PREVENTION OF PCDD/Fs DE NOVO FORMATION ON SINTERING PROCESS FLY ASH.

Céline XHROUET, Caroline NADIN, Catherine PIRARD, Edwin DE PAUW

University of Liège, Mass Spectrometry Laboratory, B6c Sart Tilman, B-4000 Liège, Belgium

INTRODUCTION

Although iron and steel industries are known to be important sources of PCDD/Fs in different countries[1,2], most studies concerning the formation of these toxic compounds deal only with MWI. Relatively few data are available for industrial and metallurgical processes, in particular for sinter plants[5-11]. Considering the very large gas flow volumes discharged from these industrial processes, the contribution of the dioxin pollution by these sources is important.

PCDD/Fs emissions can, of course, be controlled by means of flue gas cleaning systems such as electrostatic precipitators, fabric filters, activated carbon injections, etc. From a technical viewpoint, the concept of inhibition differs from flue gas cleaning techniques in that inhibition deals with prevention of PCDD/Fs formation, whereas flue gas cleaning removes PCDD/Fs already formed. Various inhibitors have been tested to reduce the PCDD/Fs formation. A first category of inhibitors is formed by basic compounds such as NH_3[12, 13], CaO[14], NaOH and KOH[15]. Another category of inhibitors includes compounds that are likely to form a complex with the transition metal ions that catalyze PCDD/Fs formation. From this category, functionalized amines are very effective[15, 16]. Concerning the mechanism of inhibition, an interaction (complexation) with the (Cu) catalyst is the most likely manner in which the functionalized amines work. Lippert et al. have observed the existence of a Cu-N bond during the reaction of bromobenzene on alumina with Cu as catalyst and ethanolamine as an inhibitor (200 °C)[17].

In this paper, we report on inhibition experiments carried out with sinter plant fly ash. We have showed[20,21] that this fly ash is very active in de novo formation of PCDD/Fs and we investigate here the possibility to prevent this formation. Two inhibitors are examined: triethanolamine (TEA) and monoethanolamine (MEA). Different parameters (amount of inhibitors, temperature and reaction time), as well as the homologue and full isomer distributions are investigated.

EXPERIMENTAL SECTION

Fly ash. Fly ash was collected in the electrostatic precipitator of a Belgian sintering plant. All experiments were conducted with extracted fly ash. Prior to experiments, all fly ashes were Soxhlet extracted with toluene (2 × 24 h), rinsed with hexane, and air-dried at room temperature.

Inhibitors. Extracted fly ash was mixed with 0.5, 1 or 2 wt % of inhibitors. The inhibitor was preliminary dissolved in methanol, then mixed with the fly ash and the methanol evaporated.

Experimental apparatus. 5g of sample was packed into a glass tube reactor with glass wool as plugs. The samples were heated under a flow of air (100mL/min). Products evaporating from the fly ash were collected using two washing bottles in series (100mL of toluene cooled with ice). Each experiment was performed in duplicate or triplicate.

Cleanup. Detailed method has been described previously[21].

Analysis. All analyses were performed by HRGC/HRMS using Mat95-XL and HP 6890 Series. The GC conditions were optimized to separate most of the PCDD/Fs (see previous study[21]). The source temperature was set to 270 °C.

Identification and quantification. Most of the T_4CDD-OCDD and T_4CDF-HpCDF congeners were analyzed. Native concentration was determined by isotopic dilution using the 2,3,7,8-Cl-substituted labeled PCDD/Fs to quantify all the native isomers within homologues. The isomers were identified according to ref[22].

RESULTS AND DISCUSSION

The summary of the experiments performed and the results obtained are presented in Table 1. Percentages of inhibition were calculated from the reference tests performed without inhibitors Figure 1 shows a part of the results (325 °C and 2 h).

