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1 2 3	1	Residues characterisation from the fluidised bed combustion of East London's
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18 Abstract

Waste thermal treatment in Europe is moving towards the utilisation of the combustible output of mechanical, biological treatment (MBT) plants. The standardisation of solid recovered fuels (SRF) is expected to support this trend and increase the amount of the generated combustion residues. In this work, the residues and especially the fly ashes from the fluidised bed combustion (FBC) of East London's NCV 3, Cl 2, and Hg 1 class SRF, are characterised. The following toxicity indicators have been studied: leachable chlorine, organochlorides expressed as pentachlorobenzene and hexachlorobenzene, and the heavy metals Cu, Cr, Cd, Zn, Ni, and Pb. Furthermore the mineralogical pattern of the ashes has been studied by means of XRD and SEM- EDS. The results suggest that these SRF derived ashes have significantly lower quantities of Cu, Cd, Pb, Zn, leachable Cl and organochlorides when compared to other literature values from traditional waste thermal treatment applications. This fact highlights the importance of modern separation technologies employed in MBT plants for the removal of components rich in metals and chlorine from the combustible output fraction of SRF resulting to less hazardous residues.

Keywords: Refuse derived fuels, thermal treatment, air pollution control residues,

trace metals, chlorine leaching

1. Introduction

Thermal treatment has been recognized as a valuable technique for the recovery of the energy content of wastes within the waste management hierarchy. Recent data (Defra, 2009) indicate that countries like Denmark, Netherlands, Belgium, Sweden, Luxemburg, Germany, France and Portugal, incinerate more than 20% of their generated municipal solid waste. In addition, or in replacement, of traditional mass grate thermal treatment, the use of the combustible output fractions of MBT plants could further support a sustainable short/middle- term approach for the management of the increasing volumes of wastes, especially in dense metropolitan areas (Caputo and Pelagagge, 2002). This integrated waste treatment approach has increased its presence in Europe, with MBT plants that reach a capacity of 2 million tons per annum (Velis et al., 2009).

Despite these facts, public opinion is sometimes against developments regarding integrated thermal treatment applications, even in developed counties (Luria, 2008). These oppositions mainly focus on direct health effects from emissions and residues of these technologies based on past experience. Issues related to chlorine and heavy metals content of waste derived fuels have resulted to limited demand of the latter during the past decade (Rotter et al., 2004).

In this context, the standardization of SRF (CEN/TS 15359, 2006) in terms of calorific value, trace metals and chlorine content, intends to facilitate the economic, emissions, and technological issues associated with the acceptance and marketability of waste derived fuels and related applications. According to the abovementioned standard, SRF is distinguished from the classical term of refuse derived fuel (RDF), as the initial characterization criterion is a non-hazardous waste source and the final criterion is a quality assured (QA) classification according to the following properties:

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The mean net calorific value

- The mean value of chlorine content •
- The mean and 80th percentile values for mercury content. Both values are • taken into account and due to the statistical distribution pattern of Hg. The highest value is used for determination of the SRF class.

Each property is divided in five classes with range values and the combination of the property classes makes up the class code for each SRF.

SRF standardization protocols can support the development and expansion of waste-fuel markets (Bernd et al., 2007). This expansion is expected to increase the quantities of the generated combustion and air pollution control (APC) residues. In the UK this amount is expected to reach 162,000 tons per annum in 2010, from about 83,000 tons in 2000 (Amutha Rani et al., 2008). Fly ash in particular, is an issue of concern as it is enriched with heavy metals, soluble salts and organic micro-pollutants (Huang et al., 2003; He et al., 2004; Hyks et al., 2009), that could be released in the environment from its utilization or landfilling. Thus, knowledge of the characteristics of these residues is of extreme importance for their treatment within good integrated waste management practices.

This work characterizes the fly ashes produced from the combustion of East London's SRF in a fluidized bed reactor. The following toxicity indicators have been studied: total organic carbon (TOC), leachable chlorides, organochlorides expressed as pentachlorobenzene (Cl₅Bz) and hexachlorobenzene (Cl₆Bz), and the heavy metals Cu, Cr, Cd, Zn, Ni, and Pb. Finally, XRD and SEM- EDS techniques are utilized for the mineralogical characterization of the produced fly ashes. These commonly applied

92 indicators have been employed to facilitate comparisons with other reported values in 93 literature. The aim of this study is to assess whether the pollutants load of SRF 94 derived fly ashes is lower than the equivalent values reported in literature, from 95 conventional waste fuels, and/ or traditional waste thermal treatment applications.

