



Ash deposit characterisation in a large-scale municipal waste-to-energy incineration plant

Awassada Phongphiphat^{a,b}, Changkook Ryu^{a,c}, Karen N. Finney^{a,*}, Vida N. Sharifi^a, Jim Swithenbank^a

^a Sheffield University Waste Incineration Centre (SUWIC), Department of Chemical and Process Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

^b The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangmod, Tungkru, Bangkok 10140, Thailand

^c School of Mechanical Engineering, Sungkyunkwan University, Suwon, 440-746, South Korea

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ABSTRACT

The deposition of ash – combustion residues – on superheaters and heat exchanger surfaces reduce their efficiency; this phenomenon was investigated for a large-scale waste-to-energy incineration facility. Over a period of six months, ash samples were collected from the plant, which included the bottom ash and deposits from the superheater, as well as flyash from the convective heat exchanger, the economiser and fabric filters. These were analysed for particle size, unburned carbon, elemental composition and surface morphology. Element partitioning was evident in the different combustion residues, as volatile metals, such as cadmium, antimony and arsenic, were found to be depleted in the bottom ash by the high combustion temperatures (1000+°C) and concentrated/enriched in the fabric filter ash (transferred by evaporation). Non-volatile elements by contrast were distributed equally in all locations (transported by particle entrainment). The heat exchanger deposits and fabric filter ash had elevated levels of alkali metals. 82% of flyash particles from the fabric filter were in the submicron range.

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1. Introduction

Energy recovery from municipal solid waste (MSW), such as through mass-burn incineration, is a well established technology and vital to reduce the amount of waste going to landfill. Previously, MSW combustion was seen simply as a waste-disposal option, although significant emphasis is now placed on recovering the energy from this process – for instance in waste-to-energy (WTE) plants; consequently, heat recovery mechanisms and equipment, like superheaters and heat exchangers are integrated within the incineration system. MSW often contains large proportions (~25%) of ash, which can become deposited on heat recovery equipment in the power station and limits their efficiency.

1.1. Ash from waste-to-energy facilities

Gas cleaning processes in all power stations control the release of various organic/inorganic pollutants to comply with the stringent emission limits set out in the EU Waste Incineration Directive (2000/76/EC). The release of submicron particulates (solid-phase

emissions) has recently been the focus of significant environmental concern. Particle formation and release is a common problem from combustion sources using solid fuels, such as coal or MSW [1,2]. These particles are composed primarily of ash, which is where metals tend to be concentrated, in addition to soot and unburned fuel particles. The generation of flyash from fossil fuel and biomass combustion are well understood [3–5].

Flyash particles from combustion sources, such as coal-fired power plants, iron ore sinter plants and biomass plants, are bimodal, with one peak in the submicron range (less than 1 μm) [6–8]. Particles in the flue gas are generated by two mechanisms: (i) the entrainment of large particles into the gas flow; and (ii) the vaporisation of volatile trace elements. The former generally contributes to particles over 1 μm, and the latter to the submicron, respirable fraction. The entrained larger particles contain the elements that do not vaporise and compose the matrix of the flyash. Their surface can subsequently be enriched by deposits of volatile materials. The elements that are partially or fully vaporised during combustion undergo transformation and partitioning as the flue gas cools during heat recovery and gas cleaning. The conversion of these elements into the solid phase involves adsorption, condensation, coagulation and chemical transformation. Some larger particles are transported to and held on the cold surfaces of the heat exchangers before entering the gas cleaning phase. The deposition mechanisms involve inertial impact, condensation and thermophoresis. Deposition is typically initiated by the conden-

Abbreviations: EDS, energy dispersive X-ray spectrometer; MSW, municipal solid waste; SEM, scanning electron microscopy; WTE, waste-to-energy.

* Corresponding author. Tel.: +44 114 2227572; fax: +44 114 2227501.

E-mail address: K.Finney@sheffield.ac.uk (K.N. Finney).

sation of alkali metal compounds, which create a sticky surface on which flyash particles can accumulate. Such deposits reduce the heat transfer to the water-steam and also cause operational problems, such as corrosion and the formation of large clinkers. Air pollution control devices, such as electrostatic precipitators or fabric filters, are used to remove particles from the flue gas, in combination with injections of activated carbon and lime for the adsorption of heavy metals and organic pollutants, including dioxins. Although these devices can have particle removal efficiencies of over 99% by mass, they are least efficient at capturing the smallest, submicron particles.

MSW differs from coal or pure biomass, such as wood and straw, due to its heterogeneity in both composition and particle size. Other key dissimilarities are the elevated ash content (as mentioned previously) and the high amounts of chlorine (~1%) compared to other fuels. Incineration directly burns large waste particles with excess air, which results in lower flame temperatures than for coal and biomass. Ash from the mass-burn incineration in WTE facilities is discharged through several pathways [9]. Most of the ash (typically 80–90% by weight) is bottom ash, discharged at the end of the grate. A negligible portion of particles in the waste bed drops through the gaps between the grate plates as grate siftings, which are usually combined with bottom ash for disposal. Ferrous metals can be recovered from this bottom ash and the rest can be used as feedstocks for construction or other industries [9–11].

Various aspects of the behaviour of particulates and trace elements during municipal solid waste incineration have been studied [12]. This includes investigations of the sources and partitioning of elements and the enrichment of the more volatile elements on fine particles [13–18]. These found that lithophilic elements, such as iron, copper, chromium and aluminium, remain mainly in bottom ash (over 90% by weight), while the enrichment of volatile elements, including heavy metals, in flyash varies depending on their volatility. These have also been found to fluctuate considerably with the feed material and plant processes. Typically, over 80% of cadmium by weight is found in the flyash, while it is about 50% for lead and zinc. Small, submicron ash particles can be highly enriched with heavy metals, which are often hazardous, as they are classed as the respirable fraction and can thus be inhaled deep into the lungs. These can be toxic and/or carcinogenic and as a result can cause a wide variety of chronic cardiovascular and respiratory illnesses. This brings significant attention to the behaviour of trace metals associated with combustion residues in general, and the ash particles generated from MSW incineration in particular.

