Characterization of fly ash from a hazardous waste incinerator in Medellin, Colombia

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ABSTRACT

Bag filter (BF) fly ash from a hazardous waste incinerator located in Medellín, Colombia was characterized. Particle size distribution, chemical composition, metal loading, surface area, morphology, and chemical environment were assessed before and after fly ash extraction with toluene. Fly ash consists of low surface area platelets of SiO_2 smaller than 0.5 μm agglomerated in spheres between 20 and 100 μm. High concentration of sodium chloride, carbon, and heavy metals such as Cu, Fe, Pb, Hg, Cd, Co and Mn are deposited over the fly ash surface. The carbon is oxidized and forms different structures such as amorphous carbon black, nano balls and more crystalline fullerenes like nano onions. The high concentration of dioxins, furans and dioxin-like PCBs (superior to 185 ng WHO-TEQ/g) is favored by oxidized carbon, chlorine and metals such as Cu and Fe on the shell of the particles. Before and after toluene extraction, fly ash samples presented similar morphology. However, after extraction their particle size increased while their surface area decreased by 35% and the carbon and metal contents decreased by 35% and 50%, respectively.

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated chlorobenzenes (DL-PCBs) are a group of toxic related compounds, commonly known as dioxins [1]. Waste incineration is an important source of these compounds that are mainly concentrated in the solid residues of gas cleaning systems [1–3]. Incineration is a traditional treatment method to handle hazardous waste in Colombia (South America) [4]. This treatment has been mostly used for reducing hazardous waste from industrial and medical activities, whereas a large fraction of municipal solid waste (MSW) is commonly disposed in landfills. Mixing industrial and medical waste prior to incineration is a common practice in Colombia and the characterization and composition of waste streams are in most cases limited or unknown. Most plants operating in Colombia have capacities below 100 kg/h and the estimated total installed capacity is 18,000 ton/year [4,5].

Several characterization studies of fly ash from municipal [6–15], medical [16] and industrial waste incineration [17] and [18] have shown the risk of these materials ascribed to high concentration of dioxins, heavy metals and soluble salts. Also, different extraction procedures with water [19] and [20] and chemical reactants [21–24] have demonstrated that fly ash components are prone to leaching under landfill conditions and alerted about the environmental risk associated to inadequate inertization and disposal. However, in Colombia fly ash is mixed with household waste and landfilled without either previous treatment or use of appropriate human protection. Although characterization studies also reveals that the levels of dioxins in fly ash vary widely depending on specific combustion parameters, particle size and the air pollutant control device (APCD) used for dust collection [19,21] and [25], 1–3 ng I-TEQ/g of PCDD/Fs is accepted as an adequate value for landfill disposal in developed countries [25,26]. Nevertheless, fly ash collected from incinerators in Colombia usually contains higher dioxin concentrations [4,5] requiring additional treatment before land filling.

Several methods for dioxin detoxification of incineration fly ash have been proposed both in solid phase [26–33] and in liquid fly ash extracts [34–37]. Among them, liquid phase catalytic hydrodechlorination (LP-HDC) over Pd supported catalyst is a promising technique for fly ash dioxin degradation since high conversions are obtained after short reaction times under moderate reaction conditions [34–37]. Fly ash extraction is carried out with toluene in a soxhlet apparatus according to EN-1948 [38] and USEPA-1613 [39] methods. As this solvent presents high affinity for dioxins and elevated thermal and chemical stability, soxhlet extraction with toluene is a reference method to extract quantitatively dioxins from fly ash samples [40–42]. The hydrodechlorination (HDC) of PCDD/Fs and DL-PCBs of liquid samples obtained after soxhlet toluene extraction of fly ash samples have been accomplished in our

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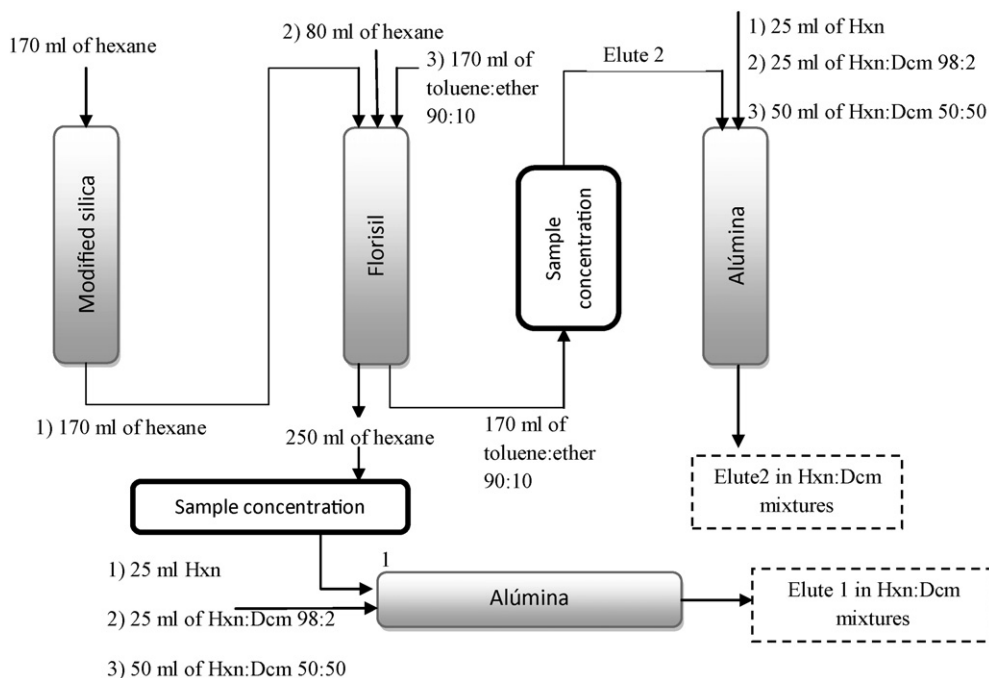cmontes@udea.edu.co (C. Montes de Correa).

Fig. 1. Cleanup procedure for simultaneous analysis of PCDD/Fs and DL-PCBs.

laboratory [43,44]. However, the extracted solid material can be still toxic and the overall impact of the treatment must be considered. Maybe, other complementary treatments must be applied to ensure assessment of fly ash environmental quality. For example, washing with water for removing soluble salts [6,44], chemical extraction for recovering heavy metals [6,10,45], and solidification-stabilization for reducing toxic leaching out of the waste matrix [6,19,32,33,46].

The present work has two main goals: (i) Determine the structure, the dioxin content and the metal loading of fly ash samples collected from a hazardous waste incinerator operated in Colombia—which mixes medical and industrial residues—and (ii) characterize fly ash samples after toluene extraction. The aim is to contribute to a better understanding of fly ash from medical–industrial waste incineration and the overall impact of hydrodechlorination for dioxin degradation of fly ash samples.

2. Experimental

2.1. Fly ash source

Fly ash samples were taken from a container filled with accumulated bag filter fly ash from several incineration batches. The incinerator burns between 40 and 70 kg/h of a mixture of industrial and medical waste. Industrial waste consists of industrial refuse materials like polymerization sludge, expired food and commercial products. Medical residues were composed of contaminated sharps, human blood and blood products, tissues and body parts, etc. The specific composition of incinerated waste is not available. The incinerator is equipped with a gas cooling heat exchanger, a wet acid scrubber, a cyclone and a bag filter for particulate collection. Finally, the system is equipped with a fixed bed of activated carbon for dioxin adsorption. Waste incineration is batch processed operating 8 h per day.

2.2. Characterization

Fly ash samples were characterized by different techniques before and after toluene extraction. Fly ash samples are denoted as FA1 (before extraction) and FA2 (after extraction). The size of

fly ash particles was determined in a Coulter LS23. CHNS elemental analysis was performed in a Carlo Erba (CHNS-OEA1108) apparatus. The chemical composition was determined by X-ray fluorescence using a Philips model PW1480. Before metal analysis fly ash samples were acid digested with 10 mL HNO_3 2% (v/v) in closed vessels using a microwave digester (O-I-Analytical). The digested sample was filtered and ppb levels of metals were analyzed by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS, Thermo Elemental, VG PQ-ExCell) and by Inductively Coupled Plasma/Optical Emission Spectrometry (ICP/OES, Perkin Elmer, 4300) in the ppm range.

