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Prevention of dioxins de novo formation by ethanolamines

Abstract Two inhibitors, triethanolamine (TEA) and monoethanolamine (MEA), were tested for their ability to prevent the de novo formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) on sinter plant fly ash. The amounts of both PCDDs and PCDFs, formed by thermal treatment of the fly ash, decreased when inhibitors were added. Up to 90% reduction of the PCDD/Fs formation was reached when 2 wt % monoethanolamine was mixed with fly ash. The temperatures tested, 325 and 400 °C, did not affect the inhibition activity. However, a longer reaction time, 4 h instead of 2 h, gave higher percentages of PCDD/Fs reduction. The laboratory results show that ethanolamines reduce the dioxins formation on sinter plant fly ash under various conditions of temperature and reaction time. Moreover, factory tests performed in parallel at a sinter plant are in good agreement with the laboratory experiments, thus confirming that the use of ethanolamine inhibitors is an appropriate technique for the prevention of dioxins emissions from sintering processes.

Keywords Polychlorodibenzo-*p*-dioxins (PCDDs) · Polychlorodibenzofurans (PCDFs) · De novo synthesis · Inhibition · Fly ash · Sinter plant

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly toxic compounds produced by some natural processes, such as forest fires and volcanic eruptions, and different human activities. Dioxins structure is depicted in Fig. 1. These pollutants consist of a group of chlorinated tricyclic aro-

matic compounds with different degrees and positions of chlorination on the molecule skeleton, thus leading to the occurrence of 75 congeners of PCDDs and 135 congeners of PCDFs, usually termed 'dioxins'. Some congeners such as 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) are known to be among the most toxic compounds with potential carcinogenic and mutagenic effects.

Anthropogenic sources of dioxins include the incineration of waste and most combustion processes. Since the discovery of PCDD/Fs in the flue gas and fly ash of municipal waste incinerators by Kees Olie (1977), the formation of these toxic compounds has been studied intensively. Some reviews summarized the most important trends and results (Addink and Olie 1995; Tuppurainen et al. 1998). Two different pathways have been proposed to explain the occurrence of dioxins (PCDD/Fs) in the emissions of incinerators and other combustion processes: the synthesis from precursors and the de novo synthesis. The first pathway involves the formation of PCDD/Fs by reactions of chemical precursors such as chlorophenols, which are formed initially by incomplete combustion. The second de novo synthesis pathway involves PCDD/Fs formation from macromolecular carbon present in the fly ash. Indeed heterogeneous reactions between the gas phase and the fly ash are catalyzed by some constituents of the fly ash such as copper and iron chlorides. Many authors postulate that this synthesis could take place essentially in the post combustion zone of the incinerators at a temperature around 300 °C (Vogg and Stieglitz 1986). The de novo formation of PCDD/Fs is supposed to be strongly correlated with the metal-cata-
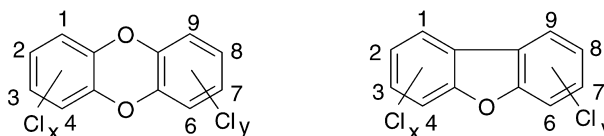
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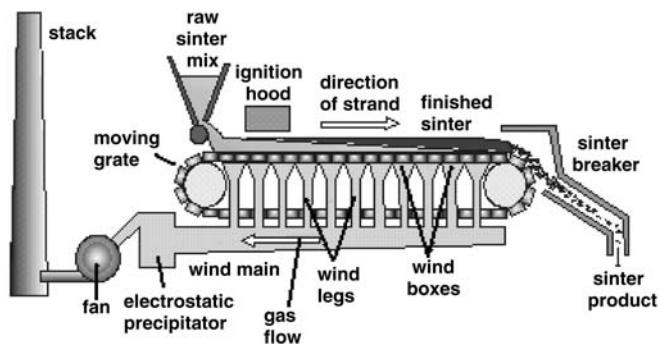B6c Sart Tilman, B 4000 Liège, Belgium
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Fig. 1 Molecular structure of dioxins. Polychlorodibenzo-p-dioxins (PCDDs) (*left*) and polychlorodibenzofurans (PCDFs) (*right*)