1.2. Objectives of the research

The main objective of this research was to characterise various ash samples taken from different locations in a mass-burn WTE incineration plant. This included determining the particle size distribution, unburned carbon content and elemental composition, as well as the mineralogy and surface morphology of the combustion residue particles.

2. Experimental methods and materials

2.1. The waste-to-energy plant

This investigation was conducted at a large-scale WTE facility – a commercial mass-burn MSW incinerator. The waste, which was fed by ram feeders, underwent combustion on the grate with primary air. Secondary air was injected in the form of jets at each sidewall above the bed, in order to aid turbulent mixing and supply additional oxygen to the residual combustion gases. These gases then passed through a pendant superheater, multi-tubular heat exchanger and economiser for energy recovery. The gas entered the fabric filters, which contained both hydrated lime sorbents for the removal of acid gases and activated carbon for the capture of dioxins/organic (micro-)pollutants and heavy metals. The amounts of lime and activated carbon injections were about 9 kg/ton-waste and 0.2 kg/ton-waste, respectively. The bottom ash, discharged from the grate, passed through a magnetic separator to recover ferrous metals. The ash was then transported for use as a capping material on landfill sites or as an aggregate substitute for the maintenance of roads. The total amount of residue was 322 kg/ton-waste. Bottom ash accounted for around 85% of the total residues, of which 7.8% was recovered as ferrous metals (equivalent to 6.2% of the total residues). Fig. 1 shows a schematic diagram of a typical WTE incineration plant.

2.2. Collection of ash samples

Over a period of six months, four samples were collected from each of the five different locations, as numbered in Fig. 1: (1) bottom ash; (2) deposits from the superheater; (3) flyash from the convective heat exchanger; (4) flyash from the economiser; and (5) flyash from the fabric filters. Approximately 1–5 kg of each residue was retrieved each time. The bottom and flyash samples represented particles generated for about an hour during each sampling period,

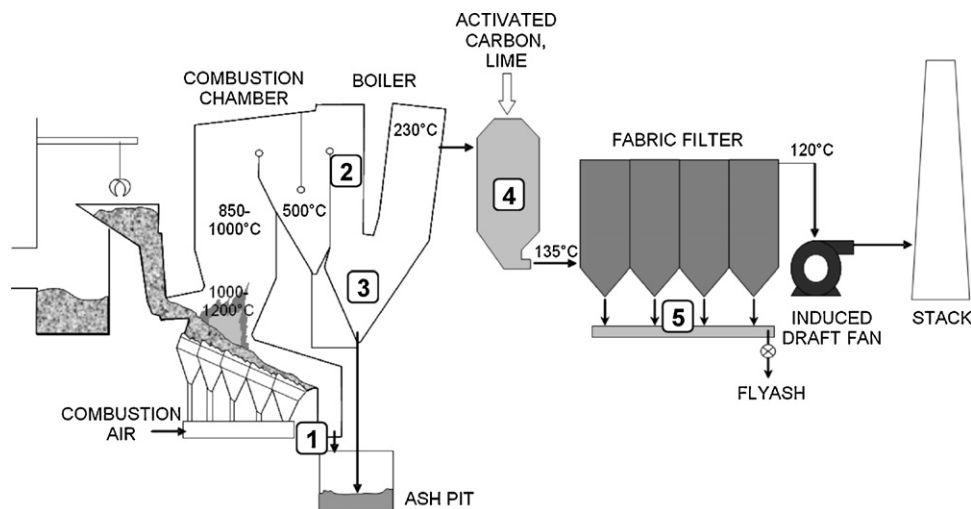


Fig. 1. A schematic overview of a typical incineration (mass-burn) process, showing the five ash sampling locations: (1) bottom ash; (2) the superheater deposit; (3) heat exchanger ash; (4) economiser ash; and (5) fabric filter ash.

while the superheater deposit was accumulated over a period of several weeks to months.

2.3. Ash sample analysis

A range of analytical techniques was used to determine the particle size distribution, unburned carbon content, elemental composition and surface morphology of each sample. As the particle sizes varied widely from the submicron to a few centimetres, the samples were first sieved to 19 size ranges, from 212 μm to 4750 μm . The amount of sample used for the sieving was 737 g for the bottom ash and about 200 g for the rest of ash samples. Mass loss during sieving was less than 1% of the initial mass. Particles smaller than 850 μm were analysed by a Malvern instrument (Mastersizer S). This used low angle laser light scattering, detecting particles by a number of photosensitive silicon detectors. It provided two methods of analysis: a polydispersed-range model (0.5–850 μm) and a compressed-range model (0.5–212 μm) with better accuracy. The results with the polydispersed-range model had a good agreement with those from sieving tests for the 212–850 μm range and the compressed-range model.

The analysis for morphology and mineralogy was completed using a SEM (Scanning Electron Microscopy) and an EDS (Energy Dispersive X-ray Spectrometer) at the Sorby Centre, University of Sheffield. The work was divided into two parts: initially, the samples were coated with gold and analysed by a Camscan Mark II – Link system SEM and subsequently, the samples were mounted in epoxy resin and then the cross-sections were diamond-polished and coated with carbon for SEM–EDS using an attached Link Analytical EXL energy dispersive spectrometer. It identified elements heavier than Na with a detection limit of approximately 0.1%. The carbon content in the ash was analysed according to British Standard 1016 Part 6 [19]. Elemental analysis was carried out using a Spectro Genesis inductively coupled plasma spectrometer. The acid solvent used in digestion was a 3:1 ratio mixture of HNO_3 and HCl.