Nitrogen absorption–desorption isotherms were obtained at 77 K in a Quantachrome Autosorb 6 apparatus. Scanning electron microscopy (SEM) studies were carried out in a Hitachi S-3000N model equipped with an XFlash 3001 Bruker EDX (Energy Dispersive X-Ray Spectroscopy). Before SEM fly ash samples were sputtered with Au ions using a Metallization (Au)/Evaporator (C) Balzers SCD 004 under vacuum conditions. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2010 apparatus equipped with an EDS (Energy Dispersive X-Ray Spectroscopy) system OXFORD instruments INCA Energy TEM100. Fly ash samples were dispersed in ethanol by ultrasonic vibration and dropped on a copper grid coated with carbon film.

XPS (X-Ray Photoelectron Spectroscopy) analysis was carried out with a VG-Microtech Multilab electron spectrometer, by using the Mg Kα (1253.6 eV) radiation of twin anode in the constant analyzer energy mode with pass energy of 50 eV. X-ray diffraction was performed in a Bruker D8-Advance diffractometer with an X-ray generator Kristalloflex K 760–80 F (output: 3000 W, voltage: 20–60 KV and stream: 5–80 mA) with Kα radiation (1.5406 Å) and $2\theta = 2$–$80°$. Database JCPDS was used for data analysis.

2.3. Analysis of PCDD/Fs and DL-PCBs

A four-gram fly ash sample was labeled with EPA1613-LCS and WP-LCS standards according to EPA-1613 method [39]. Then, it was acid digested with 30 ml of 1 M HCl during 2 h for releasing PCDD/Fs. The sample was water washed and dried for 12 h, soxhlet extracted with toluene during 48 h and rotovaporated. After that, the sample was cleaned-up by liquid–solid adsorption chromatography at

Table 1
Dioxins, furans and DL-PCBs in a fly ash sample from an incinerator in Medellín, Colombia.

Compound	pg/g	WHO-TEF	WHO-TEQ (pg/g)
Dioxins			
2378-TCDD	3770 ± 714	1.0000	3769.8
12378-PCDD	49942 ± 2211	1.0000	43539.3
123478-HxCDD	21704 ± 4600	0.1000	2170.4
123678-HxCDD	26506 ± 6151	0.1000	2650.6
123789-HxCDD	31768 ± 18735	0.1000	3176.8
1234678-HpCDD	174244 ± 70562	0.0100	1742.4
OCDD	149136 ± 5983	0.0001	14.9
Total PCDD	457070 ± 37587		57064.3
Furans			
2378-TCDF	29227 ± 2902	0.1000	2922.7
12378-PCDF	75271 ± 25922	0.0500	3763.6
23478-PCDF	120125 ± 30909	0.5000	60062.5
123478-HxCDF	158622 ± 21893	0.1000	15862.2
123678-HxCDF	152412 ± 39840	0.1000	15241.2
234678-HxCDF	141865 ± 19716	0.1000	14186.6
123789-HxCDF	31704 ± 3900	0.1000	3170.4
1234678-HpCDF	810169 ± 336630	0.0100	8101.7
1234789-HpCDF	111962 ± 40509	0.0100	1119.6
OCDF	410579 ± 50228	0.0001	41.1
Total PCDF	2041937 ± 948858		124471.5
Total WHO-TEQ PCDD/Fs (pg/g)			
DL-PCBs			
PCB 81	1758 ± 169	0.0001	0.2
PCB 77	7591 ± 2308	0.0001	0.8
PCB 123	292 ± 48	0.0001	0.0
PCB 118	3691 ± 303	0.0001	0.4
PCB 114	437 ± 93	0.0005	0.2
PCB 105	2423 ± 830	0.0001	0.2
PCB 126	14088 ± 2062	0.1000	1408.8
PCB 167	1794 ± 425	0.00001	0.02
PCB 156	4778 ± 727	0.0005	2.4
PCB 157	1327 ± 102	0.0005	0.7
PCB 169	6764 ± 1248	0.0100	67.6
PCB 189	4030 ± 157	0.0001	0.4
Total DL-PCBs	48972 ± 9397		1481.7
Total WHO-TEQ (pg/g)			183017.5 ± 20387.7

atmospheric pressure using glass columns filled with acidic/basic silica gel, florisil and basic alumina as adsorbents. The sample cleanup procedure is outlined in Fig. 1.

Cleaned samples were analyzed by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry (HRGC-QITMS/MS) in a Varian CP-3800 GC equipped with an 8400 auto sampler and coupled to a Saturn 2000 ion-trap spectrometer, using a DB-5MS column (60 m × 0.25 mm I.D., 0.25 μm film thickness). Quantification of dioxins, furans and DL-PCBs were performed using the isotope dilution method. Relative Response Factors (RRFs) were determined using calibration standards for PCDD/Fs and DL-PCBs analysis (EP1613-CS and WP-CS solutions from Wellington Labs., Canada). Toxic equivalents (WHO-TEQ) were determined using WHO-TEF factors. Three replicates of dioxin analyses were made.

3. Results and discussion

3.1. PCDD/Fs and DL-PCBs

Dioxins, furans and DL-PCBs contents of bag filter ash samples (FA1) are shown in Table 1. High WHO-TEQ values (above 185 ng/g) of PCDD/Fs compounds while low concentrations of DL-PCBs congeners (1, 2 ng/g) were found. The PCDD/Fs congener distribution showed increasing concentrations of PCDD/Fs homologues as chlorine substitution increases, with a larger concentration of 1234678-HpCDF. Except for PCB 126, the low contribution of DL-PCBs may be due to their low TEF values [47]. Even though, they have been recently included into the list of toxic com-

pounds, they appear to produce similar negative effects as PCDD/Fs [47].

It has been established that large concentrations of dioxins are usually found in long residence time devices like bag filters and electrostatic precipitators (ESPs) [1,48]. Reports of fly ash analyses from municipal solid waste incinerators (MSWIs) indicate concentrations of: 1.12 [21] and 12.2 ng I-TEQ/g [48] in bag filter ash; 0.26 ng I-TEQ/g [21] in gas scrubber ash; 6.7 [19], 8.5 and 142.1 ng I-TEQ/g [48] in ESP ash; and 0.97–1.5 ng I-TEQ/g for PCDD/Fs and 0.013–0.023 ng I-TEQ/g for DL-PCBs in a mixture of semi-dry and bag filter ash [25]. Dioxin concentrations vary among incinerators depending on their specific operating parameters, including furnace type, capacity, furnace temperature and waste input, among others, and the presence of air pollution control devices (APCS) [9,49,50]. However, ESP ash samples from an old and small-scale batch incinerator contains PCDD/Fs levels (142.1 ng I-TEQ/g) similar to those found in this study, which might suggest that the high concentration of dioxins in our fly ash samples could be related to an old and inefficient combustion operation, for instance: batch process, outdated furnace design and slow gas cooling system. Also, the composition of the waste input (medical–industrial waste mixtures) can widely contribute to dioxin formation. As dioxin data on similar industrial and medical incineration fly ash samples are not available in the literature, this work might be an incentive to generate additional results for more exhaustive comparisons.

Studies of PCDD/Fs leaching from fly ash samples have revealed that they could be easily eluted with water containing miscible organic solvents. In this way, high concentrations of dioxins found in sediments might result from irregular leaching aided by the
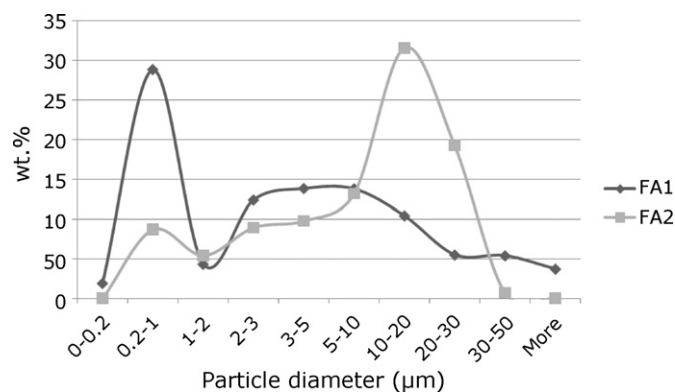
Fig. 2. Particle size distribution of fly ash before (FA1) and after (FA2) toluene extraction.

Table 2
Ultimate analysis (wt.%) and surface area of incineration fly ash before and after toluene extraction.

