive-ion mode at 34 eV energy with perfluorokerosene as the mass range calibrant.

Risk characterisation

In this study, PCDD/F and WHO-12 PCB concentrations were converted to an estimated daily intake by taking into account (i) the amount of time EAF and BOS plant workers spent in each area of the plant, (ii) daily inhalation rates of 1.5 m^3 per hour for moderate activities [5] and (iii) an 8-h working shift. The estimated daily intake was compared with the recommended tolerable daily intake (TDI). In 1998, the WHO European Centre for Environment and Health (WHO-ECEH) performed a health risk assessment of dioxin-like compounds [6], and a TDI of 1 - 4 pg WHO TEQ/kg body weight (bw) was recommended (including the WHO-12 PCBs). In November 2001, the UK committee on the Toxicity of Chemicals in Food, Consumer products and the environment (COT) issued a statement recommending that a TDI of 2 pg WHO TEQ/kg bw/d be established [7].

In this study, exposure data (monitored concentrations, inhalation doses) were also combined with inhalation cancer potency factors in order to quantify the cancer risk. For cancer risk calculations, the inhalation cancer potency for the substance, expressed as a potency slope [i.e. $(mg / kg\text{-}d)^{-1}$], and an estimate of the average daily inhalation dose in units of milligram per kilogram - day (mg / kg-d) were used. Cancer risk was calculated by multiplying the inhalation dose by the inhalation cancer potency factor to result in the potential inhalation cancer risk. The WHO-TEQ concentrations found in the workplace of the EAF and BOS plants were used for cancer risk calculations by multiplying them with the inhalation potency factor for 2,3,7,8-TeCDD of 1.3×10^5 $(mg /kg\text{-}d)^{-1}$ [8]. Daily inhalation rates of 1.5 m^3 per hour, corresponding to 172 l/kg bw for an adult of 70 kg, were used considering moderate activities. An averaging time of 365 d/year (ie. 25550 d) was used to characterise lifetime exposure. An inhalation absorption factor of 1 was used assuming 100% absorption. Finally, an exposure frequency of 250 d/year and 40-years occupational exposure duration were used.

RESULTS AND DISCUSSION

For all sampling locations, concentrations of PCDD/Fs and WHO-12 PCBs are summarised in Table 1. With regard to the EAF plant, the highest concentrations of PCDD/Fs and PCBs were found inside the melting shop area (mean = 2.71 pg WHO-TEQ / m^3), followed by the casting area and the control cabin. At Corus BOS plant A, the highest concentrations of PCDD/Fs and PCBs were found inside the BOS vessel area (mean = 0.71 pg WHO-TEQ / m^3), followed by the desulphurisation plant, the concast area and secondary steelmaking. For both steelmaking plants, total WHO-12 PCB concentrations were significantly higher than total PCDD/F concentrations; however the contribution of WHO-12 PCBs to the total WHO-TEQ typically ranged only from 5 to 20% owing to their lower toxic equivalency factors (data not shown). In the BOS and EAF processes, PCDD/Fs and PCBs are likely to be formed during charging operations owing to the presence of chlorine and carbon residuals in the scrap metal. In particular, when scrap metal is charged, chemical reactions may occur between residual molten metal (at the bottom of the EAF furnace / BOS vessel) and the new charge of scrap within a temperature range favourable for dioxin formation. At that time, significant release of fumes and particulate matter takes place. Since fumes and particulates can not be completely removed by the secondary extraction systems, it is normal to find the highest concentrations of particle-bound PCDD/Fs and PCBs in the melting shop area of the EAF and in the BOS vessel area.

When comparing steelmaking operations (EAF and BOS plants), workers exposure to PCDD/Fs and PCBs in the BOS desulphurisation, concast and secondary steelmaking areas appeared to be significantly lower than in the EAF workplaces such as the melting shop and the casting area. At Corus BOS plant A, the most exposed category of workers to PCDD/Fs and PCBs were workers from the BOS vessels area, but their level of exposure was significantly lower than workers inside the EAF melting shop. When comparing with other industrial processes, PCDD/F and PCB exposure of BOS plant workers appeared to be similar to the exposure of iron ore sintering workers (ca. 0.66 pg TEQ / m^3) [3], but significantly lower than in the aluminium recycling industry (ca. 24.2 pg TEQ / m^3) [1].