3. Results and discussion

3.1. Particle size distribution

Fig. 2 shows the cumulative particle size distribution for four ash samples. The fabric filter ash had the smallest particles sizes, although both the heat exchanger ash and the economiser ash also had particles sizes of generally less than 1000 μm (1 mm). The bottom ash was a heterogeneous mixture of coarse black dust and larger slag solids. Around 57% of the bottom ash was larger than

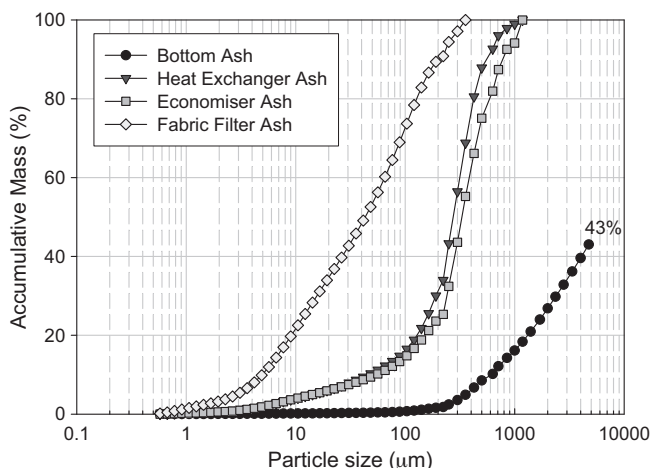


Fig. 2. Accumulative particle size distribution of the ash samples.

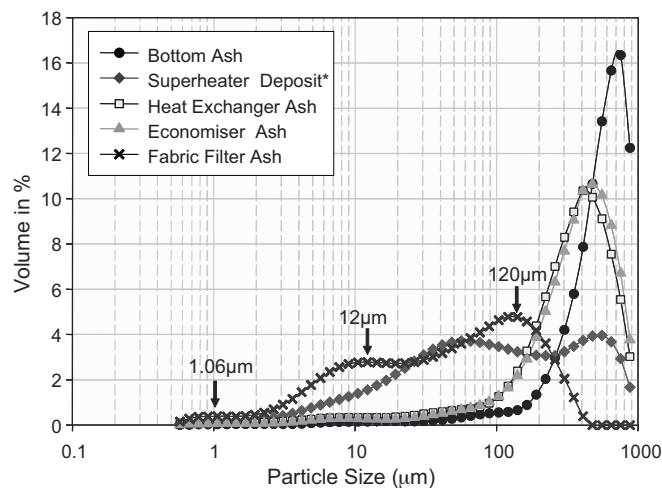


Fig. 3. Size distribution for particles smaller than 850 μm . *As collected which includes fragments from large agglomerates.

4750 μm (4.7 mm). When compared to data from Spanish incinerators reported in the literature, the bottom ash in this study had significantly fewer fine particles [10]. The particle size distribution varies between plants, depending on the MSW feed composition, particle mixing by moving grates and the subsequent treatment of the bottom ash. Furthermore, representative sampling of bottom ash is also notoriously difficult [12].

The superheater deposits were yellowish-brown in colour and due to their hard nature, moderate physical force was required to break them. It should be noted that this deposit was originally a large agglomerate on the superheater surface, but the sample consisted of both agglomerated particles and disintegrated fragments. The vibration during sieving might have further broken up the particles. The results, however, divulged that pieces larger than 4750 μm accounted for 31.1%. Fig. 3 shows the results from the Malvern instrument for particles less than 850 μm in all the ash samples. It suggests that the superheater deposits contained a greater fraction of fine particles than the heat exchanger and economiser ashes. This was related to the mechanism of deposit formation: the sticky surface of the deposit (created by the condensation of alkali metal compounds) can trap fine particles better due to their large surface area-to-mass ratio. The heat exchanger and economiser ashes, by comparison, consisted mainly of coarse (50–1000 μm) flyash entrained in the flue gas. Although the heat exchanger ash was much darker than the economiser ash, over 90% of both samples were particles smaller than 850 μm (Fig. 2) and had a peak at around 500 μm (Fig. 3). The volume-averaged diameters of the two ashes were 344.1 μm and 366.1 μm , respectively. The difference in particle shape will be discussed later with the SEM images.

The fabric filter ash, having light grey grains, combined the flyash and the material from the injected sorbents. All the particles were smaller than 350 μm and the volume-averaged particle size was 75.0 μm . From the particle size distribution of the fabric filter ash, in Fig. 3, it emerged that this type of ash was tri-modal, with a tiny peak at 1 μm , and larger peaks at 12 μm and 120 μm . Although the latter peak was for coarse flyash, hydrated lime – which accounted for 19% of the fabric filter ash by weight – also contributed to this peak, as the grain size of commercial hydrated lime is less than 125 μm . The grain size of commercial activated carbon is typically smaller than 45 μm , but the weight fraction of activated carbon in the flyash was less than 0.5%. The peak at 12 μm was for coagulated fine particles. The volume fraction at the 1 μm peak was 0.38%. In terms of particle number fractions, however, 82%

Table 1
Results of the full elemental analysis for the various combustion residues.

Bottom Ash	Superheater deposit	Heat exchanger ash	Economiser ash	Fabric filter ash	
Unburned carbon (%)	3.95	2.00	1.72	2.32	4.45
Dioxin (I-TEQ ng/g) ^a	0.06	0.07	0.08	0.12	1.62
Elements (mg/kg)					
Ag	2.1	5.7	6.6	3.9	28.4
Al	31,000	22,200	28,800	40,800	24,000
As	3.8	25.7	7.1	3.3	27.5
Ba	639	299	704	1043	477
Ca	81,320	148,300	107,600	102,100	225,000
Cd	3.7	19.8	25.6	6.25	127
Co	14.1	14.3	14.7	17.1	13.2
Cr	74.5	174	115	100	86.2
Cu	1459	713	436	1440	438
Fe	104,000	8500	18,800	17,300	6400
K	4820	17,200	17,200	10,420	23,300
Mg	7130	9790	8680	9290	6710
Mn	753	561	689	656	468
Mo	8.1	15.2	16.2	14.0	15.9
Na	5535	14,460	10,330	9600	15,250
Ni	73	41.7	52.5	102	41.1
P	4050	7550	5500	7000	3950
Pb	999	144	587	182	2060
S	5050	71,000	7200	7900	26,000
Sb	23.6	110	68.5	42.5	233
Sn	158	244	227	112	504
Sr	182.9	196.0	199.7	219.9	262
Ti	2190	2680	2430	3360	2000
Tl	<0.1	<0.1	<0.1	<0.1	1
V	51.7	41.1	57.3	83.5	59.4
Zn	2770	7850	3020	1710	6370

