



The polychlorinated dibenzofuran fingerprint of iron ore sinter plant: Its persistence with suppressant and alternative fuel addition



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HIGHLIGHTS

- Sinter pot and full scale iron ore sinter strand PCDF isomer profiles are similar.
- Full isomer profiles with and without suppressants are shown to be similar.
- Targeted isomer ratios are shown to be unaffected by coke fuel replacement.
- Observed and DFT-predicted 1,9-substituted isomer abundances are low.
- Observed non-1,9PCDF isomer abundances do not match DFT-based levels.

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ABSTRACT

An earlier demonstration that the relative concentrations of isomers of polychlorinated dibenzofuran do not vary as the flamefront of an iron ore sinter plant progresses through the bed, and profiles are similar for two sinter strands has been widened to include studies of the similarity or otherwise between full scale strand and sinter pot profiles, effect of addition of suppressants and of coke fuel substitution with other combustible materials. For dioxin suppressant addition, a study of the whole of the tetra- penta- and hexaCDF isomer range as separated by the DB5MS chromatography column, indicates no significant change in profile: examination of the ratios of the targeted penta- and hexaCDF isomers suggests the profile is similarly unaffected by coke fuel replacement. Addition of KCl at varied levels has also been shown to have no effect on the 'fingerprint' and there is no indication of any effect by the composition of the sinter mix. The recently published full elution sequence for the DB5MS column is applied to the results obtained using this column.

It is confirmed that isomers with 1,9-substitution of chlorine atoms are invariably formed in low concentrations. This is consistent with strong interaction between the 1 and 9 substituted chlorine atoms predicted by DFT thermodynamic calculations. Non-1,9-substituted PCDF equilibrium isomer distributions based on DFT-derived thermodynamic data differ considerably from stack gas distributions obtained using SP2331 column separation. A brief preliminary study indicates the same conclusions (apart from the 1,9-interaction effect) hold for the much smaller content of PCDD.

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1. Introduction

The waste gases from iron ore sintering contain minute quantities of polychlorinated dibenzofurans but because of the very large quantities of iron ore sintered worldwide, and the large

volume throughput of air involved, sintering, together with the electric arc furnace, makes steelmaking a major source of dioxins in the atmosphere (Ooi and Lu, 2011). The underlying formation process remains uncertain, although it is generally assumed that metal surface catalysis plays a larger part (Stanmore, 2004) than gas phase formation, e.g. (Fabian and Janoschek, 2006; Summoogum et al., 2012). As the full scale sinter plant is not amenable to experimental input variations, experimental studies have been

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carried out using small scale reactors (sinter pots) with variations in the fuel percentage and suction pressure (Chen et al., 2012), origin of the ore, and composition of the inorganic additives used in the interests of optimising the sintering process e.g. (Ooi et al., 2013): use of other additives for pollutant emission suppression (Anderson et al., 2001, 2007): and coke fuel substitution to address coke availability and cost issues (Ooi, 2006, Ooi et al., 2008a, 2011). Success has been achieved in terms of emission reduction but little advance in understanding the essential formation process has been achieved. Because these experiments were aimed at reduction of the emission of toxic dioxin isomers from the sinter plant, the analyses were carried out using the DB5MS chromatography column to achieve good separation of the toxic isomers before mass spectrometric identification and quantification (Gruber et al., 1995). Until recently the DB5MS column was only partially calibrated for chlorinated dibenzo-*p*-dioxins and dibenzofurans, that is, it was calibrated to the extent that all the targeted isomers could be identified and quantified, but the elution sequence of non-targeted isomers eluting away from the targeted isomers was not known. Only two measurements of the abundances of all isomers of PCDD/F in sinter plant emissions were obtained, and have been reported (Wang, 2001, Wang et al., 2003) elsewhere: these analyses were carried out using the SP2331 chromatography column, which also provides greater isomer separation than the DB5MS (Fishman et al., 2007; Ryan et al., 1991).