97 2. Materials and methods

2.1. Feedstock properties

SRF derived from East London's Waste Authority, processed by a private contractor was the feedstock for the trial. The fuel is produced in a sequential separation, shredding, and aerobically bio-drying MBT process, classified as a "NCV 3; Cl 2; Hg 1" class SRF. A batch of 100kg was sampled from the MBT plant and it was later sub-sampled as a static pile, according to the relevant standard (CEN/TS 15442, 2006) for the detailed investigation of proximate characteristics and chlorine content. The remaining data on ultimate analysis (Table 1) were provided by the SRF producer based on routine quality analysis/ quality control (QA/QC).

107 <<Table 1>>

2.2. Fluidized bed combustion rig operating conditions

The 50 kW_{th} fluidized bed combustor that was used for the trial consisted of a screw feeding hopper, the main bed chamber (dimensions $175 \times 30 \times 30$ cm), a secondary combustion chamber that leads to a vertical ash deposition compartment, a water heat exchanger, a cyclone, and an exhaust fan prior to the stack. The bed area was filled with 30.2 kg of silica sand with particle size between 1.00 - 0.5 mm (16/30 grade, density 1,556 g l⁻¹), resulting to bed static dimensions of 30*30*15.35 cm. The FBC was vacuumed the day before the experiment for the removal of residual ash and particles from previous trials. Furthermore, it was operated overnight, burning natural gas for decontamination and start-up purposes. The rig was monitored by 19 K-type thermocouples, CO, CO₂, and O₂ online gas monitoring systems. The SRF incoming flow slightly varied throughout the trial with a mean value of 117g min⁻¹ and a lambda coefficient equal to 1.6. The duration of the test was 300 minutes and the bed temperature was at 800 \pm 20 °C. The rig and the ashes sampling points are illustrated in Figure 1. Detailed information on the experimental conditions are reported in previous work (Balampanis et al., 2008).

<<Figure 1>>

2.3. Analysis

2.3.1. Inorganic chlorine & chlorobenzenes

After the experiment, the rig was disassembled and the mixed silica sand/ bed ash were collected, weighted, and emptied to a tank with deionised water. The tank was mechanically agitated for 3 hours and 6 replicate samples were taken, centrifuged and filtrated. The horizontal chamber and cyclone ash were collected separately in clean pre- weighted vacuum bags. Ashes sampled from the horizontal chamber (approximate size <1.2 mm) and ashes sampled from the cyclone (approximate size <200 µm) (Figure 2) will be referred herein and after, as coarse fly ash and fine fly ash, respectively, according to the literature definitions (IAWG, 1997; Quina et al., 2008a). Six replicates of a gram each, of coarse and fine fly ash were diluted in 250 mL of deionised water and agitated for three hours. The mix was centrifuged and decanted and the filtrate was stored in polypropylene bottles, at 4 °C for chloride anions analysis (Dionex, UK- Ion Chromatographer, column: Ion Pac As9- HC 4*250 mm).