^a Gan et al. [20].

of fabric filter ash was submicron, which makes it difficult to capture and remove these particles from the flue gas stream. This was common for the other ash samples analysed by the Malvern instrument; 78% of the bottom ash and around 80% for the rest of the combustion residue samples were found to be submicron in terms of particle numbers. The PM₁₀ content – particulates smaller than 10 µm – for the samples was 3.3% by volume for the heat exchanger ash, 2.4% for the economiser ash and 22.1% for the fabric filter ash.

3.2. Elemental analysis

Table 1 lists the unburned carbon contents (average of three tests), dioxin concentrations and trace element concentrations (average of two tests) in the ash samples. The unburned carbon content in the bottom ash was 3.95%, which is evidence of good combustion efficiencies. The unburned carbon contents for the superheater deposit, heat exchanger and economiser ashes were all around 2%. The carbon content increased to 4.45% in the fabric filter ash mainly due to the activated carbon injection and adsorbed organic micropollutants. The main inorganic elements in the ash samples were iron, calcium and aluminium, as well as silicon, which was not analysed here. These elements have high boiling points and are thus not volatile in the relatively low temperatures of the combustion chamber; these consequently form the matrix of flyash [21]. The concentrations of magnesium, sodium, potassium, sulphur, phosphorus, titanium and zinc were also significant (2000+ ppm).

The comparison of the elemental compositions between the ash samples established two distinct behaviours of trace elements, depending on their volatilities. This has also been observed by others [21,22]. Non- and less volatile elements, such as calcium, aluminium, magnesium, titanium, nickel and chromium among others, were fairly equally distributed in all the ash samples, as they were transported by the entrainment of particles in the gas flow from the waste bed. Oxides of these, particularly aluminium, magnesium and titanium, which are highly stable, were the likely

form of these metals in the bottom ash [21,23]. Considering that the bottom ash accounted for about 85% of the total ash, most of these non- or less volatile elements remained in the bottom ash. In the case of iron, which is also non-volatile, the concentration in the bottom ash was significantly higher than in the flyash, probably in the form of stable iron oxides [23]. It suggested that certain waste materials made of steel were not bound to the organic compounds but were present separately. Copper behaved similarly to iron, although this metal did have an evaporation route, through the formation of CuCl₂ (boiling point 993 °C). Calcium was the most abundant element in all the residues except the bottom ash. Its concentration in the fabric filter ash was further increased to over 24% due to the lime injection during flue gas cleaning.

The volatile elements, which were transferred by evaporation, were found to be enriched in the fabric filter ash, but their behaviour in the other samples were different [22]. These included antimony, cadmium, zinc and sulphur, which volatilised during combustion and were later able to condense on flyash particles in cooler regions of the WTE facility [21]. Antimony and cadmium were only significantly enriched in the fabric filter ash and depleted in the rest of the samples, whereas most other volatile elements still had a significant concentration in the bottom ash. The volatile elements listed above, in addition to copper, gallium, lead, zinc and selenium are not often found in significant quantities the bottom ash however [21]. Cadmium is frequently enriched in flyash particles due to the high volatility of this element; chlorides of both cadmium and lead (as CdCl₂ and PbCl/PbCl₂/PbCl₄) can also easily be volatilised at temperatures well below 400 °C, whereas the major gas species would be elemental at and above 1000 °C [22–24].

Alkali metals, like sodium and potassium, were depleted in the bottom ash and enriched in all the other ash samples. Their compounds, including hydroxides and chlorides, vaporised in the waste bed and stayed in the gas phase in the superheater region. These may have later condensed on the cooler superheater surfaces and could thus enhance the deposition of other flyash particles. Sulphur and zinc were also enriched in the superheater deposit, although

Table 2
Summary of particles and metal emissions per 1 ton of input waste into the incineration plant.

Ash	Bottom Ash	Superheater Deposit	Heat Exchanger Ash	Fabric Filter Ash	Flue Gas Particles
Weight fraction of total ash	85.3%			14.7%	
Typical particle size	>1000 μm	Agglomerates	1-1000 μm	0.1-300 μm	<1 μm
Enriched elements	Fe, Cu	Cl, S, K, Na, Zn, Sb	K, Na	All volatile metals, dioxins	
Fe	28.6 kg (99%)			0.3 kg (1%)	
Al	8.5 kg (88%)			1.1 kg (12%)	
Cu	0.4 kg (95%)			0.02 kg (5%)	< 0.067 g ^a
S	1.39 kg (53%)			1.22 kg (47%)	< 33.3 g ^a as SO
K	1.3 kg (55%)			1.1 kg (45%)	
Cd	1 g (15%)			6 g (85%)	0.041 g ^a
Pb	275 g (74%)			97 g (26%)	0.869 g ^a
Zn	761 g (72%)			299 g (28%)	
As	1 g (44%)			1 g (56%)	0.095 g ^a
Sb	6 g (37%)			11 g (63%)	
Sn	44 g (65%)			24 g (35%)	
Cr	20 g (83%)			4 g (17%)	<0.067 g ^a

^a From annual emission data of the plant.

the weight fraction of the superheater deposit in the total ash was negligible. Sulphur was found to be specifically concentrated in the superheater deposits, presumably due to sorption of SO₂ and the condensation of volatilised species, such as metal sulphates, during the prolonged exposure of the deposit to the combustion gas. Sulphates condense at relatively high temperatures compared to chlorides and are predicted to become more thermodynamically favoured as temperatures decrease – essentially delaying volatilisation at low temperatures [4,25]. These sulphates can be particularly stable at temperatures lower than 800 °C [23]. This behaviour also suggests that the elemental composition of the deposits in the superheater and heat exchangers will vary depending on the gas temperature.