Table 1 : PCDD/Fs and WHO-12 PCB concentrations in the workplace air of an EAF and a BOS steelmaking plant operated by Corus in the UK in comparison with other steelmaking plants and other industrial activities.

	Total PCDD/Fs pg/m^3	Total WHO-12 PCBs pg/m^3	TEQ (Low) pg TEQ/m^3	TEQ (High) pg TEQ/m^3	TEQ (Mean) pg TEQ/m^3
Steelmaking processes					
BOS (Corus UK, this study) † †					
BOS vessels area (n = 14)	6.6	74.0	0.13	1.80	0.71
Desulphurisation plant (n = 3)	2.9	69.1	0.16	0.48	0.28
Concast area (n = 3)	1.6	30.0	0.13	0.40	0.26
Secondary steelmaking (n = 6)	1.0	26.8	0.03	0.15	0.08
EAF (Corus UK, this study) † †					
Melting shop area (n = 20)	24.5	586.0	0.29	8.62	2.71
Casting area (n = 6)	7.2	187.2	0.48	2.45	0.75
Control room (n = 3)	4.1	99.3	0.25	0.39	0.31
EAF, Taiwan[2]					
Melting shop workers	30.1	-	-	-	1.56 *
Casting area workers	20.1	-	-	-	1.92 *
EAF, UK[1]	-	-	2.4 †	4.7 †	-
Iron ore sintering					
Sinter plant, Taiwan[3]	7.29	-	0.24	0.90	0.66
Other industrial activities					
Secondary ALS, UK[1]	-	-	2.9 †	72.7 †	24.2 †

† † Data were reported using the TEFs defined by WHO (1998), and include WHO-12 PCBs.

* Data were reported using the TEFs defined by WHO (1998), but do not include WHO-12 PCBs.

† Data were reported using the TEFs defined by NATO/CCMS (1988).

Secondary ALS : Secondary aluminium smelter plant.

Exposure assessment of Corus BOS and EAF workers to PCDD/Fs and dioxin-like PCBs via inhalation was carried out by comparing the estimated daily intake of workers to the TDI for dioxins and dioxin-like compounds, and also by calculating a potential cancer risk over a 40-year occupational exposure period. Table 2 summarises the estimated daily intake of PCDD/Fs and WHO-12 PCBs and the corresponding cancer risk. At the EAF steelmaking plant, three categories of workers were considered. After consultation with plant personnel, it was decided to estimate daily intakes for melting shop workers by assuming that they would typically spend 25% of the shift inside the melting shop and 75% of the shift inside the control cabin. In the casting department, workers would generally spend 50% of the time in the casting area, and 50% of the shift inside the control cabin. Finally, workers in charge of furnace operations would spend the totality of a shift inside the control room. At the BOS plant, daily intakes were calculated by assuming that workers would spend 50% of their shift in their respective working areas (BOS vessel, desulphurisation, concast or secondary steelmaking). Using these data, the highest estimated daily intakes by inhalation of PCDD/Fs and PCBs were determined for EAF melting shop workers. These ranged from 0.15 to 0.41 pg WHO-TEQ/kg bw. At the BOS plant, the daily intake for the most exposed category of workers (BOS vessel area workers) ranged from 0.06 to 0.18 pg WHO-TEQ/kg bw. When considering the average UK adult exposure to PCDD/Fs and WHO-12 PCBs from their dietary intake of 1.8 pg WHO-TEQ/kg bw/d, it is estimated that the daily intake of PCDD/Fs and PCBs from food and from the inhalation of air from the EAF workplace would range from 1.95 to 2.21 pg WHO-TEQ/kg bw /d for melting shop workers. These data indicate that for the most exposed category of workers (i.e. melting shop workers), the estimated daily intake would be 2.21 pg WHO-TEQ/kg bw /d, only slightly above the TDI recommended by COT, but well within the range of 1 to 4 pg WHO-TEQ/kg bw /d recommended by the WHO.