The resolution of the concentration distribution within each degree of chlorination of polychlorinated dibenzofuran is of interest in the comparison of the observed abundances with the predicted thermodynamic equilibrium concentration distribution, as an early step in attempting to elucidate the formation mechanism. Addink et al. (1998) carried out such a comparison for municipal waste incinerator (MWI) emissions, and show that there is little correlation between observations and predictions. In view of the presence of material such as chlorinated plastics in the municipal waste, which could be isomer-specific dioxin precursors, the result is not conclusive evidence of absence of equilibrium concentrations in the sinter plant, which lacks such precursors. The predictions of Addink et al. (1998) were made using an extension of the MOPAC-derived thermodynamic data obtained by Unsworth and Dorans (1993): as the predicted data is independent of the experimental system, and the results are only dependent on temperature, a similar comparison to Addink et al.'s comparison with MWI isomer profiles may be made for sinter plant emissions using their results. Thompson (1995) derived thermodynamic data using a modification of Benson's group additivity method (Benson, 1976) and these data may also be compared with observations (see below). Neither MOPAC-derived thermodynamic data nor group additivity-derived thermodynamic data are entirely reliable, but until recent years they provided the only available methods of providing thermodynamic data for compounds for which experimentally derived data were not available, as is the case for PCDD/Fs. MOPAC (Stewart, 1990) is subject to uncertainties in the results produced, the magnitude and sign of which cannot be assessed: the uncertainties can be seen in the examples presented by Stewart (Stewart, 1990) and in the results of Howard et al. (Howard et al., 1995). In the latter work, the results form the various optional versions of the program within MOPAC differ significantly. Group additivity is reliant on the contributions by interactions between groups within the compound for which data are to be derived being all available. If a potential interaction has not been assigned a contribution to the thermodynamic property because the necessary compounds containing this group interacting in the required way have not been examined experimentally, the particular interaction is necessarily neglected in the model.

For example, neither the potential for interaction between the

chlorine atoms substituted in the 4 and 6 positions in PCDD/Fs, nor the interaction between the chlorine atoms in the 4 and 6 positions and the bridging oxygen atom, can be included in the model of PCDD/F because the set of compounds containing the bridging oxygen and with and without chlorine atoms substituted at either and both sides of the bridge have not all been studied experimentally. In recent years improvements in predictive programs based on DFT have led to increased confidence in results provided from that method of derivation of thermodynamic data. Several authors have provided data for PCDD/F and related compounds (Dorofeeva and Yungman, 2007; Lee and Choi, 2003; Leon et al., 2002; Thompson and Ewan, 2007; Wang et al., 2005), including the algorithm provided by Thompson and Ewan (2007) for PCDF. Data derived using this method will be compared with experimental results in this paper.

The isomer profiles in alternate windlegs along the whole length of two sinter plant, compared on the basis of the peak heights in the chromatograms obtained using the DB5MS column for separation (Thompson et al., 2003) varied little from windleg to windleg. The similarity between the results from the two sinter strands suggests the possibility that there may be an isomer concentration distribution common to all iron ore sintering emissions. The observed near-constant concentration distribution of isomers within each degree of chlorination in emissions irrespective of the position of the flamefront in the bed means that the averaged composition measured in sinter pot studies similarly represents the emissions at all stages of the process. To broaden the study it is desirable to compare full size strand emissions with sinter pot emissions, and sinter pot emissions with variations in input sinter mix composition. This paper carries out such a study, and uses the recently published elution sequence of the DB5MS to identify the isomers (Fishman et al., 2011). In this study the profiles obtained using the SP2331 are used to compare thermodynamic predictions with experimental results because of the greater separation obtained with that column.

2. The iron ore sintering process and the sinter pot model

Beneficiation of iron ore from the mined state, together with the need for its intimate mixing with additives before it is reduced, results in it being in fine grain form, which is not suitable for introduction into the blast furnace. The purpose of the sinter plant is to convert the fines into suitable size finished products or agglomerates with sufficient mechanical strength, such that air can pass between the agglomerates, coke and lump ore, unhindered and the agglomerates positioned further down the furnace can support the upper part of the blast furnace charge imparting requisite permeability to the furnace. To achieve this end, the ore is blended with the necessary additives and typically 3–5% coke breeze, formed into pellets with typically 4% moisture content and placed on a moving bed to a depth of 0.4–0.7 m. The bed is ignited from the top and air is drawn downwards through the bed by induced draught fans, through a series of ducts (windlegs) into a combined exhaust duct (the windmain). Dust is removed from the exhaust gas by electrostatic precipitators and the cleaned gas is discharged to the atmosphere through a stack. The flame burns through the sinter bed near the end of the moving grate (strand) which is typically 4–6 m wide, and moves at 2–3 m min⁻¹, adjusted to match burnthrough requirements: much of the mix is sintered into finished agglomerates. The agglomerates, together with the inert bed on which the mix was deposited (i.e. the hearth layer) and any fines which have not sintered, are tipped off onto a carousel where they cool before grading. Undersize particles are returned to the sinter input mix, which is also used to dispose of appropriate plant waste from other units of the steelworks.

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