DESORPTION OF DIOXIN LADEN FILTER DUST
FROM METALLURGICAL PROCESSES

Nadezhda Zyaykina[1], Alfons Buekens[1], Robert Carleer[2], Johannes Czech[2],
Guy Reggers[2], Alain Brasseur[3], Jean-Paul Pirard[3]

[1] Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium, E-mail: abuekens@vub.ac.be
[2] Limburgs Universitair Centrum, IMO-Laboratory for Applied Research, 3590 Diepenbeek, Belgium
[3] Université de Liège, Institut de Chimie - B6, B-4000 Liège, Belgium

Introduction

Adsorption methods are largely used in practice for treatment of industrial gas streams contaminated with dioxins and related chloroaromatic compounds. Literature refers to numerous examples of successful applications, but much more seldom to investigations of adsorption properties with respect to such pollutants. Well-proved adsorbents are activated carbon[1] and lignite coke, either pure or with additives. Natural and synthetic zeolites are inorganic adsorbents of practical significance. Lime adsorbs chloroaromatics, but only to a limited extent, its major role is to neutralise acid gases in the effluent. Dust particles from thermal and metallurgical processes show some adsorptive capacity too. For MSW-incinerator fly ash this property has been often related to carbon content[2]. Several authors reported a positive correlation between removal of fine iron ore sinter dust particles and removal of dioxins due to the adsorption ability of the first[3-4]. However, the adsorption potential of metallurgical dusts is small and not well known yet. Therefore the present study investigates filter dust from metallurgical processes, such as iron and manganese ore sintering, and zinc oxide recovery from steel converter dust. Its aims are: (1) comparing various thermal methods to estimate the original organic load of particles, and (2) identifying and quantifying the major classes of desorbed compounds, as well as some significant individual compounds. These tasks are rather complicated, since filter dust is very heterogeneous, containing particles of distinct nature, e.g. ore, coke, salts, lime, ash, slag. Their structure and properties reflect their process of origin, but also vary with location and time within the same plant. Moreover, these particles are generally conglomerates of smaller ones, whereas their surface is modified by the presence of volatile salts, condensed from the gas phase. Adsorbed species are also very variable in vapour pressure, molecular size, polarity, and functional groups. Thus, the resulting desorption pattern is both varied and complex.

Methods and Materials

The samples treated are briefly introduced in Table 1. For a majority of them the particle load of PCDD/F, PCBz, PCPh, PCB and PAH is established during prior MINIDIP project. The elementary composition is derived by X-ray fluorescence (XRF) analysis and scanning electron microscopy/ energy dispersive X-ray spectroscopy (SEM/EDXS).

The following thermal methods are tested in order to meet the purposes stated above:

1) Temperature Programmed Desorption (TPD) and monitoring of gases with GC-FID and MS;
2) Direct thermal desorption of dusts and GC-MS analysis of the cryo-condensed volatiles;
3) Thermogravimetric analysis (TGA) either collecting the evolved volatiles into Tenax tubes with subsequent desorption by Method 2, or direct monitoring with a MS;
4) Fast high temperature treatment by pyrolysis and analysis of products with GS-MS.

A preliminary study is carried out using the TPD method by heating a sample in flow of helium (3 l/h) while applying a rise of temperature at 20 °C/min up to 500 °C, followed by an isothermal period. In all the following methods helium is used as a carrier gas as well. Up to 0.75 g dust is

placed into a U-shaped column (0.25 m long, 2 mm internal diameter) that is lowered into an electrical oven at the start of the test. Off-gases are monitored using a GC equipped with flame ionization detector, and a mass spectrometer OmniStar®, with a detection limit < 1 ppm.

Thermal desorption-GC-MS experiments (methods 2 + 3) are performed using a PE ATD 400 unit coupled to a PE Thermomass quadrupole GC-MS spectrometer. GC column: 30 m CPSil8CB-MS 0,25 mm I.D., film thickness 0,25µm (Varian Chrompack); GC program: 35 °C isothermal for 1 min; 35 - 250 °C at 10 °C/min; 250 - 320 °C at 15 °C/min; and 320 °C isothermal for 10 min. MS scan conditions: mass range 41-470 with scan rate 0.5 sec.