Fig. 2 Schematic representation of a typical sinter plant (Anderson et al. 2001). This process is the core of an integrated steel plant where ore fines and ferrous reverts are converted into a feedstock acceptable in the blast furnace. High dioxins concentrations have been measured in the stack of different plants (Bröker et al. 1993) and, in most of the European countries, sintering process is now recognized as the major source of dioxins (European Dioxin Inventory-Stage I, 1997). Most dioxins emitted by this industrial process are supposed to be formed by de novo synthesis on fly ash in the wind boxes and the pipes, in particular on fly ash immobilized on walls (Xhrouet et al. 2001a, 2002b)

lyzed oxidation of carbon in the fly ash (Huang and Buekens 1996). The oxidative degradation of the carbon structure gives mainly gaseous products such as CO_2 and CO as well as, in a minor pathway, some small aromatic compounds including PCDD/Fs.

Although iron and steel industries are known to be important sources of PCDD/Fs in different countries (Lahl 1993; Bröker et al. 1993), most studies concerning the formation of these highly toxic compounds deal only with municipal waste incineration. Relatively few data are available for industrial and metallurgical processes, in particular for sintering plants (Buekens et al. 1998, 1999a, 1999b, 1999c, 2001; Stieglitz and Buekens 1999; Stieglitz et al. 1999; Weber et al. 1999).

The sintering process is an essential step in an integrated iron metallurgical plant. In this process, the iron ore is converted to larger fragments acceptable in the blast furnace. The sinter plant consists of a 50–100 m long, 3–5 m wide, horizontal strand, which supports the feed of hematite ores, cokes and lime, and is slowly moving (see Fig. 2). Burners initiate the process by igniting the feed layer on top and ambient air is sucked through the layer that moves the burning front downwards. The sinter is then cooled and broken before its use in the blast furnace. Separate chambers, called wind boxes and located below the strand, collect the off-gas prior to filtering in appropriate dust collectors. The detailed mechanism as well as the place of PCDD/Fs formation in the sintering process remain unknown although all the necessary ingredients are present: carbon from the coke, oxygen in the air sucked through the cake, chlorine and catalytic metals available in the ores. Considering the very large gas flow volumes (up to 10^6 m^3/h) discharged from these industrial processes, the contribution of the dioxin pollution by these sources is important. In Belgium, it can be estimated from the data

by Wevers and De Fre (1995) that, in 1995, the industry sector was responsible for 34% of the total dioxin emissions; among the different industries, 24% of the dioxin emissions estimated for the industrial sector came from sintering.

PCDD/Fs emissions can be controlled by means of flue gas cleaning systems, which remove the PCDD/Fs present in the gas, or by the way of the inhibition technique, which tries to avoid or reduce the formation of PCDD/Fs in the process. A recent review presents a comparative evaluation of techniques for controlling the formation and emission of PCDD/Fs in municipal waste incinerators (Buekens and Huang 1998).

Although PCDD/Fs formation in combustion processes is being studied widely, studies on inhibition are quite sparse, especially on sinter plants. This prevention technique is, however, adequate for this particular industrial process: the inhibitors can simply be mixed with the raw material and the additional cost will be insignificant. Various inhibitors have been tested both in laboratory and in pilot plants to reduce the PCDD/Fs formation relating to incineration processes. Different studies reveal the inhibition ability of some basic compounds such as NH_3 (Ruokojärvi et al. 1998; Vogg et al.1987), CaO (Naikwadi and Karasek 1989), NaOH and KOH (Naikwadi et al. 1993). Based on the concept of "poisoning" the catalyst, another group of compounds is used as inhibitors for the PCDD/Fs formation: compounds able to form a complex with a catalyst like the functionalized amines. Ethanolamine and triethanolamine are very effective (Dickson et al. 1989; Naikwadi et al. 1993). Urea has also been examined in this way by several research teams as a potential PCDD/Fs inhibitor (Dickson et al. 1989; Ruokojärvi et al. 1999, 2001; Samaras et al. 2001; Tuppurainen et al. 1999; Xhrouet et al. 1999; Yli-Keturi et al. 1999).

