On Dioxin Formation in Iron Ore Sintering

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Iron ore sintering is an important source of "dioxins", polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/ Fs). This paper reports on attempts to identify materials, conditions, and mechanisms responsible for PCDD/F formation (i) by investigating salient properties of ores (viz., with respect to oxidation, condensation, and chlorination of model organics) and (ii) by mimicking the industrial process on a microscale with real-life materials. Principles of Design of Experiments (DOE) are employed. The reactivities of iron ores differ greatly. Limonite/goethite "soft" ore is a very active oxidation catalyst (e.g., for benzene and phenol), a property that may be useful in cleaning up crude sintering process offgases, whereas hematite/magnetite "hard" ore is not. The latter, however strongly promotes condensation of phenol to dibenzofuran. A newly built labmicroscale sintering facility could satisfactorily imitate the large-scale process, in part or as a whole. Results obtained with realistic feed mixtures point at dioxin formation in the sinter bed at levels significant enough to explain a major part of the outputs observed in the real-life process. With \sim 8 ppm (wt) of chloride added as NaCl, the PCDD/F output doubled, but with the same proportion of chlorine administered as C₂Cl₄, the dioxin output was over 2 orders of magnitude larger. The use of process reverts, etc. containing chlorinated organics should therefore be avoided. PCDD/F congener patterns are also reported and compared with those observed in practice.

Introduction

Background. Ever since the discovery of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the

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offgas of one of the Dutch municipal solid waste incinerators (MSWI) in 1977 (1), there has been a growing concern on "dioxins" formed in this and in other thermal industrial processes. In the course of time, dioxins in gaseous, solid, or liquid effluents of other processes have been reported, including the chemical industry (i.e., production of pesticides) (2), paper manufacturing (3), and the metallurgy of iron and non-iron metals (4). So far, worldwide attempts to close the gap between PCDD/F levels measured in the environment and the recognized sources of these noxious compounds have been unsuccessful (4). Nevertheless it is now sure that metallurgy in general is an important dioxin source. Where exactly in these processes and how dioxins arise are unknown. Therefore, under aegis of the European Union, in 1998 university and industrial groups from Belgium, Germany, Sweden, and The Netherlands joined to investigate pathways and mechanism(s) of formation with the ultimate aim to minimize outputs of PCDD/Fs in thermal industrial processes (MINIDIP).

This paper deals with iron ore sintering, a key largescale metallurgical process. Some preliminary results of our work have been presented earlier (5). Below a brief description is given of the process, the materials involved, and the process parameters considered relevant for dioxin formation.

Sintering Process. Sintering is a preliminary process in iron smelting with the aim to prepare a raw material for blast furnaces. The basic principle of sintering may be compared to smoking of a cigarette or a pipe: sucking air through a glowing material moves the burning front down. The design of a traditional Dwight-Lloyd type sintering plant is very simple and basically unchanged from its early beginning (see Figure 1). Iron ores mixed with cokes and some additives (1) are ignited by (natural or producers) gas-fueled burners (2) situated at the beginning of the steel belt conveyer (3); air is sucked through the sinter layer by means of wind legs (4) and the fan (5), which moves the burning front down the layer; the cooled sinter is ground (by means of rough rolls) and collected.

Environmental concern—with tighter emission limits imposed, not only for dioxins—resulted in a redesigning: instead of one APC (6) unit at the end of the process, the system was fitted with high-pressure scrubbers, air/water recycling loops, and AC (activated carbon) injection absorbers. This improved design, called the Energy Optimized Sintering (EOS), is used for example by Corus Nederland (Figure 2). It leads to a considerable drop in (trace) organic emissions at an overall higher energy efficiency.

Locally, temperatures in the sintering bed can become as high as 1200-1250 °C, but due to its inhomogenity, the actual maximum temperature may locally be less, maybe not higher than 1000 °C. The temperature in the wind legs ranges from ambient at the beginning through some tens of degrees higher values while water is evaporated from the sinterfeed to 200-600 °C when dry air breaks through and the burning front reaches the bottom near the end of the sinter belt.

