Characterisation of Releases of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Integrated Iron and Steelworks in the United Kingdom

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Preliminary studies have been carried out to investigate the emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from integrated iron and steelworks in the United Kingdom. The results show that the sintering of iron ore is the only significant source of emissions of PCDD/Fs and the average emission concentration at five sinter plants operated by British Steel was 1.3 ng (I-TEQ)/m^3 which compares favourably with the UK Environment Agency's achievable release limit of 1 ng (I-TEQ)/m^3 for brand new plants, and the concentrations found were considerably lower than those reported elsewhere. PCDD/F emissions from BOS steelmaking and coke oven battery underfiring were well below the achievable release level of 1 ng (I-TEQ)/m^3. The PCDD/F concentrations of sediments taken from effluent discharge streams or receiving waters were mostly at background levels found in UK rivers and hence it is concluded that aqueous effluents from integrated iron and steelworks do not release significant amounts of these pollutants into the aquatic environment.

Introduction

The Seveso incident in 1976 raised public awareness of the problems of environmental pollution from polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F). Since then combustion processes, particularly those associated with the incineration of chemical and municipal wastes, have been shown to be important sources of PCDD/F emissions. The production of steel is energy intensive and involves a number of high temperature processes which raise the possiblity of PCDD/F formation. In order to assess the potential for the release of PCDD/F from its operating plants, and to aid the development of appropriate control strategies, British Steel has set up a dedicated unit at its Swinden Technology Centre in Rotherham for the sampling and analysis of trace organic micropollutants. Initial work has been concerned primarily with characterising the emissions from integrated iron and steelmaking operations, such as cokemaking, iron ore sintering, and basic oxygen steelmaking (BOS). Sediments from effluent streams and receiving waters have also been analysed for PCDD/Fs. This paper presents the preliminary results of these investigations.

Integrated Iron and Steelworks' Processes

The production of steel by the integrated process route involves a series of closely related processes whereby iron is extracted from iron ores in the blast furnace, converted into steel in the BOS process. The resulting steel is then cast and rolled into various finished or semi-finished products such as strip, beams, pilings, plates etc. The complete processing route is shown schematically in Fig. 1.

Experimental

Emission samples were obtained by sampling the waste gases by use of a US EPA Method 23 sampling train comprising a heated glass-lined sampling probe and filter box equipped with a glass fibre filter, and a water-cooled XAD-2 sorbent trap. The analytical samples consisted of the filter, XAD-2 resin, and solvent washings from the glassware of the sampling train. The samples were analysed by isotope-dilution high-resolution gas chromatography-high-resolution mass spectrometry (HRGC-HRMS) on a VG Autospec Ultima system equipped with a 60 m DB-5ms column. In preparation for analysis samples were Soxhlet extracted with toluene for 20 h and the extracts were subjected to a two-stage clean-up involving a multi-layer silica column and a Florisil mini-column.

Sediment samples were air-dried and crushed to less than 200 mesh. For analysis 5 to 10 g samples were extracted with toluene at 150°C and 2000 p.s.i. by use of a Dionex ASE 200 accelerated solvent extraction system. Sulphur was removed from the extract by treatment with copper powder and the sample was cleaned up using the two stage treatment mentioned previously.

Results and Discussion

British Steel has four integrated iron and steelworks in the UK and these have a combined output of around 13 million tonnes of liquid steel per annum. At the outset of these studies it was considered important to carry out an inventory of PCDD/F emissions from the primary processes of cokemaking, sintering and BOS steelmaking. The production of iron in the blast furnace is essentially a closed system and was therefore considered to be of lower priority. The results of this initial programme of work are summarised in Table 1, from which it may be seen that the mean concentrations of PCDD/F in primary and secondary BOS emissions, coke oven battery underfiring and sinter production were 0.01, 0.004, 0.1, 1.3 ng (I-TEQ)/m^3. The data for coke oven battery underfiring are limited because of the lack of suitable sampling points in waste gas stacks. At present there are no strict limit values for PCDD/F although the Environment Agency in the UK has specified an achievable release limit for iron and steelmaking processes of 1 ng (I-TEQ)/m^3 for brand new plant. Clearly there would be no problem in meeting such a limit for the BOS process and cokemaking emissions, although PCDD/F emissions from the sintering process are, on average, slightly above the specified value. The mean PCDD/F concentration and the range, 0.4 to 4.4 ng (I-TEQ)/m^3, are much lower than the levels of 12 and 43 ng (I-TEQ)/m^3 reported by Bruckmann et al[2]. Following the preliminary measurement programme detailed studies are now being carried out into the factors that influence the formation of PCDD/Fs in the sintering process in order to establish to what extent these may be controlled by modifying the combustion process.