In the present paper, we report on a series of inhibition experiments carried out with sinter plant fly ash. We have showed in a previous study that this fly ash is very active in de novo formation of PCDD/Fs and we investigate here the possibility to prevent this formation by using inhibitors (Xhrouet 2002; Xhrouet et al. 1999, 2001a). Two different inhibitors are examined: triethanolamine (TEA) and monoethanolamine (MEA). Different parameters such as the amount of inhibitors, the temperature and the reaction time are investigated. Preliminary results of our investigation have been published before (Xhrouet et al. 2001b). To get a better understanding of the inhibition mechanism, the homologue and full isomer distributions were also examined and are detailed elsewhere (Xhrouet 2002; Xhrouet et al. 2002).

Experimental

Materials

The following materials were used: solution of 2,3,7,8-Cl-substituted $^{13}C_{12}$-labeled PCDD/Fs (EPA 1613 LCS, Campro Scientific, Veenendaal, The Netherlands); tolu-

ene (p.a., Baker); hexane (p.a., Baker); dichloromethane (p.a., Vel); dodecane (Merck); sulfuric acid (95–97%, Baker); sodium chloride (p.a., Merck); potassium hydroxide (p.a., Merck); sodium sulfate anhydrous (Baker); aluminum oxide (activated, neutral, type 507c, Aldrich); glass wool (silane treated, Alltech Europe); technical dry air (Air Liquide, Belgium), triethanolamine (97%, Acros), and monoethanolamine (99%, Acros).

Fly ash

Fly ash was collected in the electrostatic precipitator of a Belgian sintering plant. This electrofilter consists of three fields and operates at 120–130 °C. The fly ash used in this study comes from field 3 and was stored at ambient temperature prior to lab experiments. Around 72.5 wt % of the fly ash has a size under 40 µm. The fly ash composition was (wt %): Mg (1.04), Al (2.17), Si (3.62), P (0.24), S (4.07), Cl (9.55), K (9.07), Ca (7.83), Cr (0.04), Mn (0.31), Fe (49.90), Cu (0.17), Zn (0.34), Pb (5.98), C (3.34). All experiments were conducted with extracted fly ash in order to minimize potential interferences from adsorbed organic precursors and native PCDD/Fs. Prior to experiments, all fly ashes were Soxhlet extracted with toluene (2×24 h), rinsed with hexane, and air-dried at room temperature. This fly ash, cleared of native PCDD/Fs, is called "extracted fly ash" or "fly ash" in the rest of the paper as opposed to the "original fly ash", which refers to the fly ash that comes directly from the sintering plant without any pretreatment and contains the native PCDD/Fs. Only trace amounts of PCDD/Fs were found in the extracted fly ash.

Inhibitors

Two different inhibitors have been tested in this study: triethanolamine (TEA) and monoethanolamine (MEA). Extracted fly ash was mixed with 0.5, 1 or 2 wt % of inhibitors. The inhibitor was preliminarily dissolved in methanol, then mixed with the fly ash and the methanol evaporated.

Experimental apparatus

5 g of sample (fly ash or fly ash+inhibitor) was packed into a horizontal glass tube reactor (16 cm long, 3 cm diameter) with glass wool as plugs. The tube was placed in a chromatographic furnace, and the samples were heated under a flow of technical air (100 ml/min). Three kinds of experiments were performed: 325 °C during 2 and 4 h, 400 °C during 2 h. Products evaporated from the fly ash were collected using two cold-traps in series (100 ml of toluene cooled with ice). Each experiment was performed in duplicate or triplicate; mean values±range are reported.

Cleanup

The slightly modified EPA-8280 was followed for classical PCDD/Fs analysis. Detailed procedures are described elsewhere (Xhrouet et al. 2001a).