Materials. The following (raw) materials are used—with proportions typical for a plant operated in Western Europe:

Iron Ores. At least five different ores are employed. Geologically they belong to the mineral groups limonite/goethite (soft ores—low iron content, comprising ca. 15–20 wt % of the mix) or hematite/magnetite (hard ores—high iron content, in total ca. 65 wt % of the sinterfeed).

Additives. This rather ill-defined group of materials includes plant reverts from the whole of the iron metallurgical process as well as mineral flux agents and binders.

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FIGURE 1. Schematic representation of a Dwight-Lloyd iron ore sinter plant: (1) feeder, (2) burner for ignition, (3) steel belt conveyer with (4) wind legs, (5) fan, and (6) APC unit.



FIGURE 2. Schematic representation of the Energy Optimized Sinter (EOS) plant: (1) hopper, (2) burners, (3) sinter belt, (4) wind legs, (5) fan, (6) stack, (7) rough rolls, (8) ESP, (9) high-pressure scrubber/ AC injection, (10) air/dust recycling hood, and (12) fresh/recycled air supply.

Plant Reverts. the most interesting category is ball mill reverts, consisting of finely ground iron ores soaked with mineral oil. The oil content is relatively high (up to 10 wt %), which—given the proportion used in the sinterfeed, 10–15 wt %—results in a high additional organic input. Upon analysis, we have found the oil to consist of mostly linear and branched long-chain aliphatics (octane through dodecane) with trace amounts of substituted cycloalkanes (mostly cyclohexanes) as well as aromatics (naphthalenes and higher). An important fact is that this oil-containing material is only allowed to be recycled in this way in The Netherlands and Belgium (for example, in Great Britain it is subject to landfilling).

Other reverts include sludges and ashes from dedusting units. These materials, especially the ESP ashes, have substantial organic carbon contents as well as considerable chloride levels.

Some 5 wt % of the sinterfeed is actually sinter itself. As the bottom, it serves as a thermal insulator preventing the conveyer belt from excessive heat. Fine sinter, not useful for a blast furnace, is also returned, admixed with the "raw" sinterfeed.

A common flux agent is olivine (2-3 wt %). It allows melting the iron ores at temperatures of around 1000 °C rather than over 1200 °C, as we have experimentally verified. Olivine is a mixed iron/magnesium silicate. Limestone (at ca. 2 wt %) is another common additive.

Coke. In fact, the so-called "breeze", the fines fraction from the coking process, serves as the fuel in the sintering process, employed at 3-3.5 mass %. The ash content of this coke is ca. 10-13 wt % and consists mostly of silicon and aluminum oxides. On this basis, the coke-related carbon input is ca. 2-3% of the total mass. Once again, this shows the importance of the organic carbon load from the plant reverts.

Chlorine Input. Nearly all the above-mentioned materials are very poor in chlorine, typically ca. 0.05 wt %. Exceptionally high levels of chlorine were only reported for ESP ashes (from

the 3rd field) (6). Little if any data are available on the total chlorine balance of the sintering process, particularly when considering organic chlorine.

Another important ingredient is water. The sinterfeed is moistened by 6.3–6.5 wt % to prevent its falling apart while it is put onto the sinter belt as well as to allow smooth burning. It is important to consider the salinity and metal contents of the (surface) water used. For example, the average salinity of the Rhine River water is between 70 and 100 mg/L (data: Rijkswaterstaat—Dutch Water Management Council, Lobith monitoring point). At some 5 million ton per year throughput (70 Mt/yr of sinter, 6.5 wt % of water), this gives an impressive load of 350–500 t of NaCl per year.

Yet another source of chlorine may be the air used in the process. Sintering plants can be located close to, or directly on, the seashore. Sea saline aerosols are known to contain relatively high levels of chloride (7), ca. $4-5 \mu g/m^3$. However, at an estimated "consumption" of some 700 Mm³/yr, this gives a negligible amount of chlorine of ~150 kg as compared to the water-related input of hundreds of tons. The same holds for the input of atmospheric HCl, in view of an average HCl concentration in the industrial air (8) of around 0.2–3 $\mu g/m^3$.