TA Instruments Thermogravimetric Analyzer 951coupled with a FISONS Instruments quadrupole mass spectrometer VG Thermolab provided continuous monitoring of both sample weight and m/z-values in the range of 10 – 185 amu. Only during this type of test one of the samples (MnO_2) is impregnated with 2 % of $CuCl_2·2H_2O$ for comparison to the pure sample. Desorption is carried out applying heating at 20 °C/min up to 500 °C for the MnO_2 pure and limited to 350 °C for the doped sample, to avoid $(CuCl)_3$ volatilisation. After attaining the set temperature desorption is continued isothermally until the TGA response considerably decreased. Then sample is cooled down till 275 °C at ca. 20 °C/ min.

For pyrolytic treatment a dust sample (10 – 15 mg) is introduced in a quartz tube fitting into platinum heating spiral and flash heated to the set temperature. Total time of thermal treatment is only 12 sec. Heating of the wires is instantaneous, but quartz tube and sample provide resistance to heat transfer. Pyrolysis products are swept into a GC-MS Iontrap apparatus for separation and identification. As internal standard 50 ng of anthracene-10 is added. Pyrolysis tests and GC-MS are carried out on a Varian Saturn II: GC column: 50 m HT8 0,22 mm I.D., film thickness 0,25 µm (SGE); GC program: 35 °C isothermal for 1 min; 35 – 120 °C at 13 °C/min; 120 – 320 °C at 15 °C/min; 320 °C isothermal for 8 min. MS scan conditions: mass range 41- 470 with scan rate 0.6 sec.

Results and Discussion

Breathing of a dust sample refers to the desorption of highly volatile compounds, e.g. benzene, at ambient temperature. When the first portion of carrier gas flows through a column filled with fresh dust (TPD method), the FID immediately detects a narrow peak or other elevations over the baseline. This phenomenon is observed for all samples except one case, which indicates a potential occupational hazard. According to FID for metallurgical filter dusts desorption starts at temperatures as low as 100 - 125 °C. Desorption peaks differ in shape and number, reflecting the composite character of dusts. Integration of the chromatograms gives an estimate of the amounts desorbed. Comparing the samples, the weakest desorption occurred from the manganese ore sinter dust, however the load released under the same conditions from the iron ore sinter dusts is about 30 times higher. The evolution of typical for aromatic compounds m/z-values, e.g. 78, 91, 94, 112, 146, 128, etc. is monitored by MS; the temperature of the first appearance and the end of desorption peaks are noted preparing the ground for proper identifications and quantification using conventional, but more costly GC-MS techniques.

Direct desorption tests gave only partial results. Simple aromatics (benzene, toluene, xylene, thiophene) and PCBz (P = 1 to 5) are readily analysed and roughly quantified using internal standards, but detection of higher boiling compounds is impossible, because of condensation in the transfer line to the MS.

Desorption from Tenax of previously adsorbed volatiles, using the same equipment, suffered from similar problems. Prominent products recorded are CH_2Cl_2, $CHCl_3$, Bz and PCBz, toluene and PCTol, naphthalene N, limonene, PCTh (Th = thiophenes), PCBzF (BzF = benzofuran). Some mixed Cl/Br and Cl/I-Bz are also found and quantified.

The most representative results are obtained by pyrolytic high temperature treatment of dust. Routinely, more than 50 peaks of adsorbed compounds are identified and quantified, allowing to

evaluate their nature and distribution. Typically 0.2 to 50 mg/g of adsorbed organics is desorbed, but repeatability of the precise amount is not yet guaranteed. Alkanes and alkenes represent 10 to 32.5 % of this amount. Simple aromatics vary in a range of 4.7 – 28 %, di- and PAH between 1 and 20 %. Oxygen containing aromatic structures are well-represented, ranging from 11 to 34 %. Finally, the presence of heterocyclic N and S containing aromatic structures is a sample-specific feature (see Table 2).

For an iron ore sintering sample EU 2 a comparison is made between pyrolysis tests at 500, 635, and 950 °C. The first gives a relatively low response, but PCBz, phenol, DCPh, N(aphthalene), MCN are nevertheless well recorded. The pyrolysis runs at 635 and 950 °C are internally fairly comparable and give rise to structures related to dioxins, e.g. fluorenone, anthracenedione, and biphenyl contributing to the m/e-value 152; fluoren-9-one to 180, xanthone to 196.

The sample EU 12, from another field of the same electrofilter, is tested both at 650 and 950 °C, with major aromatic products (%): Bz (22), Ph (6.8), N (6), Tol (5), anthracene (4), DF (3.3), fluoren-9-one (3.3), benzonitrile (2.6), biphenyl (2.3), pyrene (2.2), N-carbonitrile (2.1), xanthone (1.9) styrene (1.7), fluoranthene (1.4), methylN (1.3), BzF (0.8), etc.