For the determination of Cl₅Bz and Cl₆Bz the following procedure was employed. Seven replicates of each ash type were spiked with extraction standards (800ng mL⁻¹ 1,3,5-tribromobenzene in toluene) and then digested with 100mL of 2M HCl. The mix was separated using vacuum filtration, and the cakes were washed with deionised water to reduce acidity, air-dried for 12h, and then extracted with Soxhlet using 200mL of toluene for 20h. The aqueous solutions were extracted three times with 100mL of dichloromethane per litre of solution, and the solvent extracts were washed twice with deionised water for pH adjustment (50% v/v). The two extracts from each sample were mixed, concentrated using a rotary evaporator (38 °C, 68 mbar), filtered through a multilayer silica gel column (anhydrous Na₂SO₄, 10% AgNO₃ silica gel, 20% H₂SO₄ silica gel, 40% H₂SO₄ silica gel, 30% KOH silica gel) and eluted with hexane, double the height of the column. The column's elutes were further evaporated (35 °C, 200 mbar) and finally concentrated to 1mL using a nitrogen flow concentrator. The samples were spiked again with recovery standards (100 µl of 1.6µg mL⁻¹ of 1,2 dichlorobenzene-d4) and analysed through GC-MS-SIM (Instrument: Perkin Elmer- Autosystem XL/Turbo Mass Gold; Column: Thames-Restek Rtx ®- 1MS- 100% dimethyl polysiloxane column (length 15m, internal diameter 0.25 mm, film thickness 0.25 µm); Injection: 1 µl at a split ratio of 100:1; Ionisation mode: positive 70 eV; Oven temperature conditions: initial 50 °C, rising 30 °C min⁻¹ up to 125 °C, and then 15 °C min⁻¹ up to 300 °C where it was held for 6 min).

3.3.2. Heavy metals

Standard methods (ASTM, 2004) for the determination of heavy metals in combustion residues, involve the utilisation of hydrofluoric acid (HF). These methods were excluded from this work due to HF's adverse effects on instrumentation, and for health and safety reasons. Furthermore, the total content of heavy metals is not directly related to the leaching potential of fly ash, when landfilled (Hyks et al., 2009). Thus, four HF free digestion methods were tested for their recoveries, using a certified reference material (CRM). The CRM was MSW incineration fly ash (BCR-176R, Joint Research Centre, Institute for Reference Materials and Measurements, EC) and a summary of the digestion methods is presented in Table 2.

<<Table 2>>

An Anton Parr Multiwave 3000 microwave oven unit was utilised for the microwave assisted digestion (MWAD) methods (A, B, and C), and compared against standard reflux with aqua regia (method D) (BSI, 1995). For method A, seven replicates of 400 ± 1 mg CRM and a method blank were placed in the PTFE pressure vessels with 8 mL of concentrated (15.8 M) nitric acid. The vessels were left 16 hours in a fume cupboard to equilibrate, to avoid elevated pressures inside the vessels at the MWAD stage. The following MWAD programme was applied: 20 minutes for the instrument to reach 18 bar and 190 °C, where held for 20 minutes and finally another 20 minutes for the vessels to cool down. The mixture was then filtered using 0.45µm Whatman cellulose filter papers and diluted with ultra pure (MilliPore) water, to a fixed volume of 100 mL.

Method B was performed exactly as method A, but with a different acid mix: 5 mL of nitric acid and 3mL of hydrogen peroxide (100 volumes). Method C was performed exactly as method A, with the difference that ultrasonic waves were applied through a 600W probe (Langford Ultrasonics- Sonomatic), to test whether ultrasonication could enhance the digestion reactions.

Method D was tested on 7 CRM replicates of 3 ± 0.001 g each, and a method blank. Twenty one mL of concentrated hydrochloric acid (12 M) were added in 250mL reaction flasks, followed by 7 mL of nitric acid. The mix was allowed to oxidise at room temperature for 16h, and then heated to reflux conditions for 2h. After cooling down, it was filtered (0.45 µm Whatman cellulose filter papers) and made up to 100 mL using ultra pure water. All chemicals were trace analysis grade and purchased from Fischer Scientific UK. The quantification was achieved through a graphite furnace/ flame- atomic absorption spectrometer (GF/F-AAS) A-Analyst 800 Perkin Elmer instrument, equipped with an air/ acetylene flame and an AS-90 autosampler.

3.3.3. XRD, TOC & SEM- EDS analysis

The coarse and fine fly ashes were also analysed for their total C,H,N, and TOC content using an elemental analyser (Vario EL III), and further examined in a SEM-EDS microscope (Philips XL 30) for their major elements determination. The mean concentration of elements (% wt> 1) in the SEM- EDS analysis was obtained from a spectrum over a 4 mm^2 and 0.16 mm^2 area for coarse and fine fly ash, respectively; Furthermore, the reported deviations represents 4 different scans in smaller areas, on each one of the quadrants of the originally scanned areas. Finally, XRD (Siemens ED 5005) analysis was employed for the determination of the ashes' crystaline phases.