Test run	ΣPCDD[a]	ΣPCDF[a]	ΣPCDF/ΣPCDD	% PCDD inhibition[b]	% PCDF inhibition[b]
325°C, 2h, no inhibitor	175 ± 24	2185 ± 431	12.5		
325°C, 2h, TEA 0.5%	95 ± 25	1918 ± 119	20.1	45	12
325°C, 2h, TEA 1%	108 ± 18	2413 ± 108	22.4	38	-11
325°C, 2h, TEA 2%	25 ± 3	485 ± 68	19.7	86	78
325°C, 2h, MEA 0.5%	154 ± 7	3406 ± 2	22.2	12	-56
325°C, 2h, MEA 1%	64 ± 11	1817 ± 214	28.5	63	17
325°C, 2h, MEA 2%	44 ± 12	775 ± 387	17.6	75	65
325°C, 4h, no inhibitor	320 ± 44	4667 ± 347	14.6		
325°C, 4h, TEA 0.5%	209 ± 105	2757 ± 2024	13.2	35	41
325°C, 4h, TEA 1%	194 ± 15	3551 ± 184	18.4	40	24
325°C, 4h, MEA 0.5%	78 ± 1.	623 ± 181	8.0	76	87
325°C, 4h, MEA 1%	79 ± 7	481 ± 38	6.1	75	90
325°C, 4h, MEA 2%	48 ± 14	459 ± 4	9.7	85	90
400°C, 2h, no inhibitor	130 ± 16	1552 ± 384	15.1		
400°C, 2h, TEA 0.5%	59 ± 11	1384 ± 157	23.6	43	11
400°C, 2h, TEA 1%	63 ± 5	1500 ± 39	23.8	39	3
400°C, 2h, MEA 1%	18 ± 8	340 ± 167	19.5	83	78

[a] Concentrations in ng/g, mean value ± range [b] Relative to the experiments without inhibitor under identical conditions

Table 1. Summary of the experimental conditions and results.

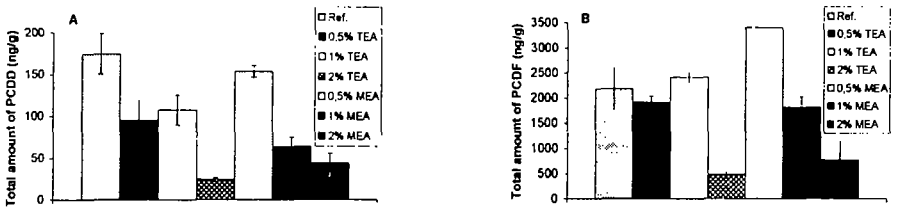

Figure 1. Total amounts of PCDDs (A) and PCDFs (B) obtained in the different inhibition tests (temperature 325 °C, reaction time 2 h). Mean value ± range.

The results indicate that a clear reduction in both PCDDs and PCDFs concentrations occurred when inhibitors are used. Depending on the temperature and the reaction time investigated, the global inhibition yields are up to 90%. The results obtained are generally better with MEA than with TEA, and with the biggest amount of inhibitor studied (2 wt %).
The PCDFs/PCDDs ratios, as well as the homologue and full isomer distributions, were investigated. Indeed, as pointed out by Olie et al.[18 19], if only one route of formation with one catalyst exists during de novo synthesis, an inhibitor can only reduce the amount of PCDD/Fs formed but not change the PCDFs/PCDDs ratios, the congener or isomer distributions. Parallel formation pathways catalyzed by various species can be affected by an inhibitor in a different way and consequently such a change in ratios or patterns can occur.
For the PCDDs/PCDFs ratios, two different trends can be established (not shown). At relatively short reaction time (2 h), the PCDFs/PCDDs ratios rise as a result of the addition of inhibitors. These results are in perfect agreement with those of Olie et al.[19], who performed inhibition tests on incinerator fly ash during 60 min. These results suggest that with a reaction time of 2 h, at 325 or 400 °C, the inhibition is better for the PCDDs than for the PCDFs and thus that PCDDs and PCDFs are formed in the de novo synthesis by different pathways. At longer reaction time (4 h), the differences between the PCDFs/PCDDs ratios of the reference and the inhibition tests become smaller. With increasing reaction time, the inhibition becomes as good for PCDFs as for PCDDs.