The potential exposure of EAF and BOS workers to PCDD/Fs and PCBs via inhalation was also investigated by estimating cancer risks. As may be seen from Table 2, cancer risks from exposure to PCDD/Fs and PCBs via inhalation for EAF workers ranged from 2.35×10^{-6} (control room area) to 7.54×10^{-5} (melting shop area). For the most exposed category of workers (melting shop), the mean cancer risk was 2.37×10^{-5}, in good agreement with the cancer risk determined at another EAF plant in Taiwan[3]. At the BOS plant, mean cancer risks were significantly lower and ranged from 1.14×10^{-6} (secondary steelmaking) to 1.36×10^{-5} (BOS vessel area). The cancer risks determined in this study were within the range 1.0×10^{-4} to 1.0×10^{-6} that is acknowledged as acceptable by regulatory agencies such as the US EPA[9]. Furthermore, for the calculation of excess cancer risk at the EAF plant, no account has been taken of the protection provided by protective respiratory equipment worn by EAF workers although melting shop workers were equipped with masks for use against particles with a low filtration efficiency (type P1), providing a protection factor of 4. If the protection factor afforded by the use of personal protective equipment was taken into consideration, the excess cancer risks for EAF workers would be 4-fold lower, and therefore considered as negligible.

Table 2 : Estimated daily intake of PCDD/Fs and WHO-12 PCBs and cancer risk via inhalation for different categories of workers at a BOS and an EAF steelmaking plants operated by Corus in the UK.

	Daily intake (Mean estimate) pg TEQ / kg bw	Daily intake (High estimate) pg TEQ / kg bw	Cancer risk (Mean)	Cancer risk (High)
Steelmaking processes				
BOS (Corus UK, this study)				
BOS vessel workers	0.06	0.18	1.36 x 10^{-5}	1.58 x 10^{-5}
Desulphurisation plant workers	0.03	0.06	3.64 x 10^{-6}	4.20 x 10^{-6}
Concast area workers	0.02	0.05	3.03 x 10^{-6}	3.50 x 10^{-6}
Secondary steelmaking workers	0.01	0.03	1.14 x 10^{-6}	1.31 x 10^{-6}
EAF (Corus UK, this study)				
Melting shop workers	0.15	0.41	2.37 x 10^{-5}	7.54 x 10^{-5}
Casting area workers	0.09	0.24	6.56 x 10^{-6}	2.14 x 10^{-5}
Control room workers	0.04	0.06	2.35 x 10^{-6}	2.96 x 10^{-6}
EAF steelmaking (Taiwan) [3]				
Melting shop workers (PCDD/F only)	-	-	3.4 x 10^{-5}	-
Casting area workers (PCDD/F only)	-	-	4.19 x 10^{-5}	-
Iron ore sintering (Taiwan) [3]				
Sinter plant workers (PCDD/F only)	-	-	1.44 x 10^{-5}	-
UK dietary intake [10]	*(Average UK food consumer)* 1.8	*(High level UK food consumer)* 3.1		

CONCLUSIONS

Occupational exposure surveys to dioxin and dioxin-like PCBs were carried out at an EAF and a BOS plant operated by Corus in the UK. In steelmaking, the highest concentrations of PCDD/Fs and PCBs were found at the EAF plant inside the melting shop area. For the most exposed category of workers, the data indicated that the total daily intake of PCDD/Fs and PCBs from both the diet and workplace exposure were well within the range of 1 to 4 pg WHO-TEQ/kg bw /d recommended by the WHO. Estimated excess cancer risks ranged from 2.05 x 10^{-5} to 7.54 x 10^{-5} for EAF melting shop workers, within the acceptable range of 1.0 x 10^{-4} to 1.0 x 10^{-6} proposed by the US EPA. For the calculation of excess cancer risks, no account has been taken of the protection provided by protective respiratory equipment worn by EAF workers inside the melting shop. When taking into account appropriate personal protective equipment, the excess cancer risks for EAF workers would be lower, and considered as negligible. Finally, exposure of BOS plant workers was significantly lower than at the EAF plant.

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