Other Elements. Apart from iron, the ores contain also other metals; the most important are alkaline metals (Ca, Mg, Na, and K up to 2 wt % as oxides), aluminum (0.1-3 wt % as Al₂O₃), titanium (0.1-0.5 wt % as TiO₂), and manganese (0.1-0.2 wt %). Phosphorus and sulfur contents are ca. 0.1 wt % each. Interestingly, copper (a notorious catalyst in MSW fly ashes) is not reported for any of the ores, whereas ESP sinter plant ashes may contain up to tens of a percent of this very subject-relevant metal ($\boldsymbol{6}$).

Dioxins and the Sintering Process. Formation of PCDD/ Fs requires the presence of carbon-containing materials either specific organic compounds or a carbonaceous matrix—and sources of chlorine and oxygen plus increased temperatures (200–800 °C, at higher temperatres PCDD/Fs will rapidly decompose), whereas the presence of catalytic metals can be essential at modest temperatures.

In the sinter bed, basically three layers can be recognized: raw material (wet and cold), the burning front, and the cool-down zone, consisting of sintered material. In the context of dioxin formation, the thin border between the burning front and the raw materials is actually the most intriguing zone. In this region, the products of incomplete combustion (PICs) surviving the heat of the burning front may condense, while the temperature is high enough to enable reactions with species in the raw materials acting as catalysts. Also, the native carbon-containing materials may react via the so-called de novo route (*6*).

Obviously, during sintering conditions are met wherein dioxins can be formed and—for some part—survive. Also downstream, in the wind legs as well as in the APC devices, dioxins may arise in a way not unlike that documented for (waste) incinerators (6, 9). Worth mentioning here is the time scale of the process. Very relevant for kinetic and mechanistic discussion is that it takes some 40 min for the materials to pass on, while in minutes the materials are subjected to a favorable temperature window, as compared with perhaps only a few seconds in the wind legs and minutes again in the APC zone.

In this paper, the possible formation of dioxins *during sintering* is considered, while other publications (*10, 11*) discuss the formation of dioxins downstream of the process. Next to orienting experiments with fixed beds of iron ores—to evaluate their reactivity with respect to model organic compounds such as benzene—a new setup has been designed and employed to mimic the sintering process as a whole on a (micro) labscale. After its optimization with the aid of Experimental Design, actual tests have been performed—



FIGURE 3. Schematic representation of the microscale sintering facility: (1) ignition burner; (2 and 3) top and bottom oven, respectively; (4) sinterfeed; (5) tubular quartz/stainless steel reactor; (6) stainless steel grid; (7) filter/demister assembly; (8) Supelco ORBO1000 cartridge; (9) polyurethane foam plug; and (10) thermo-couples.

with offline analyses—on dioxin formation, output, as a function of important operational parameters. In an attempt to detect (ultra)trace species leaving the sinter bed *online*, the setup was coupled to a JET-REMPI (Resonance-Enhanced Multi Photon Ionization) spectrometer at DLR, Stuttgart, Germany built by Dr H.-H. Grotheer.

Experimental Section

Setups. Setup A has been described earlier (*12*). It consisted of a vertical quartz tubular reactor in an electrical oven, equipped with supplies for gaseous and liquid reagents, sampling facilities, and online GC. The reactor tube (length \sim 30 cm, diameter 2 cm) has been modified to accommodate a fixed bed of iron ore (typically ca. 200 g, bed height \sim 10 cm) to investigate the properties of these materials.

The microscale sintering facility B is schematically depicted in Figure 3. The system consisted of two Watlow 300W/60V ceramic heating elements in an insulating ceramic casing, regulated by means of REX 100 temperature controllers. The tubular reactor, packed with the sinterfeed supported on a stainless steel grid resting on a Seger spring, was directly connected to the air/organic supply on the top and to a Supelco ORBO1000 PUF plug sampler at the bottom, so as to reduce the dead volume to a minimum. Gases were supplied by means of electronic mass flow controllers (Brooks 5850TR). Optionally organics were injected into the gas stream at the top of the reactor by means of a Hamilton gastight syringe on a Microdialysis injection pump. In the top assembly, a small homemade hydrogen burner was fitted, used for ignition purposes only in preliminary experiments. Stainless steel connectors, equipped with valves, in the filter/ demister assembly and the PUF plug cartridge enabled sampling of the outflowing gases through heated sampling lines by means of online gas chromatography as described below. The PUF plug cartridge was kept at -25 °C by means of a homemade cooling mantle and a cryostat.