Fly ash sample	Carbon	Hydrogen	Nitrogen	Sulfur	S_{BET} (m^2/g)
FA1	32.85	1.17	1.50	6.93	20
FA2	21.51	0.53	0.89	8.31	13

from particles between 10 and 20 μm and they presented a D [3,2] of 3.4 μm and a mean size of 11.41 μm.

3.2.2. Fly ash composition

3.2.2.1. Ultimate analysis. CHNS analyses of fly ash samples, before (FA1) and after (FA2) toluene extraction, are shown in Table 2. The FA1 sample presented carbon contents above 32 wt.%. Fly ash from a well-operated incinerator contains about 2–5 wt.% C [1]. This carbon significantly contributes to dioxin formation since the rate of formation of PCDD/F by De novo synthesis is proportional to the amount of carbon present and to its oxidation rate [1]. The decrease of carbon in FA2 samples is attributed to removal of organic compounds during toluene extraction. Apparently, sulfur did not leach during extraction. The solubility of sulfur compounds in toluene depends on their affinity with the solvent. Toluene is a non-polar solvent with a low affinity to sulfur compounds such as mercaptans and dibenzothiophenes (DBTs) [54], [55] and [56], commonly present in fuels, blocking agents, vulcanized rubber, detergents, pharmaceuticals and dyes, among others, which can be present in the input waste producing low sulfur extraction.

3.2.2.2. XRF. Table 3 shows XRF results of fly ash samples. Metal oxide composition was estimated from the total amount of analyzed elements and the basicity from the CaO/SiO$_2$ ratio [10]. Both fly ash samples exhibited similar composition and the major constituents are SiO$_2$, ZnO, Sb$_2$O$_3$, Na$_2$O, and NaCl. High Na concentration is

3.2. Fly ash characterization before and after extraction with toluene

3.2.1. Particle size

Particle size distribution of bag filter ash is shown in Fig. 2. Before extraction (FA1) fly ash is composed of very fine particles, most of them below 10 μm (75 wt.%). The major contribution is due to particles smaller than 1 μm. The particle size of MSWI fly ash is usually from 1 to 100 μm [8] and bag filters (BF) generally trap smaller particles compared to other devices. Chang and Chung [48] found that 25 wt.% of particles in BF and 12% in EP ash were lower than 37 μm. Lapa et al. [17] characterized fly ash from sewage sludge incineration in a fluidized-bed reactor and 75% of fly ash particles retained in the first cyclone were ≤40 μm and 80% in the second cyclone were ≤10 μm. In contrast, particle sizes around 300 μm are usually found in bottom ash [9,17,51].

The surface area moment mean D [3,2] or Sauter Mean Diameter (SMD) for this sample was 1.0 μm and the mean diameter was 9.5 μm. It is well known that the smaller the particle size the higher the dioxin concentration because a high specific surface area offers more adsorption sites [52], exhibiting high chlorine concentration [1]. Indeed, higher PCDD/Fs levels have been found in particles less than 1.0 μm in several studies, where the contribution of more chlorinated congeners increases significantly [1,48,53]. The important contribution of hepta- and octa-chlorinated congeners in the current sample can be observed in Table 1. As a result, more attention should be paid to PCDD/Fs contamination associated with small particles considering that they have longer residence times in the atmosphere and higher PCDD/Fs concentration compared with larger particles [48].

The equivalent surface concentrations on an external basis has been estimated by Stanmore [1] using the specific surface area $S = 3/d_p$, where d_p is the mean particle diameter in μm and assuming a density of 2000 kg/m^3. Surface concentrations calculated by Stanmore lied between 12 and 30 μg/m^2 with mean particle sizes within 29–800 μm. A surface concentration of 6.33 μg/m^2 was obtained for FA1 samples with a mean d_p of 9.5 μm and 2041937 pg/g of PCDD/Fs (see Table 1). This value is close to the equivalent surface concentration range found in Stanmore study and support the hypothesis that this parameter is relatively constant and independent of the fly ash sample. After extraction (FA2) fly ash was composed of larger particles (Fig. 2). The major contribution was

coexistence of organic matter in water, and also because of the accumulation of trace dioxins by the sediment over the long term [19]. For that reason, PCDD/Fs and PCBs in fly ash must be degraded before being disposed off to avoid further environmental contamination.

Table 3
XRF analysis of fly ash samples before and after toluene extraction (wt.%).

Component	FA1[a]	FA2[b]
Na$_2$O	15.122	14.530
Al$_2$O$_3$	0.386	N.D.
SiO$_2$	6.489	5.257
P$_2$O$_5$	4.235	3.697
SO$_3$	2.932	6.034
K$_2$O	5.693	5.688
CaO	2.247	2.641
TiO$_2$	0.235	0.283
Cr$_2$O$_3$	0.116	0.071
Fe$_2$O$_3$	3.317	3.949
NiO	0.099	0.110
CuO	0.349	0.312
ZnO	12.132	10.788
GeO$_2$	0.024	0.004
SrO	0.008	N.D.
MoO$_3$	0.092	0.094
Ag$_2$O	0.069	0.072
CdO	0.034	0.043
SnO$_2$	0.236	0.330
Sb$_2$O$_3$	8.840	11.080
BaO	0.123	N.D.
HgO	0.594	0.539
PbO	2.413	2.188
Cl	33.178	31.420
Br	0.616	0.509
I	0.421	0.278
MnO	N.D.[c]	0.057
Bi$_2$O$_3$	N.D.[c]	0.030
Basicity (CaO/SiO$_2$)	0.346	0.502

[a] FA1: bag filter ash before extraction.
[b] FA2: bag filter ash after extraction.
[c] N.D.: non-detected.

Table 4
Metal loading of incineration fly ash samples before and after toluene extraction (mg/kg) and fraction of metal leached to toluene phase (%).

Metal[a]	FA1[b]	FA2[c]	Leached fraction (%)
Zn	34464.48	23918.17	30.60
K	16470.04	12053.50	26.82
Fe	14150.32	6719.12	52.52
Sb	10465.27	6102.28	41.69
Pb	7389.98	5082.61	31.22
Ca	6926.03	4752.16	31.39
Hg	903.37	357.99	60.37
Cu	473.89	328.87	30.60
Al	465.27	253.82	45.45
Mg	395.35	261.21	33.93
Ni	240.85	113.42	52.91
Cr	228.99	123.37	46.13
Mn	154.83	69.90	54.85
Ba	110.45	58.05	47.44
Cd	93.98	46.03	51.03
Co	20.34	9.43	53.63
As	19.82	9.52	51.94
V	5.91	3.26	44.84
La	3.66	1.88	48.73
Tl	1.66	0.82	50.72
U	0.09	0.05	43.51
Th	0.06	0.03	53.36
Eu	0.03	0.02	45.88
Yb	0.01	0.01	35.25

[a] Metals detected by ICP–OES: Ca, Cu, K, Fe, Pb and Zn. The other ones were determined by ICP–MS.

[b] FA1: bag filter ash before extraction.

[c] FA2: bag filter ash after extraction.

probably linked with NaCl, typical salt in fly ash samples [10]. Also, important contributions of P_2O_5, SO_3, K_2O, CaO, and Fe_2O_3 were detected. Similar compositions were previously found in BF ash [10,11,52], which have low proportions of Si and Al and important amounts of Cl, compared with bottom ash. The low SiO_2 loading makes the fly ash structure weak and prone to leaching in contrast with the higher loading of SiO_2 reported for bottom ash [10]. The SiO_2 gives resistance to leaching since heavy metals are fixed in the net structure and they are not easily extracted [10].

The high chlorine loading in smaller particles is crucial for dioxin formation. Several studies have found that particles lower than 1.6 μm contain high levels of PCDD/Fs [1]. Additionally, Chen et al. [52] found a negative correlation between particle size and chlorine content in bottom ash samples. This chlorine may be supplied from a solid, e.g., decomposition of a metal chloride, chlorinated products of incomplete combustion, or chlorine present in the gas phase [1,10]. The input waste used in the incinerator make an important contribution to chlorine concentration in flue gas and fly ash. Good practices in health care waste management such as waste minimization and segregation are not generally implemented in Colombia [57]. Medical waste might contain all kinds of chlorinated residues from infectious, pathological, plastic and PVC wastes [58,59,60]. Industrial waste also might supply Cl to the incineration process from sewage sludge of chlorinated reactants and packing of expired products.

