Towards the comprehension of the role of copper and iron in MSWI fly ash carbon degradation

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Introduction

The formation of PolyChlorinated Dibenzo-*p*-Dioxins (PCDD) and PolyChlorinated DibenzoFurans (PCDF) from many anthropogenic sources has been noticed since the 1970s. In particular, municipal solid waste incinerators (MSWI) are a source of PCDD/F[1] and their formation has been proposed to occur by various homogeneous and heterogeneous mechanisms. In the low temperature range (200-600°C) two mechanisms generally are accepted: (i) heterogeneous reactions on the fly ash surface involving gas-phase or adsorbed precursors such as chlorinated phenols[2-4], chlorinated benzenes and polychlorinated biphenyls[5,6] and (ii) the formation, eventually catalysed, from fly ash carbon, chlorine and oxygen. In the latter, usually termed the *de novo* synthesis, contradictory conclusions are provided about the key parameters and their role. Apart from temperature and reaction time, these parameters include: the amount and structure of carbon in the fly ash; the chlorine speciation[7] together with the relative importance of gas-phase inorganic chlorine with respect to extractable organic chlorine, ash-bound chlorine, inorganic chlorides such as metal chloride[8-10] or water-soluble earth metal chloride; the oxygen percentage in the reaction atmosphere. As for the metal chlorides, copper(II) chloride has proven to be very active in promoting PCDDs/Fs formation[11-13]; even if less efficiently, iron(III) chlorides participates in or promotes formation via *de novo* synthesis.

In a previous paper[14] we reported the CO_2 evolution curves from MSWI fly ash and model systems studied by means of the TG-FTIR technique. Model systems consisted of physically ground mixtures of active carbon, C, a silica, SiO_2, matrix, and $CuCl_2$ or CuO or $CuSO_4$. It was shown that the number of peaks in the curves depended on the system studied. Thus it was possible to conclude that low temperature carbon oxidation was highly dependent on the catalyst added to the model mixtures as well as on the metals already present in the fly ash. This conclusion supported previous findings from kinetic studies[15,16].

Additional investigations on the catalytic role of copper(II) chloride and other metal oxides and salts in thermal degradation of carbon are needed to support the above findings and to give further information for the validation of the kinetic model.

Methods and Materials

Reagents: The fly ash used in this study were those named FA3 in[15]. Model mixtures, with a carbon content of 2000 ppm, were prepared mixing appropriate amounts of activated carbon (DARCO G-60, 100 mesh, powder), silica (Merck, grade 9385, 60 Å) as support and different amounts of copper(II) chloride ($CuCl_2 \cdot 2H_2O$, 99%, Riedel – de Haën), copper(II) sulphate ($CuSO_4 \cdot 5H_2O$, Carlo Erba), copper(II) oxide (CuO, 99%, Carlo Erba), metallic copper (Cu, 99%, Carlo Erba) and iron(III) chloride ($FeCl_3$, 99%, Carlo Erba). Mixtures were prepared as already described in[14] and dried before each experiment. The metal content of each mixture (expressed as metal, % w/w) is reported in Table 1. It must be observed that, to enhance the results observed, the maximum metal concentration in model systems *2 – 12* was about 2 orders of magnitude higher than in FA3.

Analytical Procedures: Total Organic Carbon, TOC, content of the samples was measured using a Dohrmann instrument. Details of the apparatus and analytical method were already reported[17,18]. The experimental TOC of each mixture is reported in Table 1.

The oxidative degradation of the carbon in the model mixtures and in fly ash was studied monitoring the CO_2 evolution at 2361 cm^{-1} by a JASCO-FTIR spectrophotometer Mod. 360 assembled with a Dupont Thermogravimetric analyser Mod. 951. Characteristics of the apparatus and analytical procedure were already reported in[14]. The experimental conditions used for the TG/FTIR analyses were: reaction atmosphere, O_2; gas flow rate, 55 mL/min; temperature scanning of 10°C/min in the temperature range 30–200°C followed by 2°C/min in the range 200-650°C. After each run, the TOC of the residual sample was measured: taking into account the experimental error of the technique, the TOC was always equal to zero.

Table 1: Chemical composition of model systems and fly ash.