Overall, the flyash from the heat exchanger and economiser had similar compositions to the bottom ash, except for the enrichment of alkali metals and the depletion of iron and copper. The superheater deposit had much higher concentrations of sulphur and zinc but similar levels of alkali metals to the heat exchanger and economiser ashes. The significant quantities of chlorine in the initial material and in the superheater deposit may have aided the volatilisation of the zinc present [23]. The fabric filter ash was enriched with various volatile metals, including among others lead, cadmium, potassium, zinc and antimony, as the temperature in the furnace (up to 1000 °C) was greater than the volatilisation temperatures of these elements (e.g. around 850 °C for antimony) [23].

Table 2 summarises the amount and weight fraction of each element in the bottom and fabric filter ashes for 1 ton of input waste. The partitioning of elements was calculated from the weight fraction of bottom ash (85.3%) and fabric filter ash (14.7%) in the total, ignoring the somewhat minor contributions of the other ash residues. Data for the flue gas acquired from the UK pollution inventory is also listed in Table 2. The mass fraction of volatile

metals in the fabric filter ash ranged from 25 to 85%. Cadmium had the highest mass fraction (85%) for the fabric filter ash, along with antimony (63%) and arsenic (56%), whereas iron and copper had the highest mass fraction in the bottom ash (99% and 95% respectively), for the reasons considered above. The partitioning for most elements was in the same range as reported in the study by Jung et al. [16], although the concentration of lead in the fabric filter ash here (26%) was slightly lower than in that study (32–57%), attributable to the differences in the MSW feed composition and operating conditions. The fractions of potassium and sulphur in the fabric filter ash in this study were about 45%. The amount of iron in the bottom ash was 28.6 kg/ton-waste (99%), of which a large proportion can be recovered by magnetic separation. The amount of ferrous metals the plant recovered was 19.9 kg/ton-waste.

3.3. Particle morphology and mineralogy

Fig. 4 shows SEM images of the superheater deposits, which were agglomerates of irregular-shaped flyash particles (cube-like, elongated, needled and plate-like particles), with some spherical/polygon particles. These were dissimilar to the flyash particles from the combustion of both coal and wood, which are mainly composed of spherical particles and long, thin, irregularly shaped particles respectively [7,26,27]. This was thought to be due to several factors, including the variable components of MSW, greater ash entrainment and the relatively low operating temperature in the incinerator. The spherical particles, identified in Fig. 4a, had typical sizes of 10–60 μm and were formed under high temperatures; these appear as smooth spheres of molten material, while those formed under lower temperatures had irregular shapes, such as those in Fig. 4b [28]. The surfaces of the polygon particles (Fig. 4c)

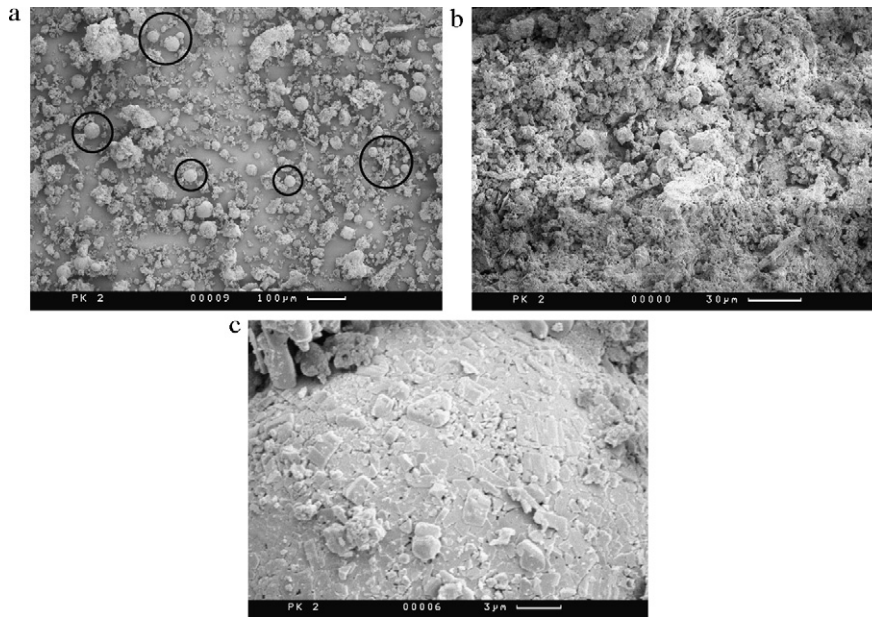


Fig. 4. SEM images of superheater deposits: (a) individual particles; (b) the surface of a large deposit; and (c) the surface of a rounded particle.

were sintered agglomerates of about 1 μm and these fine particles were attached to the surface of larger rounded/spherical particles.