207 4. Results and discussion

4.1. Inorganic chlorine and chlorobenzenes

Figure 3 demonstrates the amount of water soluble chlorides that leached from each ash type. As expected the bed ash contained the lowest levels of Cl as most of it was volatilised in the process to form HCl, Cl₂, or Cl radicals. The bed ash contained an amount of non- combustibles that was visible in the bed material. These residues were mostly glass fractions, ceramics, metals, stones etc., thus a rather abnormal and heterogeneous distribution of chlorides in these particles should be expected. Although the determination of chloride ions was made with a much greater liquid to solid (L/S) ratio than characterisation protocols suggest (BSI, 2002), the bed ash, based on the leached Cl, would be accepted for co-disposal in a non hazardous landfill (Cl⁻< 15,000 mg kg⁻¹), according to the existing legislation (EC, 2002) for granular waste. According to the same legislation the coarse fly ash would be accepted in a hazardous waste landfill without further treatment ($Cl^{-} < 25000 \text{ mg kg}^{-1}$), while fine fly ash would require further stabilisation before final disposal.

The higher chlorinated benzenes (Cl₅Bz, and Cl₆Bz) were quantified as indicators for the organochloride load of the fly ashes. Indirect measurement of dioxins like compounds using Cl₅Bz, and Cl₆Bz is useful for process optimisation, control of separation efficiencies of the flues gases in cleaning devices and the control of emissions levels. However, although indirect measurements can be performed at lower cost than determination of PCDD/Fs, the relationship between PCDD/Fs and the indicator parameters is likely to be plant specific (Öberg et al., 2008). The Cl₅Bz values ranged between 9 ± 3.9 ng g⁻¹ for coarse, and 15 ± 2.8 ng g⁻¹ for fine fly ash while the equivalent Cl₆Bz values ranged between 3.3 ± 2.8 ng g⁻¹, and 8 ± 2 ng g⁻¹,

respectively. These figures correspond to the lower range of reported values on organochlorides within the literature as it will be discussed at a later stage (section 4.4).

<<Figure 2>>

4.2. Heavy Metals

The four HF-free fly ash digestion methods were compared for their recoveries of the CRM and the results are reported in Figure 4. The overall recoveries ranged between 59% and 94%, except from Cr which ranged at lower levels ca. 19- 38%. A one way ANOVA at a confidence interval of 95%, confirmed that there was no single method that significantly recovered higher amounts for the whole range of the examined metals. However, some exceptions were found in method A, which recovered significantly higher quantities of Pb, and in the aqua regia method (D), which recovered lower amounts of Cu, Cd and Pb. Furthermore, neither the addition of H₂O₂ in the digestion vessels, or ultrasonication as post-digestion treatment, improved the recovery of the metals. Thus, single step HNO₃ MWAD proved sufficient for the solubilisation of heavy metals in waste derived fly ashes, as reported in older studies (Mester et al., 1999; Quina et al., 2008b).

<<Figure 3>>

The fly ashes were further analysed for their content in Cu, Cr, Ni, Pb, Cd, and Zn using method A and the results are presented in Figure 5. Coarse fly ash contained higher Cu, Pb and Zn quantities than the fine fly ash fraction, which had higher Cr and Ni contents. The Cd values were relatively low ranging at 3.6 ± 0.6 mg kg⁻¹ and 7.3 ± 0.2 mg kg⁻¹ for fine and coarse fly ash, respectively. Finally, it should be noted that the actual concentration of Cr in both ash types could be higher than the ones

255 presented in Figure 5, as the HF free digestion method used gives a relative poor 256 recovery of the element according to the CRM recovery values.