The homologue distributions for the different experiments performed during 2 h (not shown) seem not to be affected by the presence of the inhibitors. The inhibition yields obtained are identical for the different chlorofamilies. However, the homologue distribution obtained for experiments performed at 325 °C but during longer reaction time (4 h), are affected by the presence of the inhibitors. The lower chlorinated species (tetra- and penta-) decrease in comparison with the reference test, whereas the most chlorinated (OCDD) rise from 13 % in the reference test to values between 25 and 53 % for the different inhibition tests.

The full PCDD/Fs isomer distributions (not shown) are not influenced by the addition the inhibitors whatever is the temperature or reaction time investigated. The inhibitors appear not to be able to alter the isomer distribution within homologues. These results are consistent with earlier observations that isomer distributions of PCDD/Fs formed on fly ash do not depend on the experimental conditions (temperature and reaction time) and appear to be thermodynamically controlled[3,4,21]. The inhibitors are able to reduce the global amounts of PCDD/Fs but not to suppress the formation of the toxic 2,3,7,8-substituted isomers selectively.

Inhibition as a function of the temperature.
Figure 2 presents the percentages of inhibition obtained for some experiments as a function of the temperature of reaction. It can be observed that, for the TEA, the temperature of reaction has no

effect on the percentage of inhibition obtained. For the MEA, it seems that the inhibition is better at 400 °C than at 325 °C. The same trend was observed for the PCDFs (not shown).

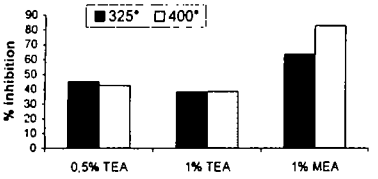

Figure 2. Inhibition yield for the PCDDs as a function of the temperature, reaction time 2 h.

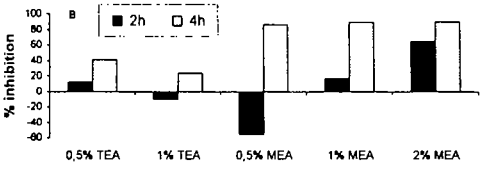

Figure 3. Percentage of inhibition for the PCDFs as a function of the reaction time, temperature 325 °C.

These results are quite surprising since we could think that a higher temperature of reaction will induce a partial vaporization or destruction of the inhibitors and thus, a decrease in the inhibition. Nevertheless, these results are very encouraging relating to the sinter plant itself. Actually, the sintering process presents a large range of temperature along the strand and in the wind boxes. The results suggest that the great variation of temperature along the process will no affect the ability of the inhibitors and that the inhibition can remain effective at different temperatures.

Inhibition as a function of the reaction time.

Figure 3 presents the percentages of inhibition obtained for some experiments as a function of the reaction time. Except for the PCDDs with TEA (not shown) for which the reaction time seems to have no influence, longer reaction time (4 h instead of 2 h) gives better inhibition results. The difference of percentages of inhibition obtained at 2 and 4 h is particularly important when the inhibition at 2 h is weak (for example with TEA or with weak amount of inhibitors). 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 industrial process, where various reaction conditions may exist, notably for the residence time.

Inhibition tests performed in a real sintering process.

In parallel to these laboratory experiments, inhibition tests were performed in an sinter plant. The same inhibitors were tested: TEA and MEA. The way of introduction of the inhibitors was however different: the inhibitors were dissolved in water and introduced in the process by the way of spraying nozzles placed in wind boxes located below the strand. Reference tests were performed without inhibitor and compared to inhibition experiments in which the inhibitor was injected continuously and measurements carried out after different times. The results obtained are in good agreement with the laboratory experiments. TEA and MEA were both effective in preventing the PCDD/Fs formation in the industrial process. MEA gives better results with inhibition yields up to 90 % (calculated on the basis of TEQ). 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 inhibitors in the process and especially on the walls where adsorbed fly ash can produce great amounts of PCDD/Fs by de novo synthesis.