Analysis

All analyses were performed by gas chromatography-mass spectrometry (GC-MS) using Mat95-XL high-resolution mass spectrometer and Hewlett-Packard 6890 Series gas chromatograph. GC conditions were optimized to separate most PCDD/Fs as followed: SP2331 capillary column [Supelco, 60 m×0.25 mm i.d., 0.2 µm film thickness, poly (80% biscyanopropyl/20% cyanopropylphenyl)siloxane]; splitless injection of 2 µL extract at 275 °C; temperature: 150 °C (1 min), 150–200 °C (15°/min), 200–273 °C (1.2°/min), then 273 °C (18 min). Helium carrier gas. The mass spectrometer was operated in the electron impact ionization mode using selected ion monitoring. The mass spectrometer was tuned to a minimum resolution of 10000 (10% valley), and was operated in a mass drift correction mode using FC5311 to provide lock masses. The two most abundant ions in the chlorine clusters of the molecular ion were recorded for each congener of native and labeled PCDD/Fs. The source temperature was 270 °C.

Identification and quantification

Most dibenzodioxins substituted with 4 to 8 Cl and dibenzofurans substituted with 4 to 7 Cl were analyzed. No analyses of the species bearing less than 4 Cl were performed. Native concentration was determined by isotopic dilution using the 2,3,7,8-Cl-substituted ^{13}C-labeled PCDD/Fs to quantify all the native isomers within homologues assuming equal response for all isomers within an isomer group and no isomer-selective losses during the cleanup. The isomers were identified according to Ryan et al. (1991).

Results and discussion

Two ethanolamine inhibitors, monoethanolamine (TEA) and triethanolamine (MEA), were tested to study their effect on the catalytic activity of the sinter plant fly ash towards the prevention of dioxins (PCDD/Fs) formation by de novo synthesis. The inhibition tests were compared to control experiments, which consisted of thermal experiments performed without inhibitors mixed with the fly ash. Percentages of inhibition were calculated from the difference with control tests. Results obtained are summarized in Table 1. Figure 3 shows a part of the results (325 °C and 2 h). The authors have paid particular attention to presenting their results with margins of error (tables and figures). These are too often absent from

Table 1 Inhibition of dioxins (PCDD/Fs) formation by ethanolamine inhibitors during thermal experiments with sinter plant fly ash. *TEA*: triethanolamine, *MEA*: monoethanolamine, $\Sigma PCDD$: sum of dibenzodioxins congeners substituted with 4 to 8 Cl, $\Sigma PCDF$: sum of dibenzofurans congeners substituted with 4 to 7 Cl

Test run	$\Sigma PCDD^a$	$\Sigma PCDF^a$	$\Sigma PCDF/\Sigma PCDD^b$	% PCDD inhibition[d]	% PCDF inhibition[d]
325°C, 2 h, no inhibitor	175±24	2185±431	12.4±0.4		
325°C, 2 h, TEA 0.5%	95±25	1918±119	21.9±3.5	45±16	12±18
325°C, 2 h, TEA 1%	108±18	2413±108	23.3±2.4	38±13	−11±22
325°C, 2 h, TEA 2%	25±3	485±68	19.6±0.4	86±2	78± 5
325°C, 2 h, MEA 0.5%	154±7	3406±2	22.2±0.5	12±13	−56±31
325°C, 2 h, MEA 1%	64±11	1817±214	28.8±0.8	63±8	17±19
325°C, 2 h, MEA 2%	44±12	775±387	16.4±2.2	75±8	65±19
325°C, 4 h, no inhibitor	320±44	4667±347	14.7±0.5		
325°C, 4 h, TEA 0.5%	209±105	2757±2024	12.2±2.0	35±34	41±44
325°C, 4 h, TEA 1%	194±15	3551±184	18.4±0.8	40±10	24±7
325°C, 4 h, MEA 0.5%	78±1	623±181	8.1±1.2	76±3	87±4
325°C, 4 h, MEA 1%	79±7	481±38	6.2±0.5	75±4	90±1
325°C, 4 h, MEA 2%	48±14	459±4	10.6±1.6	85±5	90±1
400°C, 2 h, no inhibitor	130±16	1552±384	15.1±[c]		
400°C, 2 h, TEA 0.5%	59±11	1384±157	23.4±0.7	43±14	11±18
400°C, 2 h, TEA 1%	63±5	1500±39	23.9±0.7	39±11	3±16
400°C, 2 h, MEA 1%	18±8	340±167	18.9±0.7	83±8	78±11