3.2.2.3. ICP–MS and ICP–OES. The metal loading of fly ash samples is shown in Table 4. The major constituents (>1000 mg/kg) in both samples were: Zn, K, Fe, Sb, Pb and Ca. The minor constituents (10–1000 mg/kg) include Hg, Cu, Me, Al, Cr, Ni, Mn, Ba, Cd, As and Co. Finally, traces (lower than 10 mg/kg) of V, La, Tl, U, Th, Eu and Yb were detected. Bag filter ash samples are characterized by high concentrations of volatile metals deposited over their large specific surface area [10,12]. However, high concentrations of non-volatile metals like Pb and Cu which should be mainly retained in bottom ash were found [11,12,52]. Huang et al. [13] attributed the high con-

centrations of these metals to the non-recycle policy of waste before incineration. The concentrations of toxic elements such as Pb, Zn, Cd, Cu and Sr, after leaching experiments of fly ash samples were much higher than the regulated limits of the Toxicity Characteristic Leaching Procedure (TCLP).

On other hand, the high concentration of Fe and Cu contributes to De novo synthesis which is mainly catalyzed by copper, although iron can be active at lower rates. Copper catalyses the oxidation of carbon as well as the chlorination and dechlorination of organic products. Cu in its two oxidation states also acts as a shuttle for chlorine between gas and solid. Therefore, it not only acts as a catalyst but also as a transmitter of heterogeneous chlorine [1].

The leaching fraction listed in Table 4 represents the percentage of metal transfer to the liquid phase during toluene extraction. Between 30 and 50% of metal leached in the extraction process with more important leaching of volatile elements such as Hg, Fe, Ni, Mn, Cd, Co and As. This corroborates the high leaching potential of toxic metals from solid waste incineration fly ash, which would be easily released in landfills [11].

3.2.3. Surface characteristics

3.2.3.1. BET surface area. Nitrogen adsorption and desorption isotherms of fly ash samples are shown in Fig. 3. The adsorption curve followed a type II behavior, according to the IUPAC classification. Here, the adsorbate thickness progressively increases until condensation pressure has been reached and monolayer and multilayer formation processes are overlapped [61]. The N_2 absorption–desorption curve did not show hysteresis, probably due to very irregular solid pores [61].

Very low fly ash BET surface area was found as shown in Table 2. Similar values have been reported [14,32,62,63] and suggest that the particles have negligible porosity. Therefore, De novo reaction mainly takes place on the exposed surface of the fly ash rather
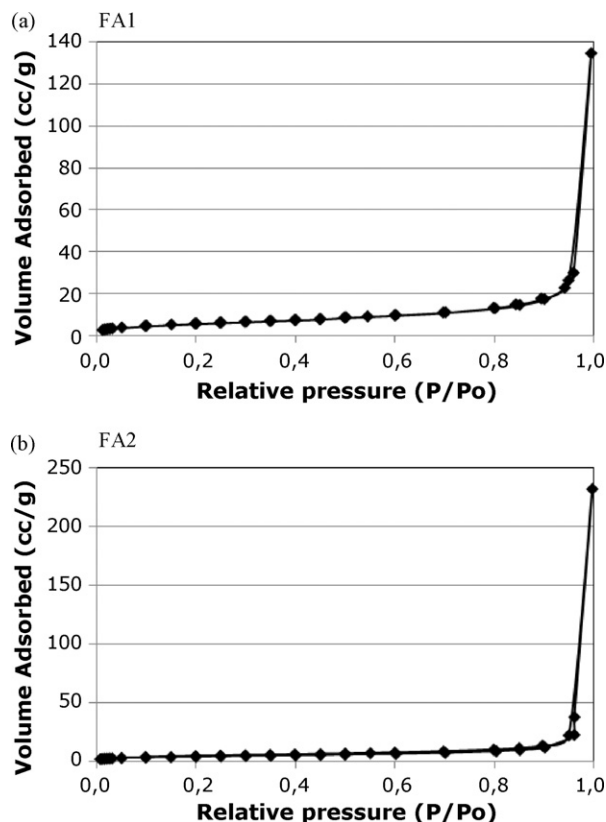

Fig. 3. Adsorption–desorption isotherms of bag filter ash before (a) and after (b) extraction.
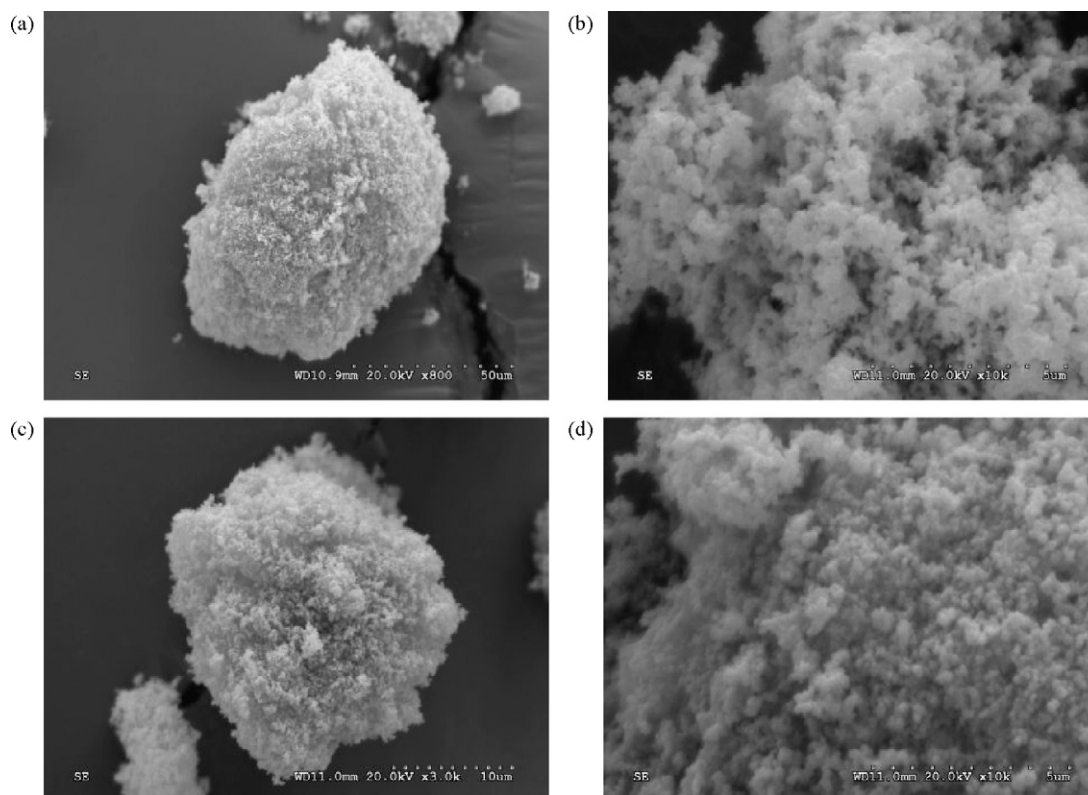
Fig. 4. SEM images of bag filter ash samples before (a and b) and after (c and d) extraction.

than in its internal pores [1]. Fly ash samples seem to lose surface area after extraction. The reduction of carbon content on the solid surface could change the textural properties of bag filter ash.

3.2.3.2. SEM–EDX. SEM images of FA1 and FA2 samples are shown in Fig. 4. Fly ash samples are composed of polycrystalline platelets smaller than 0.5 μm agglomerated in spheres between 20 and 100 μm [12]. The crystallinity of these materials may be due to high temperatures over the pathway in the flue gas stream [9]. The low porosity suggested from surface area values are confirmed in these pictures, and De novo synthesis is probably carried out on the surface of this platelets. No important differences were observed in the morphology of fly ash samples before and after extraction with toluene. However, a reduction of carbon and oxygen surface concentration detected by EDX (see Table 5) is attributed to the dissolution of organic compounds from fly ash during toluene extraction due to their high solubility in this solvent at the extraction temperature (above 250 °C) [40,41,42]. Exposure of metals overlapped by carbon (P and Fe) was found in EDX analysis of FA2 sample.

Table 5
Element content (at.%) from EDS analysis of fly ash before (FA1) and after (FA2) extraction.

Element	FA1	FA2
C	68.35	55.76
Na	0.98	9.95
Si	0.36	0.37
S	0.22	0.07
Cl	2.49	12.61
P	0.49	0.52
Zn	1.20	1.29
Sb	0.74	0.40
O	25.15	18.64
P	N.D.[a]	0.20
Fe	N.D.[a]	0.17

[a] N.D.: non-detected.