The congener profiles of the emissions from the three sources are quite different as shown in Figs 2a to 2c. In sinter plant emissions the congeners present in highest proprtions are 1,2,3,4,6,7,8-heptachlorodibenzofuran and 2,3,4,7,8-pentachlorodibenzofuran which constitute 16.5 and 16% by weight respectively of the total concentration of the targeted compounds, whereas octachlorodibenzo-p-dioxin is the main component in emissions from both coke oven battery underfiring and the BOS process. However, in each instance the main contributor to the overall I-TEQ of the sample is 2,3,4,7,8-pentachlorodibenzofuran which is reponsible for 56.6, 65, and 48% of the I-TEQ in emissions from sintering, coke making and steelmaking respectively. It is also evident from Fig 2a that the there is a predominance of PCDFs rather than PCDDs in the sinter plant emission, with the former compounds constituting 85 and 89% of the total dioxin concentration and of the I-TEQ respectively. With coke oven battery underfiring there is a more or less 50:50 split between the concentrations of targeted PCDDs and PCDFs, but PCDFs contribute almost 96% of the I-TEQ. For BOS process emissions the overall concentrations of targeted PCDDs outweigh the concentrations of PCDFs largely because of the relatively high proportion of octachlorodibenzo-p-dioxin, but the PCDFs contribute more than 83%of the I-TEQ. An interesting finding of the work to date is that the congener profiles of emissions from all of the five sinter plants operated by British Steel are substantially the same and appear to be characteristic of the process, regardless of the overall I-TEQ value of the emission, which suggests that congener profiles are thermodynamically controlled.

The PCDD/F concentrations found in sediment samples are presented in Table 2. The total concentrations of tetra through to octa PCDD/Fs and I-TEQ values were in the ranges 37 to 3583 and 0.4 to 17.1 ng/kg respectively. In order to put these results into perspective they may be compared with data obtained in a survey[1] of PCDD/F levels in UK rivers that was carried out by the UK Environment Agency. The total concentrations of PCDD/F across 36 different sampling sites were in the range 300 to 16 000 ng/kg and 2 to 120 ng(I-TEQ)/kg, and background total concentrations and I-TEQ values in rural locations were 300 to 400 and 2 to 4 ng/kg respectively. The PCDD/F concentrations found in samples taken from British Steel's integrated works sites are mostly at background levels, and those sediments which fall outside background levels would be classified as being slightly polluted using the categories suggested in the Environment Agency's report. On the basis of these initial investigations it would appear that integrated iron and steelmaking plants do not release significant amounts of PCDD/Fs into the aquatic environment via effluent discharges. The sediment sample with the highest concentration of PCDD/F of 3583 ng/kg was composed mainly of octachlorodibenzo-p-dioxin (approximately 66% by weight) and hence had an I-TEQ value of 7.5 ng/kg that was close to background level.

Conclusions

The results of a preliminary investigation of emissions from integrated iron and steelworks in the UK show that the sintering of iron ore is the only significant source of emissions of PCDD/Fs. The average emission concentration was 1.3 ng (I-TEQ)/m^3 which compares favourably with the UK Environment Agency's achievable release limit of 1 ng (I-TEQ)/m^3, but the concentrations found were considerably lower than those reported elsewhere. PCDD/F emissions from BOS steelmaking and coke oven battery underfiring were well below the achievable release level of 1 ng (I-TEQ)/m^3 for new plant. The PCDD/F concentrations of sediments taken from effluent discharge streams or receiving waters were mostly at background levels found in UK rivers and hence it is concluded that aqueous effluents from integrated iron and steelworks do not release significant amounts of these pollutants into the aquatic environment.