Model system (*sample number*)	**Me (%)**	**TOC**	**Model system** (*sample number*)	**Me (%)**	**TOC**
C + SiO_2 (*1*)	–	1790±50	C + SiO_2 + $CuCl_2$ (*7*)	5.0042	1610±10
C + SiO_2 + $CuCl_2$ (*2*)	0.2009	1660±40	C + SiO_2 + $CuCl_2$ (*8*)	10.0008	1560±30
C + SiO_2 + $CuCl_2$ (*3*)	0.3001	1790±40	C + SiO_2 + $CuSO_4$ (*9*)	5.0075	1960±60
C + SiO_2 + $CuCl_2$ (*4*)	0.5006	1780±40	C + SiO_2 + CuO (*10*)	4.9591	1880±30
C + SiO_2 + $CuCl_2$ (*5*)	0.6190	1770±30	C + SiO_2 + Cu (*11*)	5.0446	1870±50
C + SiO_2 + $CuCl_2$ (*6*)	0.9996	1870±30	C + SiO_2 + $FeCl_3$ (*12*)	5.1369	1740±50
			Fly ash, FA3 (*13*)	a)	3520±80

a) Cu % and Fe % were 0.14 % and 0.88 %, respectively (Table 1 in[19])

Some TG/FTIR analyses were performed three times to control the reproducibility of the experiment: in terms of total area, the reproducibility was always better than 16%.

To locate the maxima in each experimental CO_2 evolution curve, a deconvolution procedure (Grams Resource^{tm} from system 2000 FTIR; version 3.01A), more efficient than the one in[14] in detecting shoulders, was applied. Starting from guess values, the optimal number of Gaussian functions (one or two) and the "best" values of the parameters were determined minimising the residual sum of squares. Figure 1 shows examples of deconvolution results.

When two peaks were detected, the peak at the earlier time, t_1, was called Peak 1, the one at the later time was called Peak 2. From the deconvoluted Gaussian functions, the times (t_1 and t_2) and temperatures (T_1 and T_2) of the maxima as well as the area of each peak (A_1 and A_2) were calculated. Table 2 reports the experimental total area of the peaks (A), A_1 (%) and A_2 (%), *i.e.* the percentages of A_1 or A_2 with respect to the deconvoluted total area (A_1 + A_2), together with times and temperatures of each maximum.

Results and discussion

The TOC values, measured on each model system before and after a TG-FTIR run, showed that active carbon was always completely oxidised. The experimental total area, A, of the peaks, proportional to the produced CO_2, was therefore proportional to total active carbon amount, too.

The CO_2 evolution curve of the active carbon – silica mixture (sample *1*) was deconvoluted with only one Gaussian function. The time and the temperature of the single peak maximum (assumed as Peak 2) were the higher observed for the model systems (Table 2). The CO_2 evolution curves in model systems *2 – 12* showed a peak and a shoulder, which were resolved in two peaks with the deconvolution procedure (Figure 1a).