The reactor system could be heated very rapidly while it was also possible to cool it down (within ca. 5 min) by quenching with countercurrent nitrogen. Moreover, the reactor was mounted inside the oven in a way allowing removing and opening it in a matter of minutes. The originally all-quartz reactor was soon replaced by a passivated stainless steel one as the melted sinter grains were very difficult to remove, leading to destruction of the reactor. However, stainless steel has another drawback: with too high fuel contents the reactor wall can melt through, which damages the heater and of course ends the experiment.

Procedure. After filling with a fresh portion of sinterfeed, the reactor was placed in the oven. The PUF plug unit was then connected, after which the system was checked for leaks. Next, a background gas sample was analyzed to ensure proper performance of the GC facility, eventually followed by the ignition of the system. As mentioned above, the hydrogen burner was only used in the first series of experiments. In the course of the investigation it turned out that the water produced by the burner not only clogged the cryostatted PUF plug but also quenched the sintering. Therefore in later experiments the temperature of the top oven was initially set to 800 °C, allowing for self-ignition of the coke. Upon ignition, the temperature of the top oven was lowered to 600 °C (or a value designated by the ED spreadsheet), while monitoring the advancing burning front by means of thermocouples placed inside the top, middle, and next to the bottom layer of the sinterfeed. The temperature of the bottom oven was set initially at 150°C (or again, a value dictated by the ED) to avoid condensation of water and organic products. When the burning front passed the middle part of the reactor, the temperature of the bottom unit was raised to 600 °C, while the top temperature was set to ambient, allowing the sintered material to cool in a natural way.

The experiment was finished when the burning front passed the bottom thermocouple. The reactor was then quickly removed and cooled in a stream of air. The PUF plug cartridge was also removed and allowed to thaw and subsequently extracted as described below.

Analysis. Details on online gas chromatographic analysis of gas-bound products are described elsewhere (*12*).

Thawed PUF plugs were subjected to 18-h Soxhlet extraction with 110 mL of a 10/1 (v/v) mixture of *n*-hexane/ acetone. The extraction turnover was ~ 10 cycles/h. The solution was concentrated on a rotary evaporator to a volume of a few milliliters. Next, it was condensed to 0.50 mL by means of TurboVap gas stream evaporator. The extracts were analyzed for organic products in Leiden by means of an offline gas chromatography (HP 5890 II series, split/splittless inlet capillary CP-SIL5CB/MS column, HP6890 autoinjector, carrier gas: He) combined with a mass spectrometer (HP MSD 5972). Dioxin analyses were performed in Umea by means of HRGC/HRMS in the following way: 10% of the extract was taken to the cleanup process and spiked with labeled internal standards (IS). The cleanup is based on sequential use of open liquid chromatographic columns. Three types were used for PCDD/F analysis; first a multilayer silica gel column; basic (SiO₂-KOH, 20%), neutral activated $(SiO_2, 130 \degree C)$, and acidic gel $(SiO_2 - H_2SO_4, 40\%)$ eluted with *n*-hexane. This was followed by a super-grade alumina column eluted with cyclohexane:dichloromethane (1:1), and finally a carbopack C column (carbon:Celite) eluted with toluene. Tetradecane was added as a keeper before each concentration with a rotary evaporator. Finally, recovery standard addition completes the cleanup, and the $30-\mu L$ sample is ready for analysis by high-resolution gas chromatography coupled with high-resolution mass spectrometry (HRGC/HRMS). PCDD/Fs were analyzed on a VG-250S (GC: HP 5890 with an SP2330-column, 60 m, 0.32 mm i.d.).