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PROCESS	PCDD/F CONCENTRATION ng (I-TEQ)/m^3			NUMBER OF RESULTS
	RANGE	MEAN	STANDARD DEVIATION	
Sintering	0.4-4.4	1.3	0.8	35
Cokemaking	-	0.1	-	2
BOS Steelmaking Primary Emission	0.004-0.021	0.01	0.006	8
BOS Steelmaking Secondary Emission	0.001-0.013	0.007	0.005	6

TABLE 1 PCDD/F IN EMISSIONS FROM INTEGRATED IRON AND STEELWORKS' PROCESSES IN THE UK

WORKS	SOURCE	PCDD/F CONCENTRATION ng/kg		
		TOTAL	TOTAL TARGETED	I-TEQ
A	Effluent stream	227	179	2
	Effluent stream	98	76	0.4
B	Effluent stream	2 743	2 061	17.1
	Effluent stream	130	82	2.6
C	Effluent stream	3 583	2 364	7.5
	Receiving water - Surface - Sub-surface	 473 614	 371 493	 1.6 2.6
	Receiving water	37	26	0.2
D	Effluent stream	633	199	16.4

TABLE 2 PCDD/Fs IN SEDIMENTS FROM EFFLUENT STREAMS AND RECEIVING WATERS AT INTEGRATED IRON AND STEELWORKS IN THE UK

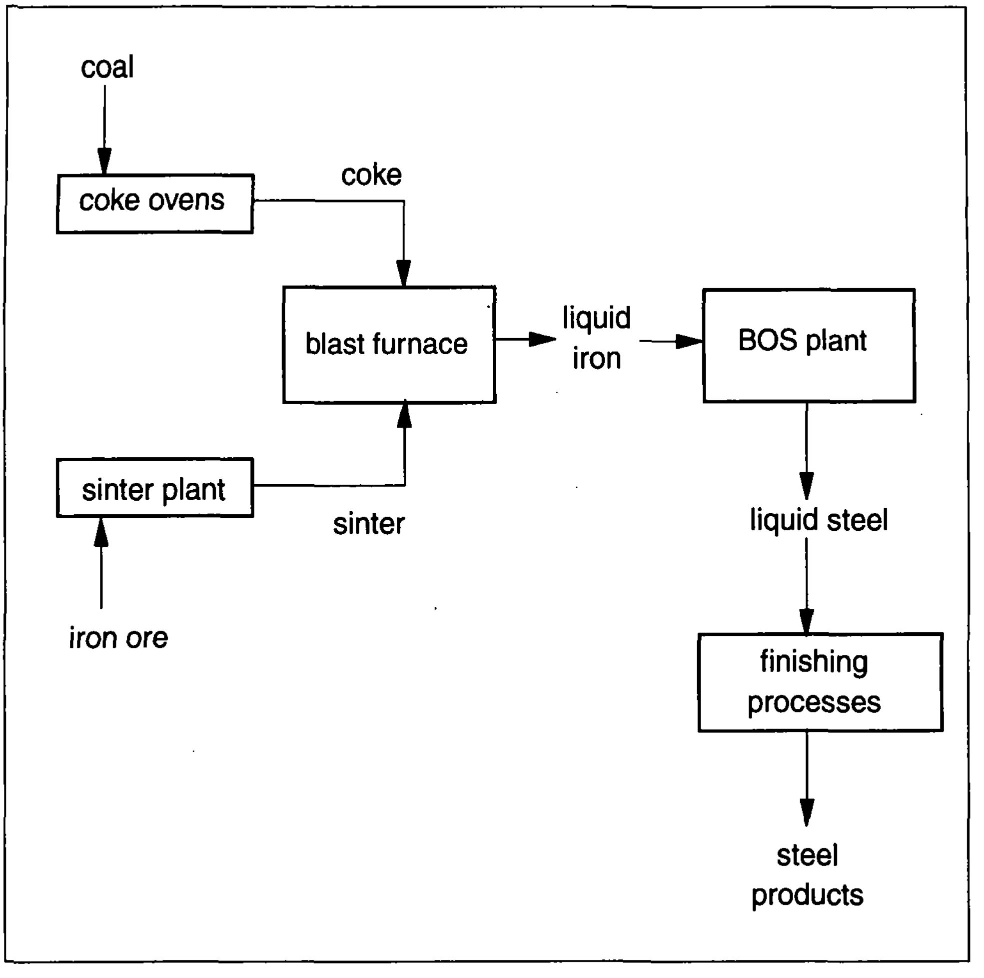

FIGURE 1 PROCESS ROUTES IN AN INTEGRATED IRON AND STEELWORKS

(A)
(B)
(C)