3.2.3.3. TEM–EDS. TEM pictures of fly ash samples before extraction (FA1) are shown in Fig. 5. Different structures of carbon were detected. Most carbon species were found as small carbon nano balls with diameters below 100 nm (see Fig. 5a). The fractal arranged aggregates vary in size and exhibit a microtexture consisting of roughly concentrically stacked graphitic layers (see Fig. 5b). This kind of microtexture is very similar to that of diesel soot or carbon black, found in other combustion sources and in ambient air [64–67]. Occasionally, spherical balls with diameters higher than 500 nm corresponding to soot or carbon black with concentrically stacked graphitic layers [65] were also observed in the sample (Fig. 5c). This is a form of amorphous carbon that gives fly ash characteristics of dark and wet powder. It is a major component of smoke from the combustion of carbon-rich organic fuels in the absence of sufficient oxygen [65]. All such soot aggregates are believed to be formed via a vaporization–condensation mechanism during combustion, for instance, burning diesel, coal, residual oil, biomass, etc. Its presence in fly ash samples indicates an incomplete combustion.

Other carbon structures like those shown in Fig. 5d are observed by TEM. They might be characterized as onion structured or related concentric, multishell carbon nanopolyhedra [68]. These are reminiscent of high temperature treatments of soot—catalyzed by metals—that transform the typical amorphous soot aggregates of these samples to the more regular fullerenes. In this process, the precursor fragments are curved around the metal catalyst, but flat sheet fragments also form an aggregate into nanospherules or spherule aggregates. Larger, more ordered or crystalline graphitic aggregates can also be formed by longer range or higher order graphite crystals intermixed with initial fullerenes such as C60 or C70 and higher order fullerene polyhedra (Cn) [68]. EDS analyses of FA1 samples are shown in Fig. 5e. The spectrum is typical of primary soot particles derived from combustion of coal, residual oil, gasoline and diesel oil. They contain a strong carbon peak, a lower intensity oxygen peak and a low intensity but discernible sulfur
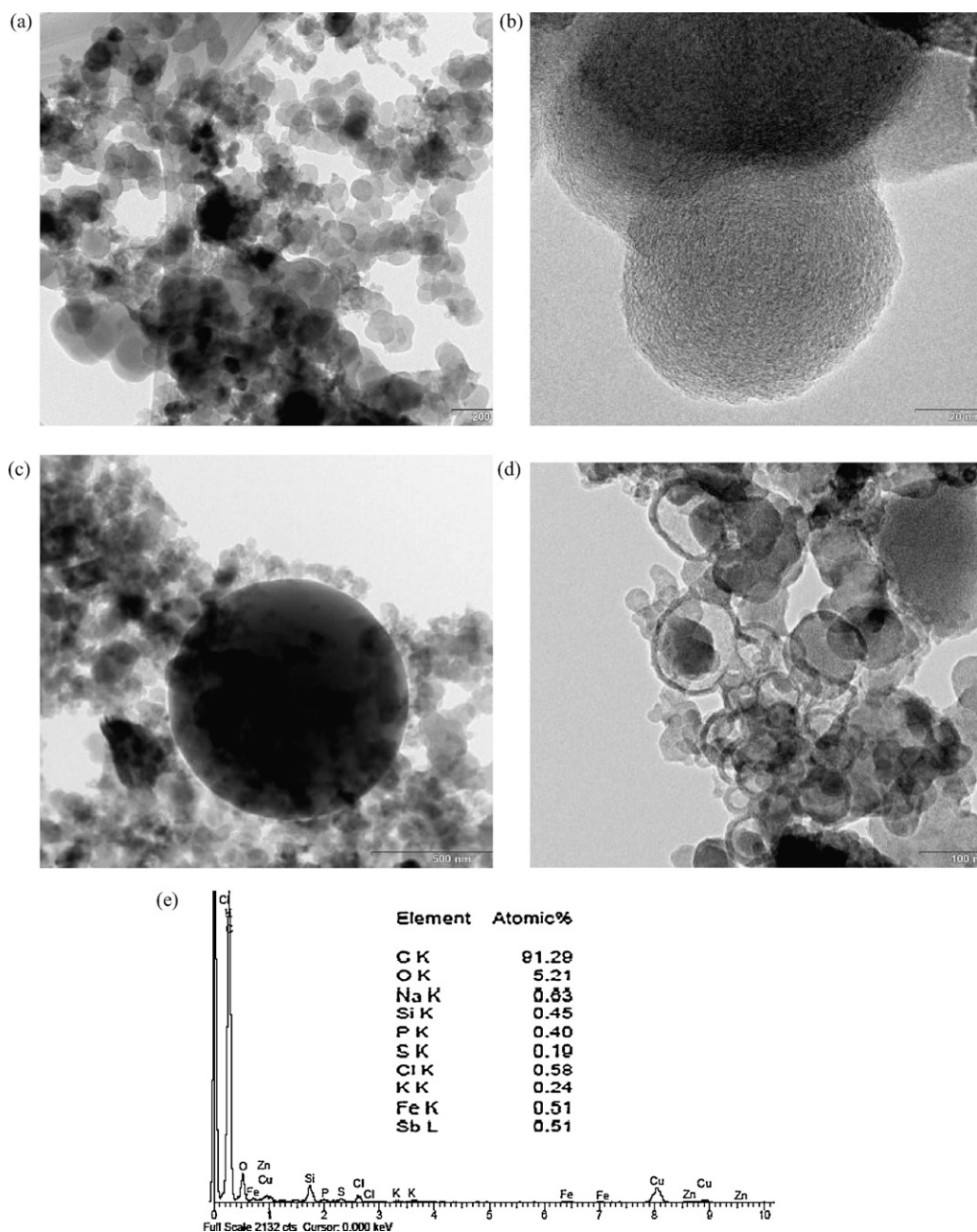
Fig. 5. Selected TEM pictures (a–d) and EDS spectrum (e) of incinerator fly ash sample before toluene extraction.

peak [65]. The sulfur was also detected by ultimate analysis and its presence is due to the combustion of fuel containing relatively high amounts of this compound. Moreover, the presence of metals previously detected, such as Si, P, Fe, and Sb, was also found by EDS.

TEM–EDS pictures of fly ash samples after extraction with toluene (FA2) are shown in Fig. 6. Soot carbon spheres were also observed in these samples, however Fig. 6a shows silicon arrangement under a carbon shell. Taylor et al. [12] found small spherical particles attributed to aluminosilicate structure of fly ash in SEM images after leaching with water and inorganic acid solutions. In this case, fly ash seems to be formed only by silicate structure. SiO_2 was not detected by SEM due to the carbon shell. However, after FA2 ultrasonic vibration in ethanol it was possible to detect SiO_2 by TEM–EDX. Additionally, other metal structures constituted by Fe and Ca were observed (see Fig. 6b and c).