Fig. 5 shows the SEM–EDS results for a superheater deposit. Fig. 5a shows the cross-section of a large spherical (broken hal-

low) particle, with a diameter of 200 μm. This is not monolithic, as partially fused particles have enclosed other particles and the voids inside, while transforming into a sphere due to heat and surface tension. The EDS spectra of the surface and the interior of this particle were very similar, both having calcium and sil-

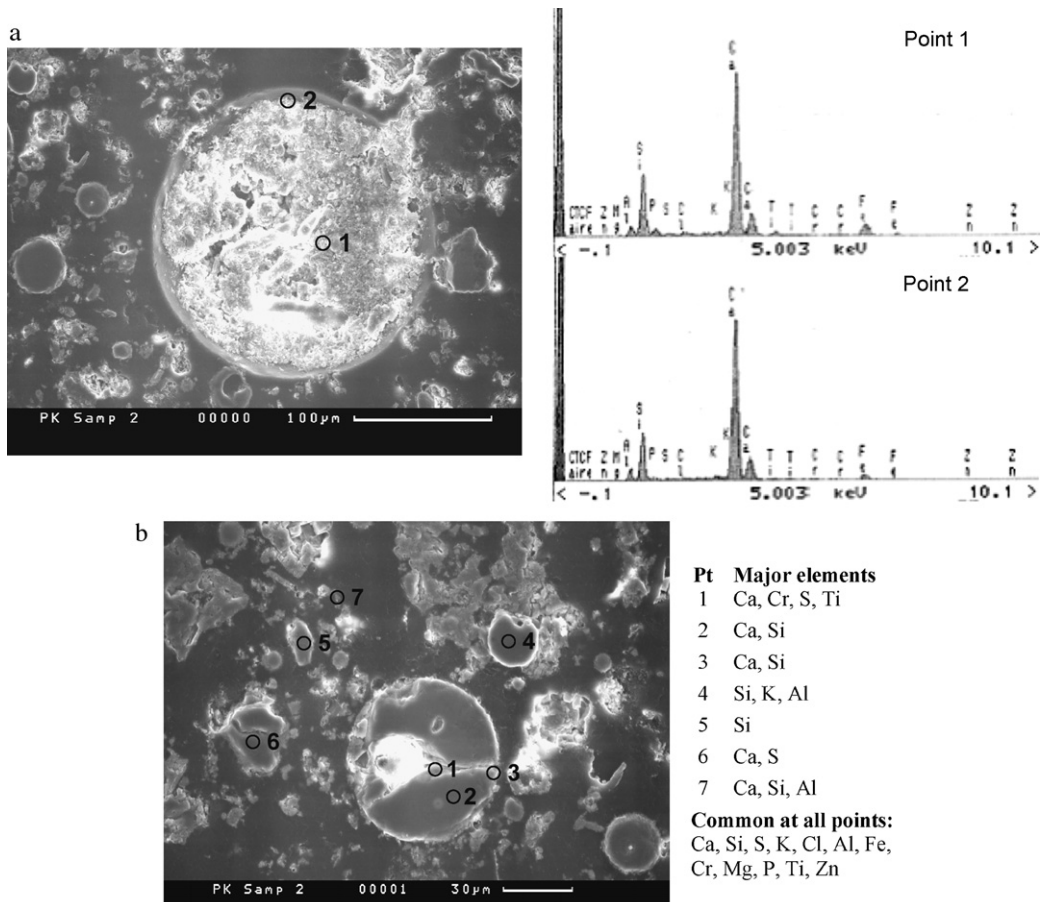


Fig. 5. SEM–EDS analysis for a superheater deposit.

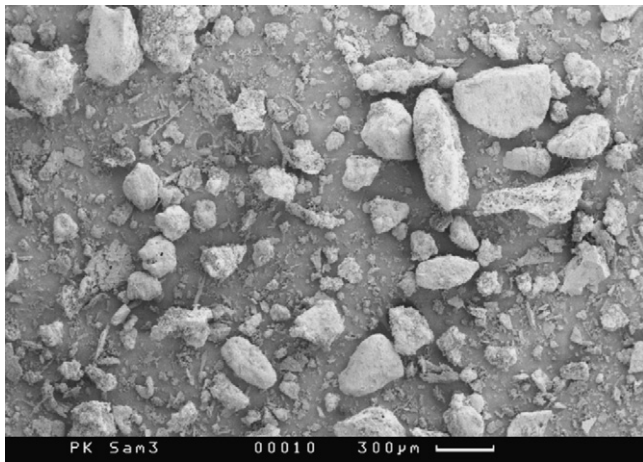


Fig. 6. SEM image of heat exchanger ash.

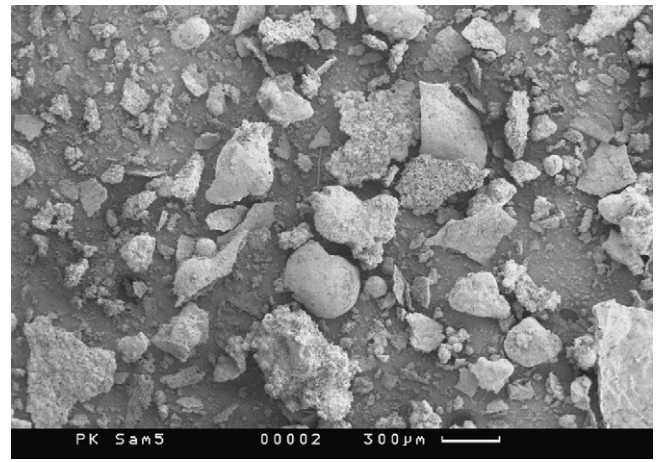


Fig. 7. SEM image of economiser ash.

icon as major elements, as shown, which is a typical elemental composition of combustion residues. Potassium, chlorine, sulphur, aluminium, iron, chromium, magnesium, phosphorus, titanium and zinc were also found at all points. In Fig. 5b, the small spheres had smooth cross-sections due to complete fusion. All the elements that appeared in Fig. 5a were also found here (typical ash-forming elements), but the major elements varied between points. The main components of the particles were Ca–Si–Al and/or Si–K–Al. Ca–S were also the main elements found at some points, which was expected mainly to be CaSO_4 . Again, no clear difference was found between the surface and the interior of the spherical particles shown in Fig. 5b.