257 <<Figure 4>>

4.3. Minerals and carbon

The rough (% wt >1) composition of the elements in the ashes, as recognised in SEM-EDS analysis is presented in Table 3. Calcium, silicon, aluminium, chlorine, sodium, potassium, iron, sulphur, and phosphorus were the most common elements, besides carbon, which ranged at 8.6 ± 0.1 % and 9.6 ± 0.2 % for the coarse and fine fly ash, respectively. This slight difference in the total carbon content is probably due to the greater residence time of the bigger and heavier coarse particles (Figure 2 a and b) in the combustion zone, resulting to higher C to CO₂ conversion. This finding is confirmed by the TOC levels that ranged at $6 \pm 0.4\%$ and $6.8 \pm 0.1\%$ for coarse and fine fly ash particles. In respect to the SEM-EDS sensitivity, another conclusion is that fine fly ash had about double the amount of chlorine than the coarse one. This finding is confirmed by the amount of water soluble chlorides that leached from each ash type (section 4.1).

The mineralogical analysis recognised the main crystal phases of the ashes by means of XRD and the diffractograms are presented in Figure 6. These were similar for both ash types: Calcite (CaCO₃), quartz (SiO₂), halite (NaCl), sylvite (KCl), and calcium sulphate ($CaSO_4$); except from calcium silicate ($CaSiO_4$), which was only detected in fine ash particles. The XRD pattern is similar to most MSWI fly ashes as reported in other works (Wan et al., 2006; Quina et al., 2008b; Wang et al., 2008; Shi and Kan, 2009) with the exception of calcium silicate. This finding is of particular importance as layers of CaSiO₄ can interfere as heat transfer barriers in flame retardant applications (Hamdani et al., 2009), however its presence was not confirmed at the
heat- exchange tower (coarse fly ash sampling point), but only at the cyclone (fine fly
ash collection point.

282 <<Table 3>>

283 <<Figure 5>>

284 <<Figure 6>>

4.4. Comparison of SRF fly ash with literature values

Comparisons against literature values are often limited by the heterogeneity of available data, due to the complexity of the ash products, and the high number of available methods for residues characterisation, leaching protocols etc. Table 4 presents the toxicity indicators determined in this work, against equivalent values from MSWI derived fly ashes in literature. The selection of the literature data was based on the quality of the reported results, and the methods used to obtain them.

The results indicate lower levels of some pollutants in SRF- derived fly ashes compared to the reported values in literature. The chlorobenzenes in the examined samples range at an order of magnitude lower than other reported figures. The same result is obtained when comparing the heavy metals content of the SFR fly ashes with the equivalent metals load from other works; The levels of, Cd, Cu, Pb and Zn were significantly lower than other reported values. Furthermore, the leached chlorides levels lay on the lowest reported ranges within literature. However, no particular difference was observed for Cr and Ni and TOC, which ranged at the same levels as other researchers report.

The reported values in literature might involve data from thermal treatment technologies different than FBC, e.g. mass grate incineration, and can enhance the heterogeneity of data. As reported in other works (Lind et al., 2007) when comparing grate firing and FBC, there were differences in the levels of As and Sb in the generated fly ashes. However, the low Cl, Cd, Cu, Pb, Zn, Cl₅Bz, and Cl₆Bz presented in Table 4 clearly reflect the low chlorine and metals content of the particular fuel. This fact indicates the importance of modern separation technologies that are used in MBT plants for the removal of components rich in metals and chlorine like electronic waste and hard plastics, respectively, resulting to the removal of heavily polluted components from the combustible output fractions (Rotter et al., 2004).

311 <</Table 4>>

5. CONCLUSIONS

The coarse and fine fly ashes produced from the fluidised bed combustion of a NCV 314 3, Cl 2, and Hg 1 class SRF have been characterised using commonly tested toxicity 315 indicators like TOC, Cd, Pb, Zn, Ni, Cr, Cu, $Cl_{5,6}Bz$, and water soluble Cl. Our 316 findings indicate that SRF derived fly ashes have a similar mineralogical pattern with 317 other waste- derived fly ashes, with the exception of calcium silicate, which was only 318 detected in the fine particles.

The results, when compared with other literature values indicate that, these SRF derived fly ashes have significantly lower values in Cu, Cd, Pb, Zn, leachable Cl and organochloride load than other traditional thermal treatment applications. This fact highlights the importance of modern separation technologies employed in MBT plants for the removal of components rich in metals and chlorine from the combustible output fraction of SRF.