Chemicals. The following chemicals were utilized: benzene (Merck p.a., 99%, distilled), acetone (Baker, >99.5%), naphthalene (Janssen Chimica, >99%), benzonitrile (Merck, >99%), chlorobenzene (Baker Analysed, >99%), phenol (Aldrich, >99%), phenanthrene (>99%), trichloroethane (Baker Analysed, >95%), benzaldehyde (Baker Analysed, >95%), dibenzofuran (Fluka, >95%), monobenzofuran (synthesized, >95%), toluene (Merck p.a., >99%), 2-chlorophenol (Merck, >95%), 2,4,6-trichlorophenol (Aldrich, >95%), tetrachloroethylene (Baker Analysed, >95%), hydrogen (Air Products, 99.995%), methane (Air Products, 99.995%), nitrogen (Air Products 99.995%), oxygen (Air Products 99.995%), and sodium chloride (Merck, >99%). Dioxin analyses were performed using the following solvents: cyclohexane, cyclopentane, dichloromethane, *n*-hexane, tetradecane, toluene (all Fluka, HPLC/GC-grade) and standard solutions for analysis: 13 C-labeled and native with 16 2,3,7,8-substituted PCDD/F congeners (CIL, >99%).

Iron ores, olivine, limestone, millscale, and plant reverts were used as received from Corus Nederland. Genuine sinter and cokes were ground prior to use—courtesy of Corus R&D Department.

Results

Reactivity of Iron Ores. Using setup A (see Experimental Section) benzene per se and solutions of phenol or dibenzofuran (1/9 mol in benzene) have been passed at a feed rate of ca. 1.7 g/h in 2.5-5 L/h of synthetic air (20% O₂ in nitrogen), void residence times of the carrier gas about 4 s, over a fixed bed (ca. 6 cm thick) of two different common iron ore materials: a limonite (ca. 60% Fe, hereafter called the "soft ore") and a magnetite (ca. 80% Fe, the "hard ore"). The temperature was varied from 200 to 700 °C. Salient results are depicted in Figures 4 and 5. It is immediately clear that the two types of ore differ greatly in their catalytic activity and properties; the soft ore is much more active-as an oxidation catalyst-while the hard ore promotes the condensation (of phenol) to dibenzofuran (DBF). Next to DBF, traces of naphthalene and phenanthrene were detected in the liquid catch of the runs with the hard ore.

In two more experiments an amount of Cl equivalent to phenol—as aqueous HCl or as C_2Cl_4 —was added to the feed solution and reacted at 220 and 380 °C (~50% conversion of phenol) with the soft and the hard iron ores as the bed material, respectively. This resulted in very limited outputs of (mono)chlorophenols. No other chlorine-containing products could be identified.

When looking at the conversion of phenol over a soft ore bed (Figure 4), one may see that complete conversion takes place at temperatures of ca. 250 °C, while the $T_{50\%}$ lies outside the experimental range of temperatures, somewhere around 200 °C. Worth mentioning is the fact that next to unconverted substrates no heavier products were detected in the liquid samples. Also, the total CO_x yields are closely following the conversion curves, although the output of carbon monoxide is somewhat higher when using benzene per se.

Lab-Microscale Iron Sintering. *Introductory Experiments.* The performance of the microscale sintering setup B has been evaluated and optimized using the principles of the DOE (*13*). Table 1 summarizes the binary experimental parameters (variables) together with the experimental ranges. Measured outputs (responses) included fuel (coke) burnout efficiency, oxygen consumption, degree and quality of sintering, and possible outputs of organics.

The results will not be presented here in detail as no dioxin data have been obtained. By using the DOE technique, the performance of the system could be optimized. Also, the obtained results were easy to interpret by means of the used DOE software (Umetrics Modde, tryout version). The factors required for the sintering to occur and determining the quality of the sinter have been identified, so providing an optimized set of conditions used in the following investigation.

Dioxin Formation in Microsintering. Next, a series of eight experiments at standard, optimized conditions has been conducted with different sinterfeeds (Table 2). Throughout,