[a] Concentrations in ng/g, mean value±range.
[b] Calculated for each experiment; mean value±range is given.
[c] Less than 0.05.
[d] Relative to the experiments without inhibitor under identical conditions using $\frac{A \pm a}{B \pm b} = \frac{A}{B} \pm \sqrt{\frac{1}{B^2}a^2 + \frac{A^2}{B^4}b^2}$, for example: PCDDs

325°C, 2 h, TEA 2%: (25±3)/(175±24)=14±2%, corresponding to an inhibition yield of 86±2%.
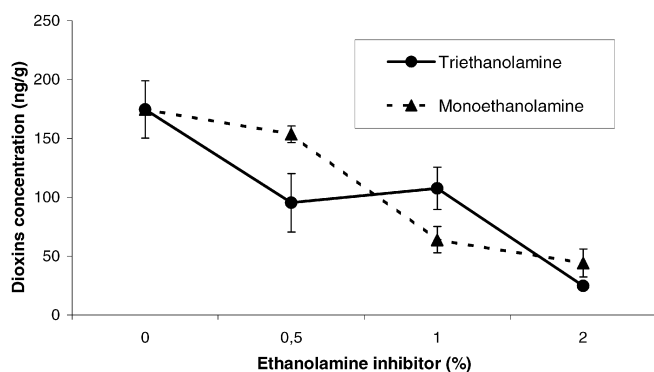

Fig. 3 Total amounts of dioxins (PCDDs: dibenzodioxins congeners substituted with 4 to 8 Cl) formed in the different inhibitors tests (temperature 325 °C, reaction time 2 h). Mean value±range

publications in the field, although it is known that such experiments are not easy to reproduce. In our case, the margins of errors are generally acceptable except for one test run (325 °C, 4 h, 0.5%TEA). This result has, in spite of that, been included in the table. However, the reader should be aware of the margin of error reported.

The results indicate that a clear reduction in both PCDDs and PCDFs concentrations occurred when inhibitors are used (Table 1, Fig. 3). Depending on the temperature and the reaction time investigated, the global inhibition yields are up to 90%. The results obtained are generally better with monoethanolamine (MEA) than with triethanolamine (TEA), and with the highest amount of inhibitors studied (2 wt %). Surprisingly, the inhibition test run at 325 °C, 2 h, with 0.5% MEA, shows an increase in PCDFs concentrations (inhibition yield: −56±31%). The margin of error relating to the PCDFs amount is however very small, only ±2 ng/g, corresponding to a relative error of 0.06%. This error is not realistic since errors of 10–20% are generally accepted for the only measure of PCDD/Fs in samples. It is indeed odd that MEA at low concentrations increases PCDD/Fs formation since it is supposed to block the de novo catalyst and can not easily be considered as a precursor to PCDD/Fs. Problems with the experimental conditions in this test run are thus strongly suggested.