3.2.4. Chemical environment

3.2.4.1. XPS. Table 6 shows XPS analyses of FA1 and FA2 fly ash samples. For each detected element, atomic concentration, binding energies, relative abundance, and possible chemistry are specified. The atomic concentration of carbon on the fly ash surface was high and similar to that detected by SEM–EDX (55–68 at.%) and TEM–EDS (91 at.%). C 1s shows a peak around 284.3 eV in both fly ash samples attributed to adventitious carbon (AC) [12], [69] and [70]. This species represents most carbon present over the samples (around 70 at.%). Also, a peak with B.E. at 286 eV corresponds to oxidized carbon species bonded to oxygen (C—O) [71] and [72]. This peak can be ascribed to the presence of hydrocarbon compounds [12]. Additionally, a small peak ascribed to more oxidized carbon was observed in FA2 [12], [71] and [72]. Oxidation catalyzed by the large amount of Cu in fly ash samples may occur during toluene extraction at 250 °C.
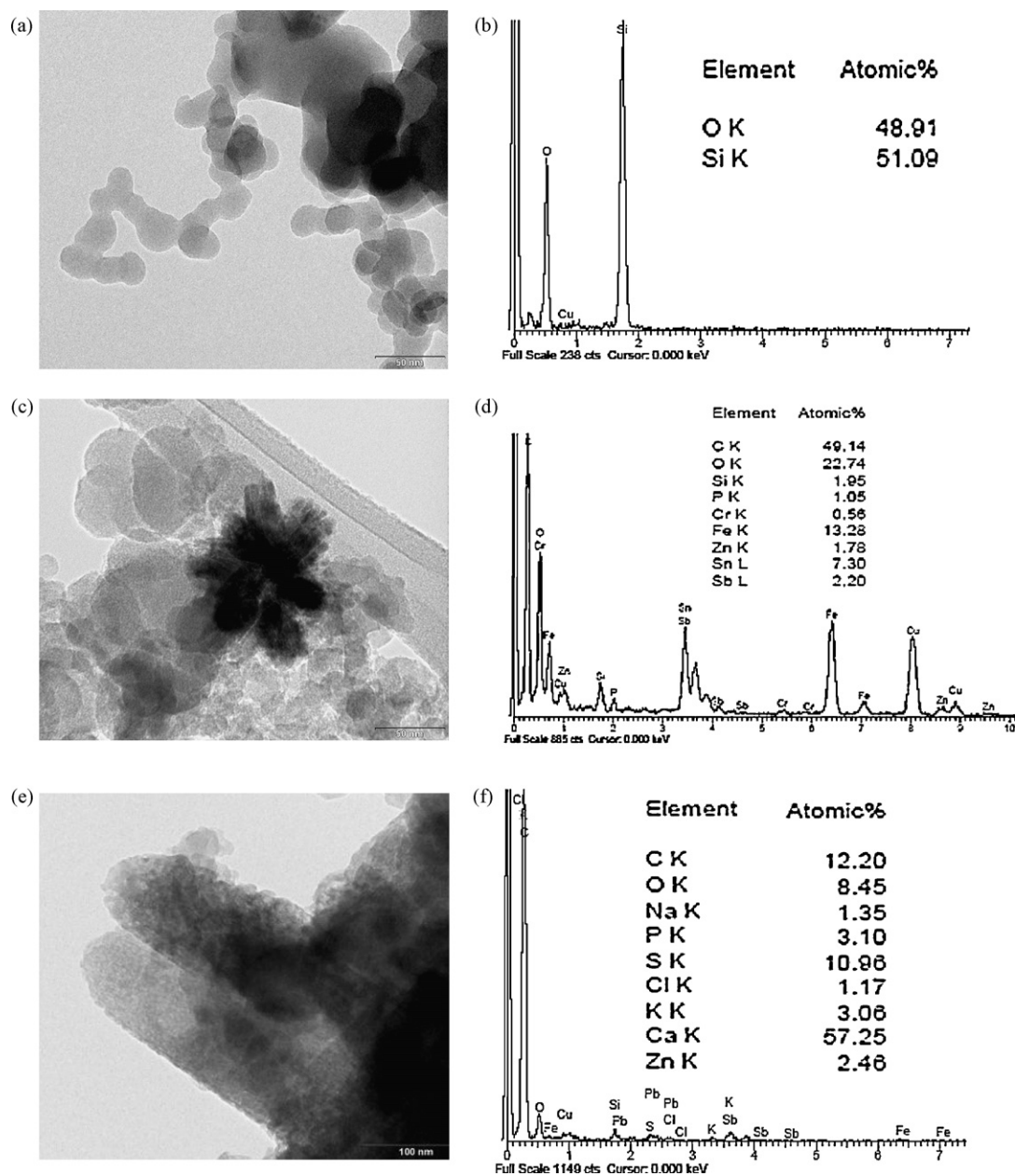
Fig. 6. Selected TEM pictures (a, c and e) with its corresponding EDS spectra (b, d and f) of incinerator fly ash samples after toluene extraction.

Table 6
XPS analysis of fly ash samples.

Element	Type of electron	Atomic conc. (at.%)		B.E. (eV)		Relative abundance (%)		Possible chemistry
		[a]FA1	[b]FA2	[a]FA1	[b]FA2	[a]FA1	[b]FA2	
C	1s	71.9	76.3	284.4	284.3	75.3	70.4	AC[c]
				286.0	285.9	24.7	23.1	C–O
				N.D[d].	288.8	0.0	6.4	C=O
O	1s	17.2	18.2	531.4	531.4	49.9	49.0	C–O, ZnO, MgO
				532.8	533.2	50.0	51.0	C=O, SiO₂
Na	1s	2.4	0.9	1072.2	1071.8	100	100	NaCl
Cl	2p₃/₂	4.7	2.1	199.1	199.2	100	100	NaCl
Si	2p₃/₂	2.5	2.4	103.5	103.9	100	100	SiO₂
Zn	2p₃/₂	1.3	0.3	1022.8	1022.4	100	100	ZnO
Mg	2p₃/₂	N.D[d].	2.2	N.D[d].	51.6	0	100	MgO

[a] FA1: bag filter ash before extraction.
[b] FA2: bag filter ash after extraction.
[c] AC: adventitious carbon.
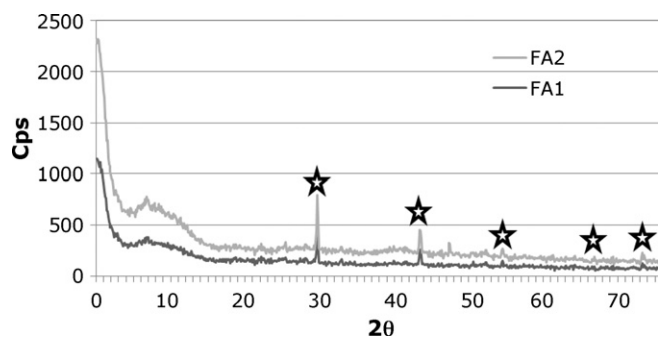[d] N.D.: not detected.

Fig. 7. X-ray diffraction patterns of fly ash samples before and after extraction. (☆) NaCl.

Na 1s spectrum showed a peak around 1072 eV ascribed to NaCl. Additionally, a peak about 199 eV in the Cl 2p$_{3/2}$ spectrum corresponds to sodium chloride. Other structures probably present in fly ash samples such as sodium carbonates, sulfates, different chlorinated salts and hydrocarbons [73] may be present in a lower proportion, so they were not detected. Metals such as silicon, zinc and magnesium were found as metal oxides: SiO$_2$, ZnO and MgO, respectively. Binding energies of oxygen correspond to metal oxides and hydrocarbons. Additionally, fly ash samples showed similar oxygen concentrations. The absence of Mg in FA1 sample may be explained by the presence of a carbon shell on the surface. After toluene extraction this shell is partially removed and Mg could be detected in FA2 samples. Other elements such as Al, Ca, Fe and Ti were not detected by SEM scanning and were probably buried into the fly ash structure.

3.2.4.2. XRD. Fig. 7 illustrates XRD profiles of fly ash samples. The fly ash surface presented an important contribution of crystalline NaCl (halite) which is maintained after toluene extraction. Other mineral phases usually found by XRD, including KCl (sylvite), SiO$_2$ (quartz), CaCO$_3$ (anhydrite) and CaCO$_4$ (calcite) [9,10,15,52,74,75] were not observed in these samples probably due to the high amount of NaCl.

4. Conclusions

Bag filter ash samples from a hazardous waste incinerator in Medellín, Colombia were characterized before and after toluene soxhlet extraction. Fly ash samples consist of platelets smaller than 0.5 μm agglomerated in low surface area spheres between 20 and 100 μm. They are composed of a silicon structure and important contributions of metal oxides and sodium chloride. Additionally, Cl, Zn, K, Fe, Sb, Pb, Ca, Ti, P were detected above 1000 mg/kg; Hg, Cu, Mg, Al, Cr, Ni, Mn, Ba, Cd, As and Co in concentrations within 10–1000 mg/kg; and traces of V, La, Tl, U, Th, Eu and Yb. Toluene extraction does not significantly affect fly ash morphology but increases particle size and reduces about 35% of C, 50% of metals and 35% of its surface area.

Dioxins, furans and dioxin-like PCBs analyses give about 180 ng WHO-TEQ/g. The high concentration of dioxins is favored by the small size of fly ash particles and large amounts of chlorine. Additionally, surface fly ash samples contained 32.8 wt.% C probably as a result of an incomplete combustion. The carbon is oxidized and forms different structures such as amorphous carbon black and nano balls, and more crystalline fullerenes like nano onions. The presence of metals such as Cu and Fe can favor the carbon oxidation and catalyze De novo synthesis leading to high dioxin levels.

Acknowledgments

References

[1] B.R. Stanmore, The formation of dioxins in combustion systems, Combust. Flame 136 (2004) 398–427.

[2] H. Fiedler, National PCDD/PCDF release inventories under the stockholm convention on persistent organic pollutants, Chemosphere 67 (2007) S96.