TABLE 1. DOE Spreadsheet for Evaluation/Optimization of the Microsintering Setup

ехр	N ₂ flow (mmol/h)	O ₂ flow (mmol/h)	top oven temp (°C)	bottom oven temp (°C)	burner ^a	organ- ics ^{a,b}	coke (%)	soft ore (%)
1	4012	408	300	100	1	0	5	5
2	2643	408	600	100	0	0	3	5
3	4012	408	600	400	0	0	5	25
4	2643	849	300	100	0	0	5	25
5	4012	408	300	100	0	1	3	25
6	2643	849	600	400	0	1	3	25
7	2643	408	600	100	1	1	5	25
8	4012	849	600	100	0	1	5	5
9	2643	408	300	400	1	0	3	25
10	2643	849	600	400	1	0	5	5
11	4012	849	300	400	1	1	5	25
12	4012	849	300	400	0	0	3	5
13	2643	849	300	100	1	1	3	5
14	3328	628	450	250	0	0	4	15
15	3328	628	450	250	0	0	4	15
16	2643	408	300	400	0	1	5	5
17	4012	849	600	100	1	0	3	25
18	4012	408	600	400	1	1	3	5
19	3328	628	450	250	0	0	4	15

^a Zero means absent, 1 means employed. ^b Mixture of 14 compounds corresponding with a primary combustion offgas (9), admixed with the sinterfeed at a level of ca. 800 ppm (wt) (mostly benzene), details in ref 14.

	ation	Format	Dioxin	on	Focusing	Runs	IN	Parameters	2.	IABLE
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exp name/code	coke (wt %)	hard ore (wt %)	soft ore (wt %)	chlorine form ^a
Standard 1/I	3	15	20	NaCl in H ₂ O
Standard 2/II	3	15	20	NaCl in H_2O
no chlorine/III	3	15	20	none
organic Cl ₂ /IV	3	15	20	C ₂ Cl ₄
hard ore/V	3	30	10	NaCl in H_2O
soft ore/VI	3	5	30	NaCl in H_2O
5% coke/VII	5	15	20	NaCl in H ₂ O
7% coke/VIII	7	15	20	NaCl in H ₂ O

^a Chlorine was supplied in the "process water" or as tetrachloroethylene admixed with the (200 g) sinterfeed at ca. 1.5 mg of Cl/experiment (7.5 ppm).

the temperature of the top and bottom ovens was set at 600° C while the gas flow was kept at 100 L/h.

Runs I–IV focus on the role of chlorine (amount, form); the respective total PCDD/F outputs are shown in Figure 6. Figure 7 depicts relative yields of dioxins in runs V–VIII with different sinterfeed composition. In Figures 8–10, congenerspecific data are given.

Discussion

Properties of Iron Ores. Figures 4 and 5 substantiate that the two ores used in the investigation have very different properties regarding oxidation and condensation of organics. The soft iron ore helps to smoothly oxidize benzene, and even better phenol, at rates very much higher than in absence of the ore. Remarkably, benzene admixed with (10%) phenol reacts faster, as its conversion curve is shifted to 50-60 °C lower temperatures. Such a synergistic effect, with two compounds of different nature, is not uncommon and can be beneficially used for example in the catalytic combustion of chlorinated benzenes with added aliphatic hydrocarbons (*15*). Anyway, it can be concluded that the soft iron ore is a potent oxidation catalyst, comparable even with sophisticated noble metal-based catalysts (*15*).



FIGURE 4. Experimental results on runs with "soft" iron ore.



FIGURE 5. Experimental results on runs with "hard" iron ore.

The hard iron ore also exhibits some catalytic activity, but of a different nature. For example the conversion of phenol sets in around 300 °C, still some 150° less than in the blank run—and needed for its gas-phase slow combustion (*16*). Next to CO_x (now with much more CO than CO_2), relatively large amounts of the condensation product dibenzo-furan are detected. Around 330 °C, the DBF output reaches even some 35% on the converted phenol, much higher than the 1–2% levels observed in gas-phase slow combustion (*17*). Figure 5 shows a second peak in the output curve of DBF, correlating with the onset of benzene conversion. This can be understood if benzene is in first instance oxidized to a phenolic entity, again subject to condensation. As mentioned earlier, in runs with HCl added to the original mixture, only

traces of (mono)chlorophenols have been detected, suggesting that both ores have a small but distinct potential for chlorination of organics.