Figs. 6 and 7 are SEM images of heat exchanger deposits and the economiser flyash. A variety of particles, sized from the submicron to over $300\ \mu\text{m}$, were seen in both samples. Although their particle size distributions were similar, as demonstrated in Figs. 2 and 3, the economiser ash contained more plate-like particles. As the drag force on such particles is higher than on round particles, they can be carried much further. The SEM–EDS results for the economiser ash, shown in Fig. 8, revealed a very simple elemental composition compared to the superheater deposit shown in Fig. 5b, which is typical of ash residues from combustion. The main elements in the large ash particles were Ca–Si–Al and Si–K–Al, likely to be present as amorphous silicates.

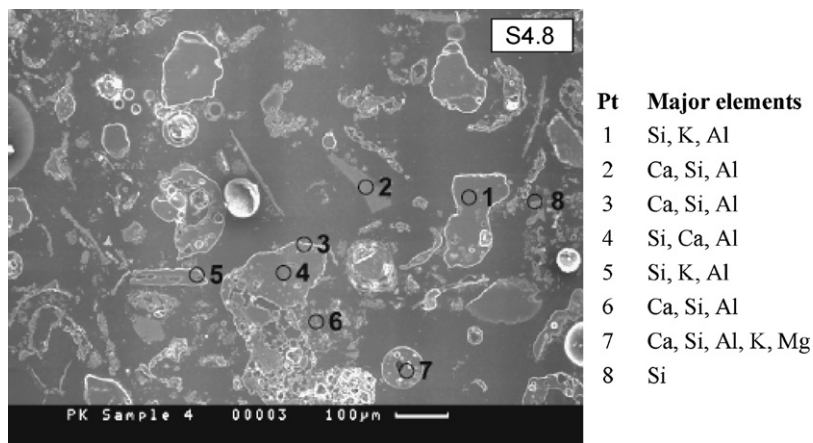


Fig. 8. SEM–EDS analysis for economiser ash.

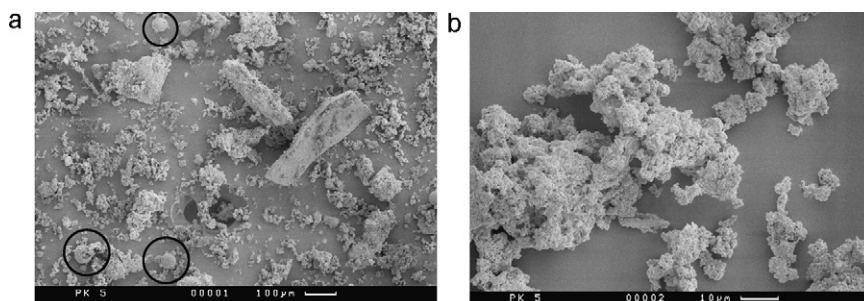


Fig. 9. SEM images of fabric filter ash.

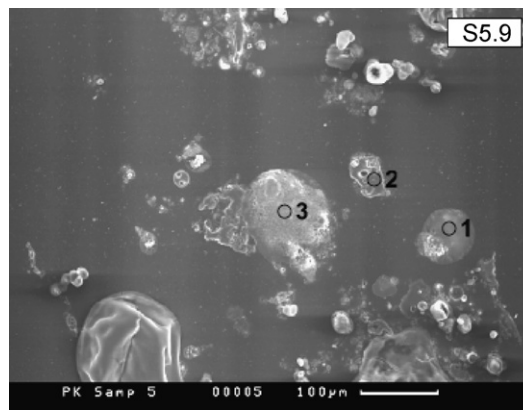


Fig. 10. SEM–EDS analysis for fabric filter ash.

Pt Major elements

- | | |
|---|---------------------------|
| 1 | Cl, Ca, K, Fe, Si, Al, Mg |
| 2 | Ca, P, Si, K, Ti, Zn |
| 3 | Cl, Ca, K |

The fabric filter ash contained significantly fewer large particles (over 100 μm) and a high proportion of porous, smaller and irregularly shaped particles, as revealed in Fig. 9a. Several spherical particles around 50 μm were also identified (as shown), of which some were lime, from the lime injection that occurred just prior to the flue gas entering the fabric filter. There were both spherical and plate-like particles present here, as found in previous samples. Fig. 9b shows the agglomeration of finer flyash particles, while Fig. 10 outlines the results of the SEM–EDS analysis of the fabric filter ash. This identified that potassium was present, which along with other alkali metals can form ‘sticky’ alkali metal compounds, such as sulphates; this can initiate bonding from the condensing of these vapours on cooler surfaces, which can in turn aid the accumulation of particles through impaction. Both potassium and sodium were found in high concentrations in the flyash collected in the fabric filter. This figure also reveals that lime particles were able to adsorb chlorine (at Points 1 and 3). Lime contains a few impurities, such as Al_2O_3 , Fe_2O_4 and MgO , which were detected together as trace [29]. The SEM–EDS for Point 2 was on a typical, large ash particle. These results compare well to those of Table 1 for the elemental analysis for this ash sample; calcium and potassium in particular were generally present in high concentrations.

3.4. Addressing the issues posed by metals in particulate matter and applications of the research

As shown by the above results, many of the more volatile elements, such as the heavy metals, like cadmium and antimony, were enriched in the flyash and 82% of this ash was submicron. These smallest particles are the most easily respirable and have been shown to contain the highest concentrations of toxic metals; these can have significant health impacts, especially on the respiratory and cardiovascular systems, if inhaled. This is further evidence that highly efficient flue gas cleaning is required to ensure that these smallest particles are removed before the gases are released to the atmosphere. As the temperature rises up to 1000 $^\circ\text{C}$ in the combustion chamber of the WTE incineration facility, many of these elements in the waste stream are able to volatilise, thus cooling the gases and removing the entrained particles, as shown Fig. 1 (in the boiler, superheater, heat exchanger, economiser and the fabric filters), are essential. As stated in Section 1, it is these smallest, submicron particles that are most difficult to remove from the gas flow and particulate removal technologies, such as cyclones, scrubbers, electrostatic precipitators and fabric filters are least efficient at capturing submicron particles; the collection mechanism is often by particle inertia, which is a function of particle mass.