[3] E. Finocchio, G. Busca, M. Notaro, A review of catalytic processes for the destruction of PCDD and PCDF from waste gases, Appl. Catal. B 62 (2006) 12–20.

[4] B. Aristizábal, M. Cobo, C. Montes de Correa, K. Martínez, E. Abad, J. Rivera, Dioxin emissions from thermal waste management in Medellín, Colombia: present regulation status and preliminary results, Waste Manag. 27 (2007) 1603–1610.

[5] B. Aristizábal, M. Cobo, A. Hoyos, C. Montes de Correa, M. Ábalos, K. Martínez, E. Abad, J. Rivera, Baseline levels of dioxin and furan emissions from waste thermal treatment in Colombia, Chemosphere 73 (2008) S171–S175.

[6] T. Sabbas, A. Polettini, R. Pomi, T. Astrup, O. Hjelmar, P. Mostbauer, G. Cappai, G. Magel, S. Salhofer, C. Speiser, S. Heuss-Assbichler, R. Klein, P. Lechner, Management of municipal solid waste incineration residues, Waste Manag. 23 (2003) 61–88.

[7] R. Li, L. Wang, T. Yang, B. Raninger, Investigation of MSWI fly ash melting characteristic by DSC–DTA, Waste Manag. 27 (2007) 1383–1392.

[8] S. Gilardoni, P. Fermo, F. Cariati, V. Gianelle, D. Pitea, E. Collina, M. Lasagni, MSWI fly ash particle analysis by Scanning Electron Microscopy–Energy Dispersive X-Ray Spectroscopy, Environ. Sci. Technol. 38 (2004) 6669–6675.

[9] F.Y. Chang, M.Y. Wey, Comparison of the characteristics of bottom and fly ashes generated from various incineration processes, J. Hazard. Mater. B138 (2006) 594–603.

[10] G.J. Song, K.H. Kim, Y.C. Seo, S.C. Kim, Characteristics of ashes from different locations at the MSW incinerator equipped with various air pollution control devices, Waste Manag. 24 (2004) 99–106.

[11] X. Wan, W. Wang, T. Ye, Y. Guo, X. Gao, A study on the chemical and mineralogical characterization of MSWI fly ash using a sequential extraction procedure, J. Hazard. Mater. B134 (2006) 197–201.

[12] T. Taylor, J. Dykstra, J. Krzanowsk1, D. Domingo, D. Stampfli, J. Martin, P. Ericksona, Comprehensive approach toward understanding element speciation and leaching behavior in municipal solid waste incineration electrostatic precipitator ash, Environ. Sci. Technol. 29 (1995) 629–646.

[13] S.J. Huang, C.Y. Chang, D.T. Mui, F.C. Chang, M.Y. Lee, C.F. Wang, Sequential extraction for evaluating the leaching behavior of selected elements in municipal solid waste incineration fly ash, J. Hazard. Mater. 149 (2007) 180–188.

[14] E. Collina, M. Lasagni, M. Tettamanti, D. Pitea, Kinetics of MSWI fly ash thermal degradation. 2. Mechanism of native carbon gasification, Environ. Sci. Technol. 34 (2000) 137–142.

[15] A. Polettini, R. Pomi, The leaching behavior of incinerator bottom ash as affected by accelerated ageing, J. Hazard. Mater. B 113 (2004) 209–215.

[16] L. Zhao, F.-S. Zhang, K. Wang, J. Zhu, Chemical properties of heavy metals in typical hospital waste incinerator ashes in China, Waste Manag. 29 (2009) 1114–1121.

[17] N. Lapa, R. Barbosa, M.H. Lopes, B. Mendes, P. Abelha, I. Gulyurtlu, J. Santos Oliveira, Chemical and ecotoxicological characterization of ashes obtained from sewage sludge combustion in a fluidised-bed reactor, J. Hazard. Mater. 147 (2007) 175–183.

[18] R. Pöykiö, H. Rönnkömäki, H. Nurmesniemi, P. Perämäki, K. Popov, I. Välimäki, T. Tuomi, Chemical and physical properties of cyclone fly ash from the grate-fired boiler incinerating forest residues at a small municipal district heating plant (6 MW), J. Hazard. Mater. 162 (2009) 1059–1064.

[19] A. Yasuhara, T. Katami, Leaching behavior of polychlorinated dibenzo-p-dioxins and furans from the fly ash and bottom ash of a municipal solid waste incinerator, Waste Manag. 27 (2007) 439–447.

[20] B.-Y. Chen, K.-L. Lin, Biotoxicity assessment on reusability of municipal solid waste incinerator (MSWI) ash, J. Hazard. Mater. B136 (2006) 741–746.

[21] H.C. Hsi, L.C. Wang, T.H. Yu, Effects of injected activated carbon and solidification treatment on the leachability of polychlorinated dibenzo-p-dioxins and dibenzofurans from air pollution control residues of municipal waste incineration, Chemosphere 67 (2007) 1394–1402.

[22] A. Smeda, W. Zyrnicki, Application of sequential extraction and the ICP–AES method for study of the partitioning of metals in fly ashes, Microchem. J. 72 (2002) 9–16.

[23] Y. Matsuzawa, K. Mae, S. Kitano, S. Yoshihara, S. Ueno, J. Nishino, N. Kubota, Leaching behavior of heat-treated waste ash, Fuel 85 (2006) 401–409.

[24] K.-Y. Chiang, C.-C. Tsai, K.-S. Wang, Comparison of leaching characteristics of heavy metals in APC residue from an MSW incinerator using various extraction methods, Waste Manag. 29 (2009) 277–284.

[25] P.J. He, H. Zhang, C.G. Zhang, D.J. Lee, Characteristics of air pollution control residues of MSW incineration plant in Shanghai, J. Hazard. Mater. B116 (2004) 229–237.

[26] P. Gabarra, A. Cogollo, F. Recasen, I. Fernandez-Escobar, E. Abad, J.M. Bayon, Supercritical fluid process for removal of polychlorodibenzodioxin and dibenzofuran from fly ash, Environ. Prog. 18 (1999) 40–49.

[27] E. Collina, M. Lasagni, D. Pitea, Degradation of ochchlorodibenzofuran and octachlorodibenzo-p-dioxin spiked on fly ash: kinetics and mechanism, Environ. Sci. Technol. 29 (1995) 577–585.

[28] R. Weber, T. Takasuga, K. Nagai, H. Shiraishi, T. Sakurai, T. Matuda, M. Hiraoka, Dechlorination and destruction of PCDD, PCDF and PCB on selected fly ash from municipal waste incineration, Chemosphere 49 (2002) 127–134.

[29] A.M. Cunliffe, P.T. Williams, Influence of temperature on PCDD/PCDF desorption from waste incineration flyash under nitrogen, Chemosphere 66 (2007) 1146–1152.

[30] Y. Misaka, T. Abe, K. Takeuchi, K. Ohba, K. Sawabe, K. Shobatake, Dechlorination/hydrogenation and destruction reactions of PCDDs in OCDD-added fly ash heated under vacuum, Chemosphere 65 (2006) 419–426.

[31] G.J. Song, S.H. Kim, Y.C. Seo, S.C. Kim, Dechlorination and destruction of PCDDs/PCDFs in fly ashes from municipal solid waste incinerators by low temperature thermal treatment, Chemosphere 71 (2008) 248–257.

[32] J.E. Aubert, B. Husson, N. Sarramone, Utilization of municipal solid waste incineration (MSWI) fly ash in blended cement Part 1: Processing and characterization of MSWI fly ash, J. Hazard. Mater. B136 (2006) 624–631.

[33] J.E. Aubert, B. Husson, N. Sarramone, Utilization of municipal solid waste incineration (MSWI) fly ash in blended cement Part 2. Mechanical strength of mortars and environmental impact, J. Hazard. Mater. 146 (2007) 12–19.

[34] P. Tundo, C. Marques, M. Selva, A mild catalytic detoxification method for PCDDs and PCDFs, Appl. Catal. B 32 (2001) L1–L7.

[35] Y. Ukisu, T. Miyadera, Dechlorination of dioxins with supported palladium catalysts in 2-propanol solution, Appl. Catal. A 271 (2004) 165–170.

[36] Z. Yang, C. Xia, Q. Zhang, J. Chen, X. Liang, Catalytic detoxification of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in fly ash, Waste Manag. 27 (2007) 588–592.