Inhibition as a function of the temperature

Effect of the temperature on the inhibition of dioxins formation was also investigated. It can be observed from Table 1 that, for TEA, the temperature of reaction has no effect on the percentage of inhibition obtained. For example, the inhibition yields observed for the PCDDs with 1 wt % of inhibitor are 38 and 39% for experiments performed at 325 and 400 °C, respectively. For MEA, it seems that the inhibition is slightly better at 400 °C than at 325 °C (inhibition yield of 83% versus 63% for the PCDDs with 1 wt % of MEA). The same trend was observed for the PCDFs. These results are quite surprising since we thought that a higher temperature of reaction would induce a partial vaporization or degradation of the inhibitors and thus, a decrease in the inhibition. Nevertheless, these results are very encouraging relating to the sinter plant itself. Indeed, the sintering process presents a large range of temperature along the strand and in the

Table 2 Inhibition of dioxins formation by monoethanol-amine (MEA). Effect of reaction time (temperature 325 °C, mean value±range, *PCDDs*: sum of dibenzodioxins congeners substituted with 4 to 8 Cl, *PCDFs*: sum of dibenzofurans congeners substituted with 4 to 7 Cl)

	MEA (wt %)	% inhibition					
		PCDDs			PCDFs		
		0.5	1	2	0.5	1	2
Reaction time	2 h	12±13	63±8	75±8	−56±31	17±19	65±19
	4 h	76±3	75±4	85±5	87±4	90±1	90±1

different wind boxes located below the strand that collect the off-gas. The results suggest that the great variation of temperature along the process will not affect the performance of the inhibitors and that the inhibition remains effective at different temperatures.

Inhibition as a function of the reaction time

Table 2 summarizes the inhibition yields obtained for experiments with MEA as a function of the reaction time. Results show that longer reaction time (4 h instead of 2 h) gives better inhibition yields. The difference between the percentages of inhibition obtained at 2 and 4 h is particularly significant when the inhibition at 2 h is low (with a small amount of inhibitors). The percentage of PCDDs inhibition with MEA goes up from 12% at 2 h to 76% at 4 h for 0.5 wt % of inhibitor, although it goes only from 75% at 2 h to 85% at 4 h for 2 wt % of inhibitor. The same trend was observed with TEA for the PCDFs: inhibition yields go up from 12% at 2 h to 41% at 4 h for 0.5 wt % of TEA. For the PCDDs, there is no clear influence of the reaction time: with 1 wt % TEA, the inhibition yields obtained for the PCDDs are 38% at 2 h and 40% at 4 h. It can be concluded that longer reaction times do not involve loss of inhibitory activity through evaporation or destruction of the inhibitor, which is an advantage for the use of this technique in the industrial process, where various reaction conditions may exist, notably for the residence time.

Inhibition tests performed at a real sintering process

Parallel to these laboratory experiments, inhibition tests were performed in an industrial sinter plant. The same two inhibitors were tested: TEA and MEA. The way the inhibitors were introduced, however, was totally different: the inhibitors were dissolved in water and introduced into the operating process by way of spraying nozzles placed in wind boxes located below the strand. Reference tests were performed without inhibitor injection and compared to inhibition experiments in which the inhibitor was injected continuously and measurements carried out after different times.

The results obtained at the sinter plant are in good agreement with the laboratory experiments. Mono- and triethanolamines were both effective in preventing the dioxins (PCDD/Fs) formation in the industrial process.

Monoethanolamine gives better results with percentages of inhibition up to 90% (the inhibition yields were calculated on the basis of dioxins concentrations taking only the 17 toxic congeners of dioxins affected by their toxic equivalent factor into account, Van den Berg et al. 1998). Better results were obtained for longer times between the beginning of the inhibitor injection and the sampling. This latency is not surprising since time is necessary to obtain a good spreading of the inhibitor in the process and especially on the walls where adsorbed fly ash can produce great amounts of PCDD/Fs by de novo synthesis.

Conclusions

Mono- and triethanolamines are both effective inhibitors to prevent the de novo formation of dioxins (PCDD/Fs) on sintering fly ash. Longer reaction times or higher temperatures do not involve loss of inhibitory activity through evaporation or destruction of the inhibitor, which is an advantage for the use of this technique in industrial processes, where various reaction conditions may exist. This study confirms that inhibition is a suitable and very cheap technique, necessitating only a few technical devices, for the reduction of PCDD/Fs emissions from sintering process, the major source of these pollutants in the environment.

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