Microscale Sintering. Even with a relatively large spread between the two standard runs 1 and 2, dioxin outputs vary more than 2 orders of magnitude when comparing experiments with organic, inorganic, and without chlorine (Figure 6). With the same input levels in both "chlorine in" series, it shows the high potential of organic-bound chlorine for dioxin formation. Consequently, in practice, contamination of the sinterfeed with even trace levels of organic chlorine should be avoided. Interestingly, despite this large variation, the toxicity factor of the resulting mixture stays relatively constant; the ratio between the total masses of the formed PCDD/Fs and their TEQ is around 40.

Proper attention has been paid to the overall chlorine balance. When feeding chlorine in the process water, some 65% was found back afterward in the sinter bed upon extraction with slightly alkaline aqueous solution. This shows that chloride is to a large extent immobilized by the materials present in the sinterfeed, most likely by the alkaline minerals (limestone) in addition to the iron oxides. The 65% mentioned above should be considered a minimal value since a part of the chlorine may have become occluded inside sinter particles and, therefore, is inaccessible for the extraction. Only ca. 10% of the chlorine was found in the water condensate frozen on the PUF plug. As other chlorine-containing organic products could not be found, as yet some 25% in the chlorine balance is unaccounted for.

Figure 7 compares outputs of dioxins for various compositions of the sinterfeed, but with the same chlorine form and amount. The overall DD/DF ratio is remarkably constant, with about twice as much DDs as DFs. The dioxin outputs increase with 30-40% when the coke content is doubled. This suggests an increased production of organic precursors, not excluding formation of "complete" PCDD/F structures. Remarkably, the dioxins from runs 7 and 8 have \sim 15 times higher TEQ levels. This can be traced back to the congener distributions (Figure 8). The overall lower chlorination degree as observed in the runs with more fuel and in the case of the hard ore has a pronounced effect on the overall toxicity of the relatively constant output of the tetra- through octa-DD/DF congeners. This may be due to a limited chlorination potential of the involved materials, which is consonant with the results of our "reactivity" study. However, the question remains how in such dilute chlorine streams and with such "impotent" catalysts multiple chlorination occurs, leading to even hepta- and octachloro derivatives.

In Figure 9, outputs of 2,3,7,8-substituted species are depicted for the runs with the different chlorine levels and forms. Surprisingly, the overall chlorination degree in the run with only the "native" chlorine is much higher than in those with HCl or organic chlorine in the feed. The latter experiments gave much higher outputs, but with a roughly comparable distribution. Figure 10 gives "Hagenmaier" charts (with fractions of a specific congener in the total of 2,3,7,8-chlorinated DD or DF family) together with that for the real-life pattern from the work of Calcagni et al. (*18*). How experimental data compare with those from a real sinter plant is broader discussed in the next section.

After coupling of the microscale sintering facility with the JET-REMPI analyzer of DLR in an attempt to observe online species leaving the active sinter bed, an experiment analogous to Standard 1, Table 2 led to the identification of a number of trace products previously not seen in our low-resolution analyses. These were phenol, monochlorophenols, dibenzo-furan, (chloro)benzenes, and various polycyclic aromatic hydrocarbons. Unfortunately, due to the instability of the REMPI system, a proper quantification of the obtained data was not possible. Nevertheless it has been proven that species



FIGURE 6. Summary of PCDD/F outputs in experiments with different chlorine form/quantity.



FIGURE 7. Relative outputs of PCDD/F as a function of the sinterfeed composition.

relevant for dioxin formation can survive the fierce conditions of the sinter bed, staying available for catalytic reactions.

Experimental Results versus Real-Life Data. With the data at hand—using the average of the dioxin outputs in the two standard runs with water-bound chlorine—an attempt is made to compare these outputs to those of real-life processes. (Table 3). Given that pertinent data on large-scale sintering processes are confidential, hence unavailable, several important parameters have been estimated.

The calculated total numbers of nanograms of TEQ per ton of sinter produced in the (model) real facility and in our microscale setup differ (only) by some 30%; indeed a close match, also because dioxin outputs from various sinter plants will not be identical, let alone that fluctuations can occur within a plant (22).

In an excellent recent publication, Kasai et al. (20) also favor dioxin formation in the sinter bed itself, although in experiments with sinterfeed spiked with labeled dioxins the answers were not clear. Obviously the observed PCDD/Fs are a net result of formation and destruction through catalytic processes inside the bed.