ACKNOWLEGMENT

The authors would like to thank Mr. J.-M. Brouhon from the C.R.M (Centre de Recherches Métallurgiques de Liège) for interesting discussions and critical reading of the manuscript. C.Xhrouet was funded as fellow by the F.N.R.S (Fonds National de la Recherche Scientifique Belge).

REFERENCES

1. Lahl, U. *Organohalogen Compd.* **1993**, 311-314.
2. Bröker, G.; Bruckmann, P.; Gliwa, H. *Organohalogen Compd.* **1993**, 303-306.
3. Addink, R.; Govers, H. A. J.; Olie, K. *Environ. Sci. Technol.* **1998**, *32 (13)*, 1888-1893.
4. Addink, R.; Drijver, D. J.; Olie, K. *Chemosphere* **1991**, *23 (8-10)*, 1205-1211.
5. Buekens, A.; Stieglitz, L.; Huang, H.; Cornelis, E. *Environ. Eng. Sci.* **1998**, *15 (1)*, 29-36.
6. Buekens, A.; Huang, H.; Stieglitz, L. *Organohalogen Compd.* **1999**, *41*, 109-112.
7. Stieglitz, L.; Buekens, A. *Organohalogen Compd.* **1999**, *41*, 129-132.
8. Weber, R.; Buekens, A.; Segers, P.; Rivet, F.; Stieglitz, L. *Organohalogen Compd.* **1999**, *41*, 101-104.
9. Buekens, A.; Prakhar, P.; Rivet, F.; Stieglitz, L. *Organohalogen Compd.* **1999**, *41*, 121-124.
10. Buekens, A.; Prakhar, P.; Stieglitz, L.; Jacobs, P. *Organohalogen Compd.* **1999**, *41*, 97-99.
11. Stieglitz, L.;Polzer, J.;Hell, K.;Weber, R.;Buekens, A.;Prakhar,P.;Rivet,F. *Organohalogen Compd.* **1999**, *41*, 113-115
12. Vogg, H.; Metzger, M.; Stieglitz, L. *Waste Manag. Res.* **1987**, *5*, 285-294.
13. Ruokojärvi,P.H.;Halonen,I.A.;Tuppurainen,K.A.;Tarhanen,J.;Ruuskanen,J. *Environ. Sci. Technol.* **1998**, 3099-3103
14. Naikwadi, K. P.; Karasek, F. W. *Chemosphere* **1989**, *19*, 299-304.
15. Naikwadi, K. P.; Albrecht, I. D.; Karasek, F. W. *Chemosphere* **1993**, *27*, 335-342.
16. Dickson, L. C.; Lenoir, D.; Hutzinger, O.; Naikwadi, K. P.; Karasek, F. W. *Chemosphere* **1989**, *19*, 1435-1445.
17. Lippert, T.; Wokaun, A.; Lenoir, D. *Environ. Sci. Technol.* **1991**, *25 (8)*, 1485-1489.
18. Addink, R.; Paulus, R. H. W. L.; Olie, K. *Organohalogen Compd.* **1993**, *11*, 27-30.
19. Addink, R.; Paulus, R. H. W. L.; Olie, K. *Environ. Sci. Technol.* **1996**, *30 (7)*, 2350-2354.
20. Xhrouet, C.; Pirard, C.; De Pauw, E. *Organohalogen Compd.* **1999**, *41*, 307-310.
21. Xhrouet, C.; Pirard, C.; De Pauw, E. *Environ. Sci. Technol.* **2001**, *35(8)*, 1616-1623
22. Ryan, J. J.; Conacher, H. B. S.; Panopio,L.G.;Lau,B.P.-Y.;Hardy,J.A.;Masuda,Y. *J. Chromatogr.* **1991**, *541*, 131-183.