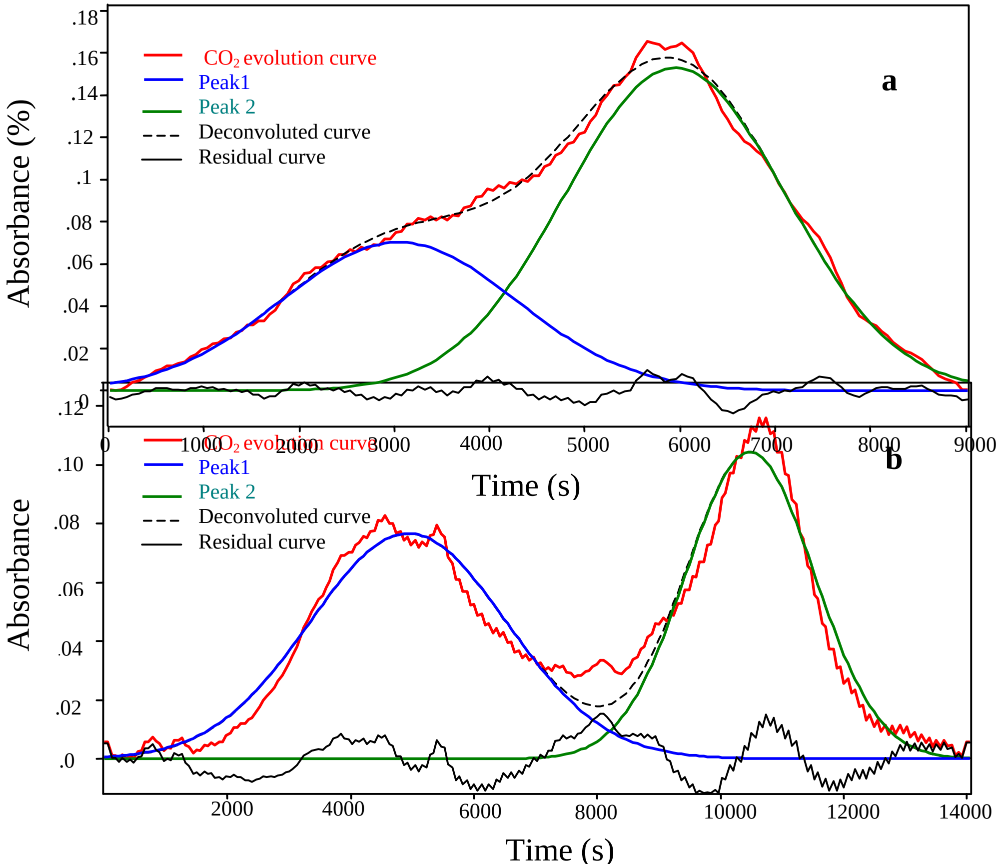

Figure 1: Experimental CO_2 evolution and calculated deconvolution curves for C – SiO_2 – $CuCl_2$ (0.3% w/w) model system (**a**) and for fly ash FA3 (**b**).

When $CuCl_2$ was the added compound, the dependence of percentages A_1 (%) and A_2 (%) on Cu (% w/w) showed the trends reported in Figure 2: A_1 (%) clearly increased with the Cu (%) increase, whereas the opposite trend was obviously observed for A_2 (%).

As far as the influence on A_1 (%) and A_2 (%) of the added metal and its speciation was concerned, two groups were identified: the first included the model systems with $CuSO_4$, Cu and $CuCl_2$ (5 %), the other those with CuO and $FeCl_3$, their behaviour being more similar to $CuCl_2$ (10%). FA3 showed intermediate A1 (%) and A2 (%) values.

Table 2: Total experimental area, A, of the peaks together with calculated percentage areas, A_1 (%) and A_2 (%), of each peaks, times (t_1 and t_2) and temperatures (T_1 and T_2) of the maxima.

Sample	**A**	**A_1 (%)**	**A_2 (%)**	**t_1 (s)**	**t_2 (s)**	**T_1 (°C)**	**T_1 (°C)**
1	534	0	100	-	10527	-	551
2	385	12	88	2270	6051	276	402
3	640	30	70	2871	5919	307	393
4	609	29	71	2673	5007	289	367
5	613	31	69	2886	4778	296	359
6	608	24	76	2607	4316	287	344
7	552	42	58	2509	3449	284	319
8	580	56	44	2641	3667	288	326
9	601	46	54	7038	8441	453	481
10	529	63	37	7586	9029	453	501
11	550	39	61	6111	9039	404	501
12	633	60	40	6023	7705	401	457
13	1078	52	48	4950	10500	370	550

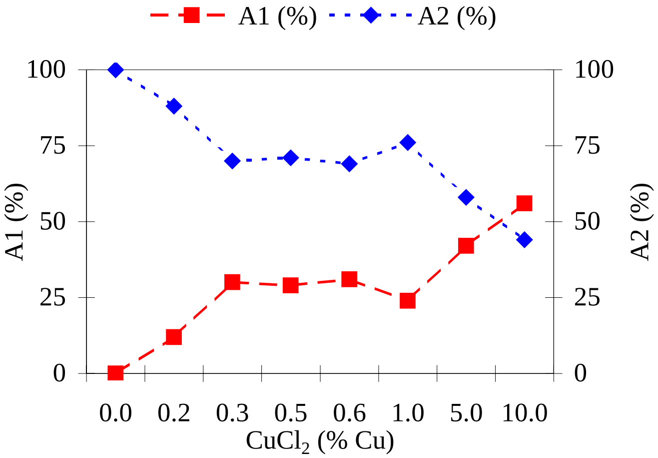

Figure 2: The dependence of percentages areas A_1 (%) and A_2 (%) on $CuCl_2$ concentration (as % w/w Cu).