The ZnO-sample is quite particular since its pattern is entirely dominated by PCBz, rather than by non-chlorinated aromatics, as most other samples (see Table 3). Other important peaks in the GC-MS analysis of this sample are monobromo-PCBz, various plasticisers and a flame retardant: all trace compounds surviving thermal treatment of electronic scrap. This way the method allows to study the destruction and removal efficiency of a metallurgical smelting process.

The sample MnO_2 is from a process, which applies urea for inhibition of dioxin formation. It is enriched in a number of aromatic nitrogen compounds, such as benzonitrile, benzenedicarbonitrile, benzoacridine, isoquinoline, toluene isocyanate and naphthalene isocyanate as well as aliphatics (octane- and nonanenitrile). The amount of N-containing compounds remarkably increased to almost 20 % of the total desorbed load. Apparently, the reacting structures incorporate a CN or a CNO group derived from urea as a substitute. TGA tests with this sample (pure sample and the one with 2 % of $CuCl_2 \cdot 2H_2O$ addition) show that desorption up to 350 °C is enhanced by adding copper chloride, which increases initial rate of weight loss. Possibly the desorbing organics remove part of the added chlorine: m/e-monitoring of doped sample shows far less benzene, but more chlorinated benzenes during desorption. On the contrary, for the standard sample desorption peaks of m/z 78, 112, 146 and 180 decline with increase of chlorination level. MS monitoring shows that the signals 44 (CO_2) and 64 (SO_2) have pronounced desorption peaks for both samples. Aromatic m/z-signals 78, 91, 105 (BTX), 118 benzofuran, 128 naphthalene, 168 dibenzofuran, 178 phenanthrene and anthracene also show desorption activity.

In general, a conclusion can be made that samples from an iron ore sintering belt are particularly rich in aromatic structures parent to those of interest in dioxins research (PAH, PCBz, phenol, etc.), the non-chlorinated representatives prevailing. In the case of ZnO, however, the full range of chlorobenzenes dominated the desorbed organics.

Acknowledgements

References

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Table 1. Origin and description of the samples

	Sample name	Process	Unit	Carbon content, %
1	EU 12	Iron ore sintering	2nd field ESP	3.38
2	EU 13	Iron ore sintering	3rd field ESP	2.53
3	EU 2	Iron ore sintering	3rd field ESP	
4	MnO$_2$	Manganese ore sintering (Sample taken during urea inhibition runs)	1st + 2nd fields ESP	14.5
5	Waelz oxide	Zinc oxide recovery from steel dust	Baghouse	Traces

Table 2. Products of pyrolysis at 950 °C: distribution (%) by groups of compounds

Sample	EU 2	EU 13	EU 12	ZnO	MnO$_2$
Alkanes, %	5.5	14.9	9.6	19.9	21.8
Alkenes, %	7.2	10.2	0.4	2.0	6.2
Simple aromatics, %	18.5	14.8	28.2	8.0	4.7
PAH (di- and polycyclic), %	16.7	17.2	20.2	1.0	5.2
O-containing, $C_XH_YO_Z$, %					
Aromatic	33.8	29.0	25.3	11.2	21.2
Non-aromatic	0.8	-	-	0.6	1.6
S-containing, $C_XH_YS_Z$, %					
Aromatic	2.0	1.0	1.6	-	0.4
N-containing, $C_XH_YN_Z(O_A)$, %					
Aromatic	9.3	9.5	6.5	0.6	19.2
Non-aromatic	-	-	-	-	0.5
Halogen-containing, $C_XH_Y(Cl, Br)_Z$					
Aromatic	4.0	3.0	0.8	48.0	7.9
Non-aromatic	-	-	-	8.0	5.1
Non-identified, %	2.2	0.4	7.4	0.7	6.2
Total, mg/g	**3.5**	**56.6**	**0.49**	**0.51**	**10.6**

Table 3. Analytical results for PCBz from pyrolysis of the samples at 950 °C

Sample	EU 2	EU 13	EU 12 Test 1	EU 12 Test 2	ZnO	MnO$_2$
PCBz, µg / g of sample	**17.9**	**231**	**2.0**	**3.3**	**351**	**233**
MCBz, % of PCBz	40	44	56	58	11	63
DiCBz, % of PCBz	23	23	24	21	17	28
TrCBz, % of PCBz	19	20	13	14	20	7
TeCBz, % of PCBz	18	11	7	6	23	2
PeCBz, % of PCBz	n/d	2	n/d	1	18	n/d
HxCBz, % of PCBz	n/d	n/d	n/d	n/d	11	n/d

n/d : not detectable