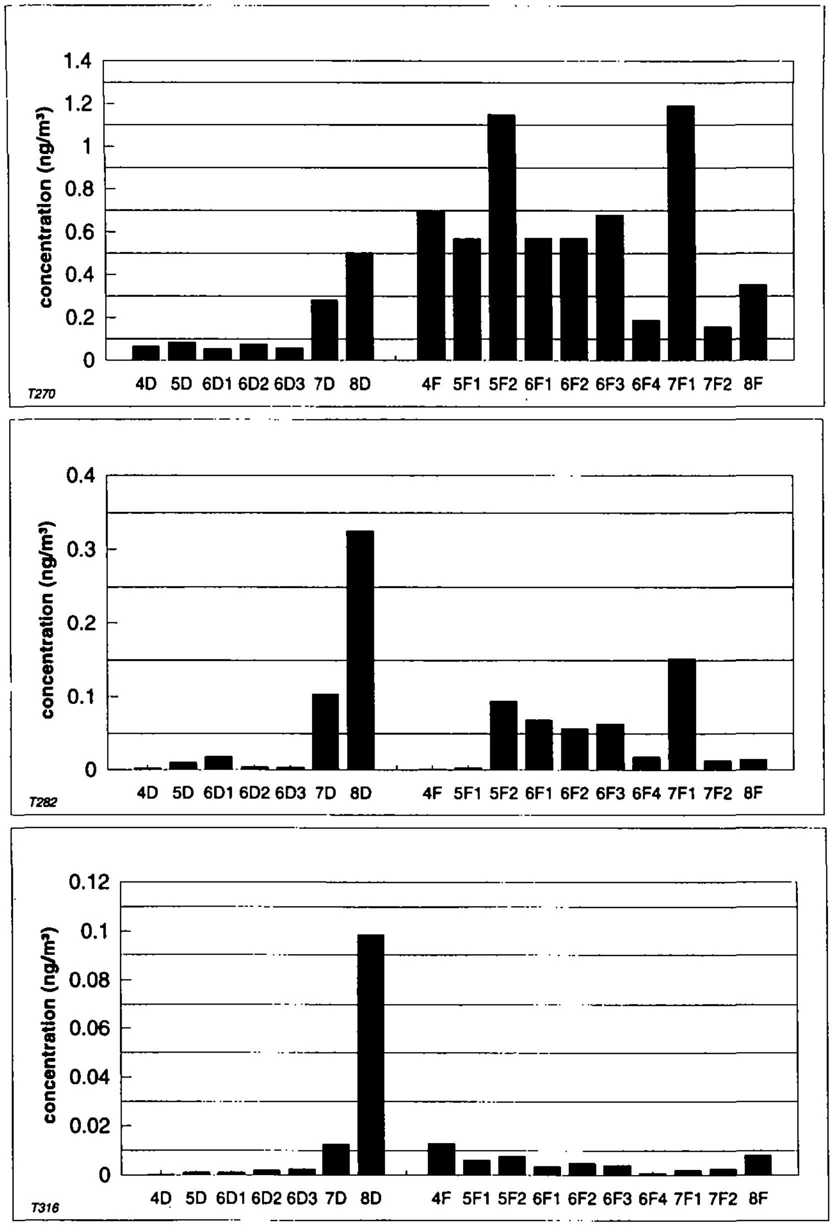

FIGURE 2 TYPICAL CONCENTRATION PROFILES OF TARGETTED PCDD / F COMPOUNDS IN EMISSIONS FROM (A) SINTERING, (B) COKE OVEN UNDERFIRING AND (C) BOS STEELMAKING.

4D, 2,3,7,8-TCDD; 5D, 1,2,3,7,8-PeCDD; 6D1, 1,2,3,4,7,8-HxCDD; 6D2, 1,2,3,6,7,8-HxCDD; 6D3, 1,2,3,7,8,9-HxCDD; 7D, 1,2,3,4,6,7,8-HpCDD ; 8D, OCDD; 4F, 2,3,7,8-TCDF; 5F1, 1,2,3,7,8-PeCDF; 5F2, 2,3,4,7,8-PeCDF; 6F1, 1,2,3,4,7,8-HxCDF; 6F2, 1,2,3,6,7,8-HxCDF; 6F3, 2,3,4,6,7,8-HxCDF; 6F4, 1,2,3,7,8,9-HxCDF; 7F1, 1,2,3,4,6,7,8-HpCDF; 7F2, 1,2,3,4,7,8,9-HpCDF; 8F, OCDF.