The dependence of the calculated times (t_1 and t_2) and temperatures (T_1 and T_2) of each maximum on $CuCl_2$ concentration is shown in Figure 3. Both time and temperature of Peak 2 maxima showed a regular decrease with the Cu (%) increase, whereas t_1 and T_1 were quite independent from Cu (%), their calculated mean values (± standard deviation) being t_1 (s) = 2600 ± 200 and T_1 (°C) = 290 ± 10. Moreover, t_2 and T_2 for FA3 were almost coincident with those determined for $C - SiO_2$ system. Finally, the differences $(t_2 - t_1)$ and $(T_2 - T_1)$ approached zero from FA3 to $CuCl_2$ (10 %). As shown in Table 2 the behaviour of model mixtures with 5% of $CuSO_4$, CuO, Cu or $FeCl_3$ was quite different from that with 5 % $CuCl_2$: in fact, both temperatures and times were noticeable higher.

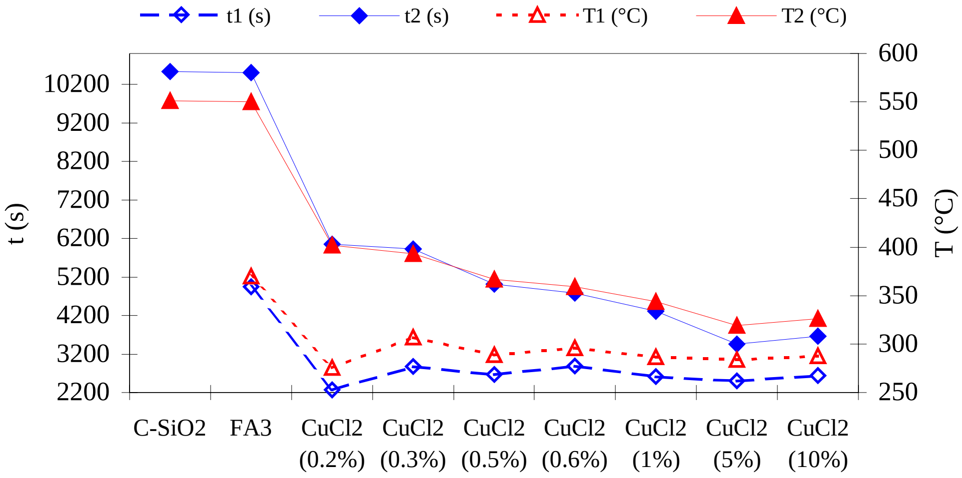

Figure 3: The dependence of the calculated times (t_1 and t_2) and temperatures (T_1 and T_2) of each maximum on $CuCl_2$ concentration (as % w/w Cu). Data for C-SiO_2 (“blank”) and for FA3 (real system) are also shown.

Two important considerations derived from the experimental data analysis on C – SiO_2 – $CuCl_2$ model systems.

The first concerned the mass balance: the carbon was completely oxidised to CO_2 in all the model systems; in all mixtures except C – SiO_2 mixture, the deconvoluted curves indicated that CO_2 produced was the result of two processes, process 1 and process 2. Process 1 was related to Peak 1, while process 2 was related to Peak 2.

The second point concerned the times and temperatures of the peaks maxima. With Cu increasing, t_2 and T_2 clearly decreased. This observation indicated that process 2 was catalysed. The presence of metal species was a prerequisite for process 1 taking place, but t_1 and T_1 were almost independent from Cu concentration.

To explain the different role of the metal in processes 1 and 2, we took into account our previous hypotheses on the kinetics and mechanism of native carbon oxidation[16]. We believed that process 2 was related to the direct native carbon gasification (eq. 6 in[16]) which was uncatalysed in the C-SiO_2 systems and became catalysed in the presence of a metal. The catalytic effect depended on the nature of the metal and on its speciation. On the basis of the proposed mechanism[16], process

1 was related to the oxygen dissociative chemisorption and/or the subsequent intermediate desorption as gaseous CO_2 (eq. 5 and 7 in[16]). The presence of the metal was indispensable for oxygen dissociative chemisorption. At the lowest experimental temperatures, the oxidation rate of the intermediate complex was slower than the chemisorption. By this way, intermediate C(O) complexes accumulated, depending on the number of available metallic sites *i.e.* on the metal percentage. Around 290°C, intermediate C(O) oxidation took place and the amount of gaseous CO_2 produced was proportional to the previously accumulated complexes. So, t_1 and T_1 did not vary with metal percentage, whereas A_1 (%) increased (Table 2).

The behaviour of model mixtures with metal compounds other than $CuCl_2$ was qualitatively consistent with that of mixtures with $CuCl_2$ (samples *2-8*) but it was quite different from a quantitative point of view. Therefore, it was questionable whether the mechanism proposed also applied for samples *9-12*.

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