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414	Table 1	
415	SRF properties	
	Proximate analysis mean± s (%wt ^{**})	
	Moisture content	13.2 ± 1.5
	Ash content	13.7 + 2
		1017 = 2
	Ultimate analysis mean \pm s(% wt dm)	
	С	47.4 ± 4.2
	Н	5.7 ± 2.9
	Ν	0.8 ± 0.3
	S	0.1 ± 0.02
	Cl	0.4 ± 0.02
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420 Table 2421 Summary of digestion methods

Method	Reagents	Digestion conditions
A	8 mL HNO ₃	MWAD 190°C, 18 bar
В	$3 \text{ mL H}_2\text{O}_2 + 5 \text{ mL HNO}_3$	MWAD 190°C, 18 bar
С	8 mL HNO ₃	MWAD 190°C, 18 bar + ultrasonication
D	21 mL HCl+ 7 mL HNO ₃	Equilibration 16 hr, reflux 2 hr
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423	SEM-EDS results on element	nai compositioi	1 70 W > 1(X. II)	icali, s. staliual	u ueviation)
	Composition	Coarse	fly ash	Fine f	'ly ash
	(wt%)				
		Х	S	Х	S
	Na	1.3	0.7	1.7	0.3
	Al	1.7	0.5	2.5	0.3
	Si	5	2.7	5.5	2.8
	Р	1.3	0.8	1	0.2
	S	1.2	0.6	1.4	0.2
	Cl	2.2	0.7	5.5	0.7
	K	1.4	0.5	2.3	0.4
	Ca	11	1.2	9	0.7
	Fe	1.3	0.5	1.6	0.3

425 SEM-EDS results on elemental composition %wt> 1(x: mean, s: standard deviation)

Table 4

429	Comparison of East London'	s SRF fly ash indicative	toxicity indicators v	with literature
100	•			

values

100	(dideb					
		This study	MSWI fly ash	MSWI fly ash	MSWI fly ash	MSWI fly ash
		-	UK ^a	Sweden ^b	other ^c	other ^d
	Cl [*] mg g ⁻¹	15-45	140-170	6-81	45-380	nd
	TOC mg g ⁻¹	56-69	10-250	Nd	4.9-17	1.6-400
	Cd mg g ⁻¹	0.003-0.007	0.1-0.15	0.0035-0.31	0.016-1.6	0.2
	Pb mg g ⁻¹	0.76-1.22	2.5-3.5	0.73-36	0.25-27	0.88
	Zn mg g ⁻¹	0.8-1.23	4-8.5	4.9-44	4.3-104	21.3
	Cu mg g ⁻¹	0.36-0.47	0.35-0.6	0.22-1.8	0.016-2.22	1.74
	Cr mg g ⁻¹	0.41-1.07	0.012-0.2	0.2-1.6	0.072-0.57	0.121
	Ni mg g ⁻¹	0.18-0.42	0.015- 0.035	0.036-0.11	0.02-0.71	nd
	Cl ₅ Bz ng g ⁻¹	5.1-17.8	nd	43-610	nd	189-355
	Cl ₆ Bz ng g ⁻¹	0.5-10	nd	47-260	nd	113-249

nd- not determined

*Water soluble or total

^a Aqua regia total metals (Amutha Rani et al., 2008)
^b Total content (Öberg et al., 2007)
^c Total (Quina et al., 2008a)
^d Total (Huang et al., 2003)



Figure 1. Fluidized Bed Combustor- 1: screw feeding hopper, 2: bed area, 3: FB
chamber, 4: vertical secondary combustion chamber, 5: horizontal chamber- ash
deposits area, 6: heat exchange tower, 7: cyclone, 8: exhaust fan, 9: stack



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452 Figure 4: Recoveries of metals from CRM between different MWAD methods (error453 bars indicate minimum and maximum values, n=7)



456 Figure 5: Concentration of metals in SRF coarse and fine fly ash (error bars indicate
457 minimum and maximum values, n=7)
458



460 Figure 6. X-ray diffractograms (a) coarse, (b) fine fly ash. Crystal phases recognised:
461 1. Calcite; 2. Quartz; 3. Halite; 4. Sylvite; 5. Calcium sulphate; 6. Calcium silicate



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Bed ash Coarse fly ash Fine fly ash