Much work within the frame of the MINIDIP project (6, 10) and by others (11) has been done on the possibility of dioxin formation in the air ducts and in the APC zone of a common sintering facility. In the course of these investigations, it was found that some process-derived materials have



FIGURE 8. PCDD/F congener distributions as a function of feed composition.



FIGURE 9. PCDD/F congener distribution as a function chlorine form and concentration.

a very high PCDD/F formation potential through de novo reactions (i.e., conversion of carbonaceous matter on ash/ sinter particles at elevated temperatures). For example, Buekens et al. (10) report on extremely high dioxin levels, in the range of 10 000 ng/g, obtained by reacting some electrostatic precipitator ashes at temperatures of around 300 °C. In practice, however, the temperature in the ESP never exceeds 170 °C, so this result, though very interesting, must be treated with caution. Also, computer-generated temperature/dust concentration profiles in the sinter plant air ducts (22) indicate that particles reside at temperatures exceeding 300 °C for at best a few seconds. By combining these results with experimental findings of Buekens et al. (10), a model was generated indicating that the de novo activity on fly ashes cannot be held responsible for the overall dioxin outputs from sintering.

Finally, it should not go without comment that the experimental PCDD/F congener distributions (Figure 10) are at (sometimes considerable) variance with the real-life charts. The dibenzo-*p*-dioxins constitute almost 75% of the total of formed PCDD/Fs as compared to \sim 70% of PCDFs in the real-life samples; also the chlorination degree is different. It should be pointed out that the real sinter plant and our lab facility, based on an hourly sinter output, differ not less than 6 orders of magnitude in scale. This and the process mechanics (flows, sintering efficiency, perhaps some wall



FIGURE 10. PCDD/F toxic congener distribution charts, compared.

TABLE 3. Comparison of Experimental and Real-Life Data on Dioxin Formation^a

real life	value	units	value	Leiden experiments ^b
		ng/exp	11	total PCDD/Fs in PUF plug
		ng TEQ/exp	0.25	TEQ in PUF plug
TEQ measured at stack (19)	43	ng TEQ/Nm ³		
PCDD/F concn at wind boxes (20)	190	ng/Nm³	73.3	PCDD/F concn
concn after APC devices (20)	7.3	ng/Nm³		
TEQ after APC (20)	0.04	ng TEQ/Nm ³		
daily output (sinter) (20)	9 600	Mg/d, g/exp	150	sinter output
daily input ^c	10 500	Mg/d, g/exp	200	sinterfeed input
air flow/ton of sinter (21)	2 200	Nm ³ /Mg of sinter	1 000	extrapolated total air flow/ton of sinter
total daily air flow	21 120 000	Nm³/d, Nm³/exp	0.15	total air throughput
dioxin output/ton of sinter ^d	418 000	ng of PCDDF/Mg of sinter	73 333	extrapolated PCDD/F output/ ton of sinter
TEQ/ton of sinter at the stack ^e	88	ng TEQ/Mg of sinter		
total TEQ wind boxes ^f	1.04	ng TEQ/Nm ³	1.67	TEQ in gas
total TEQ/ton of sinter ^g	2 290	ng TEQ/Mg of sinter	1 667	extrapolated TEQ/ton of sinter

^a Estimated values are in italics. ^b Based on the "standard" experiments (code I and II) with water-bound chlorine. ^c Daily output + 6.5% water + 2% carbon (output + "volatilized weight"). ^d (Concentration at wind boxes × air flow)/sinter output. ^e (TEQ after EPC × air flow)/sinter output; ^f (Total TEQ after APC)/(total PCDDF after APC)(PCDDF concentration at wind boxes). ^g (Estimated TEQ in wind boxes × air flow)/sinter output.

effects, etc.) may be comparable but not exactly the same. Also, the sinterfeeds did not include (models for) substances such as millscale oil-containing refuse, ESP ashes/sludges, etc. that are likely to have a distinct effect on the formation of PCDD/Fs. Moreover, the congener distribution from a real plant depends strongly on the sampling point (*18*), as can be seen in Figure 10 (compare Calcagni's "scrubber" and "baghouse" data).

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