[37] K. Ishii, T. Furuichi, Development of bioreactor system for treatment of dioxin-contaminated soil using Pseudallescheria boydii, J. Hazard. Mater. 148 (2007) 693–700.

[38] US EPA 1613, Tetra-Through Octa-Chlorinated Dioxins and Furans by Isotopic Dilution HRGC/HRMS, Washington, 1995.

[39] EN-1948-1,2,3, European Standard, Stationary Source Emissions—Determination of the mass concentration of PCDDs/PCDFs, European Committee for Standardization, Brussels, 1996.

[40] Y. Sun, M. Takaoka, N. Takeda, T. Matsumoto, K. Oshita, Application of microwave-assisted extraction to the analysis of PCBs and CBzs in fly ash from municipal solid waste incinerators, J. Hazard. Mater. A137 (2006) 106–112.

[41] O. Kiguchi, T. Kobayashi, K. Saitoh, N. Ogawa, Pressurized liquid extraction of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls from contaminated soil, J. Chromatogr. A 1108 (2006) 176–182.

[42] O. Kiguchi, K. Saitoh, N. Ogawa, Simultaneous extraction of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls from contaminated soil using pressurized liquid extraction, J. Chromatogr. A 1144 (2007) 262–268.

[43] M. Cobo, A. Quintero, C. Montes, Liquid phase dioxin hydrodechlorination over Pd/γ-Al₂O₃, Catal. Today 133–135 (2008) 509–519.

[44] M. Cobo, J.A. Conesa, C. Montes de Correa, The effect of NaOH on the liquid-phase hydrodechlorination of dioxins over Pd/γ-Al₂O₃, J. Phys. Chem. A 112 (2008) 8715–8722.

[45] K.-J. Hong, S. Tokunaga, T. Kajiuchi, Extraction of heavy metals from MSW incinerator fly ashes by chelating agents, J. Hazard. Mater. B75 (2000) 57–73.

[46] M.-S. Wang, L.-C. Wang, G.-P. Chang-Chien, Distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in the landfill site for solidified monoliths of fly ash, J. Hazard. Mater. 133 (2006) 177–182.

[47] E. Abad, K. Martinez, J. Caixach, J. Rivera, Polychlorinated dibenzo-p-dioxins, dibenzofurans and 'dioxin-like' PCBs in flue gas emissions from municipal waste management plants, Chemosphere 63 (2006) 570–580.

[48] M.B. Chang, Y.T. Chung, Dioxin contents in fly ashes of MSW incineration in Taiwan, Chemosphere 36 (1998) 1959–1968.

[49] W.M. Sierhius, C. de Vries, J.G.P. Born, PCDD/F emissions related to the operating conditions of the flue gas cleaning system of MWI-Amsterdam, Chemosphere 32 (1991) 159–168.

[50] M. Reimerink, D. Van der Klett, B. Vand der Akker, Norit powdered activated carbon in flue gas clean up, Organohalogen Compd. 27 (1996) 177–182.

[51] S. Bethanis, C.R. Cheeseman, C.J. Sollars, Properties and microstructure of sintered incinerator bottom ash, Ceram. Int. 28 (2002) 881–886.

[52] C.K. Chen, C. Lin, L.C. Wang, G.P. Chang-Chien, The size distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in the bottom ash of municipal solid waste incinerators, Chemosphere 65 (2006) 514–520.

[53] P. Ruokojarvi, M. Aatamila, K. Tuppurainen, J. Ruuskanen, Effect of urea on the fly ash PCDD/F concentration in different particle sizes, Chemosphere 43 (2001) 757–762.

[54] L.F. Ramírez-Verduzco, E. Torres-García, R. Gómez-Quintana, V. González-Peña, F. Murrieta-Guevara, Desulfurization of diesel by oxidation/extraction scheme: influence of the extraction solvent, Catal. Today 98 (2004) 289–294.

[55] M.C. Iliuta, F. Larachi, Solubility of dimethyldisulfide (DMDS) in aqueous solutions of Fe(III) complexes of trans-1,2-cyclohexanediaminetetraacetic acid (CDTA) using the static headspace method, Fluid Phase Equilib. 233 (2005) 184–189.

[56] A. Coker, Ludwig's Applied Process Design for Chemical Petrochemical Plants, vol. 1, 4th Edition, Elsevier, 2007, p. 856.

[57] A. Hoyos, M. Cobo, B. Aristizábal, F. Córdoba, C. Montes de Correa, Total suspended particulate (TSP), polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions from medical waste incinerators in Antioquia, Colombia, Chemosphere 73 (2008) S137–S142.

[58] M.E. Birpınar, M.S. Bilgili, T. Erdoğan, Medical waste management in Turkey: a case study of Istanbul, Waste Manag. 29 (2009) 445–448.

[59] A. Coker, A. Sangodoyin, M. Sridhar, C. Booth, P. Olomolaiye, F. Hammond, Medical waste management in Ibadan, Nigeria: obstacles and prospects, Waste Manag. 29 (2009) 804–811.

[60] Y.W. Cheng, F.C. Sung, Y. Yang, Y.H. Lo, Y.T. Chung, K.-C. Li, Medical waste production at hospitals and associated factors, Waste Manag. 29 (2009) 440–444.

[61] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, Surface area and pore texture of catalysts, Catal. Today 41 (1998) 207–219.

[62] H. Matzing, W. Baumann, B. Becker, K. Jay, H.R. Paur, H. Seifert, Adsorption of PCDD/F on MWI fly ash, Chemosphere 42 (2001) 803–809.

[63] B. Rubio, M.T. Izquierdo, M.C. Mayoral, M.T. Bona, J.M. Andres, Unburnt carbon from coal fly ashes as a precursor of activated carbon for nitric oxide removal, J. Hazard. Mater. 143 (2007) 561–566.

[64] J.O. Muller, D.S. Su, R.E. Jentoft, J. Krohnert, F.C. Jentoft, R. Schlogl, Morphology-controlled reactivity of carbonaceous materials towards oxidation, Catal. Today 102–103 (2005) 259–265.

[65] Y. Chen, N. Shah, F.E. Huggins, G.P. Huffman, Microanalysis of ambient particles from Lexington, KY, by electron microscopy, Atmosph. Environ. 40 (2006) 651–663.

[66] O. Mathieu, G. Frache, N. Djebaıli-Chaumeix, C.E. Paillard, G. Krier, J.F. Muller, F. Douce, P. Manuelli, Characterization of adsorbed species on soot formed behind reflected shock waves, Proceed. Combust. Inst. 31 (2007) 511–519.

[67] N. Nejar, M. Makkee, M.J. Illan-Gomez, Catalytic removal of NOₓ and soot from diesel exhaust: oxidation behaviour of carbon materials used as model soot, Appl. Catal. B 75 (2007) 11–16.

[68] L.E. Murr, K.F. Soto, A TEM study of soot, carbon nanotubes, and related fullerene nanopolyhedra in common fuel–gas combustion sources, Mater. Charact. 55 (2005) 50–65.

[69] B.S. Ahn, S.G. Jeon, H. Lee, K.Y. Park, Y.G. Shul, Hydrogenolysis of CFC-12 (CF₂Cl₂) over Pd/γ-Al₂O₃ pretreated with HCFC-22 (CHF₂Cl), Appl. Catal. A 193 (2000) 87–93.

[70] I. Czekaj, F. Loviat, F. Raimondi, J. Wambach, S. Biollaz, A. Wokaun, Characterization of surface processes at the Ni-based catalyst during the methanation of biomass-derived synthesis gas: X-ray photoelectron spectroscopy (XPS), Appl. Catal. A 329 (2007) 68–78.

[71] NIST XPS database, http://srdata.nist.gov/xps/Bind_E.asp (accessed August 15, 2008).

[72] Lasurface XPS database, http://www.lasurface.com (accessed August 15, 2008).

[73] A. Kida, Y. Noma, T. Imada, Chemical speciation and leaching properties of elements in municipal incinerator ashes, Waste Manag. 16 (1996) 527–536.

[74] C.S. Kirby, J.D. Rlmstldt, Mineralogy and surface properties of municipal solid waste ash, Environ. Sci. Technol. 27 (1993) 652–660.

[75] Y. Yu-Fen, G. Guo-Sheng, C. Zhen-Fang, C. Qing-Ru, Surface modification of purified fly ash and application in polymer, J. Hazard. Mater. B 133 (2006) 276–282.