The behaviour of trace metals associated with the ash generated from waste incineration and the partitioning of elements within

the different ash locations is thus clearly an area warranting further research. Any additional knowledge of this partitioning and enrichment of the more volatile elements in the smaller fractions of the flyash, for example, are vital for advancements to take place. Knowing where specific elements are likely to be concentrated can enhance our understanding of the behaviour of these metals under different conditions, predominantly in terms of the deposition of ash on superheaters and heat exchangers, and can in turn aid the development of flue gas cleaning methods and the handling of these residues. Furthermore, this may also assist the recovery of some of these heavy and/or toxic metals to ease their disposal, provide the option of additional treatments or processing techniques and even help identify potential uses for the solid residues from incineration at WTE plants.

4. Conclusions

Ash samples from various locations at a waste-to-energy mass-burn incineration plant were characterised through a range of techniques analysing for unburned carbon, particle size, surface morphology and elemental composition. These tests clearly identified the partitioning of elements in the different combustion residues. While volatile metals were depleted in the bottom ash by the high temperatures achieved during combustion (1000+ $^\circ\text{C}$), iron and copper were enriched here. Other non-volatile elements were distributed equally in all locations, transported by particle entrainment. Deposits on the superheater contained large amounts of sulphur and some volatile metals, such as zinc, but were otherwise similar in composition to those found on the heat exchanger and economiser. Deposits from the heat exchanger and fabric filter revealed increased alkali metal concentrations. Further analysis of the flyash from the fabric filter identified that 82% of particles were in the submicron range and thus respirable. Volatile elements appeared to be concentrated here, such as cadmium (85% of the total), antimony and arsenic (both over 50% of the total), which were transferred by evaporation. Lead and zinc, however, were not found in significant concentrations, despite their high volatility, which agreed reasonably well with the findings from other studies.

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References

- [1] L. Morawska, J. Zhang, Combustion sources of particles. 1. Health relevance and source signatures, *Chemosphere* 49 (2002) 1045–1058.
- [2] J. Zhang, L. Morawska, Combustion sources of particles. 2. Emission factors and measurement methods, *Chemosphere* 49 (2002) 1059–1074.
- [3] G. Couch, *Understanding Slagging and Fouling in PF Combustion*, IEA Coal Research, London, 1994.
- [4] W.P. Linak, J.O.L. Wendt, Toxic metal emissions from incineration – mechanisms and control, *Prog. Energy Combust. Sci.* 19 (1993) 145–185.
- [5] M. Jöller, T. Brunner, I. Obernberger, Modeling of aerosol formation during biomass combustion in grate furnaces and comparison with measurements, *Energy Fuels* 19 (2005) 311–323.
- [6] R. Davison, F.S. Natusch, J.R. Wallace, Trace elements in fly ash – dependence of concentration on particle size, *Environ. Sci. Technol.* 8 (1974) 1107–1113.
- [7] Y.C. Ahn, J.K. Lee, Physical, chemical, and electrical analysis of aerosol particles generated from industrial plants, *J. Aerosol. Sci.* 37 (2006) 187–202.
- [8] I. Obernberger, T. Brunner, Fly ash and aerosol formation in biomass combustion processes – an introduction, in: I. Obernberger, T. Brunner (Eds.), *Aerosol in Biomass Combustion: Formation, Characterisation, Behaviour, Analysis, Emissions, Health Effects*, vol. 6, Medienfabrik Graz, Steiermarkische Landesdruckerei GmbH, 2005, pp. 1–11.
- [9] C.C. Wiles, Municipal solid waste combustion ash: state-of-the-knowledge, *J. Hazard. Mater.* 47 (1996) 325–344.
- [10] I. Maria, V. Enric, Q. Xavier, B. Marilda, L. Angel, P. Felicia, Use of bottom ash from municipal solid waste incineration as a road material, in: 2001 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, 2001.
- [11] C. Ferreira, A. Ribeiro, L. Ottosen, Possible applications for municipal solid waste fly ash, *J. Hazard. Mater.* 96 (2003) 201–216.
- [12] IAWG, International Ash Working Group, A.J. Chandler, T.T. Eighmy, J. Hartlen, O. Hjelmar, D.S. Kosson, S.E. Sawell, H.A. van der Sloot, J. Vehlow, *Municipal Solid Waste Incinerator Residues Studies Environ. Sci.*, vol. 67, Elsevier Science, Amsterdam, 1997.
- [13] S.L. Law, G.E. Gordon, Source of metals in municipal incinerator emissions, *Environ. Sci. Technol.* 13 (1979) 432–437.
- [14] K. Nakamura, S. Kinoshita, H. Takatsuki, The origin and behavior of lead, cadmium and antimony in MSW incinerator, *Waste Manage.* 16 (1996) 509–517.
- [15] D.O. Reimann, Heavy metals in domestic refuse and their distribution in incinerator residues, *Waste Manage. Res.* 7 (1989) 57–62.
- [16] C.H. Jung, T. Matsutoa, N. Tanakaa, T. Okadaa, Metal distribution in incineration residues of municipal solid waste (MSW) in Japan, *Waste Manage.* 24 (2004) 381–391.
- [17] A. Wadge, M. Hutton, P.J. Peterson, The concentrations and particle size relationships of selected trace elements in fly ashes from U.K. coal-fired power plants and a refuse incinerator, *Sci. Total Environ.* 54 (1986) 13–27.
- [18] M.B. Chang, C.K. Huang, H.T. Wu, J.J. Lin, S.H. Chang, Characteristics of heavy metals on particles with different sizes from municipal solid waste incineration, *J. Hazard. Mater. A* 79 (2000) 229–239.
- [19] British Standards Institution, *British Standard 1016: Part 6: 1977, Methods for Analysis and Testing of Coal and Coke, Ultimate Analysis of Coal*, British Standards Institution, London, 1977.
- [20] S. Gan, Y.R. Goh, P.J. Clarkson, A. Parracho, V. Nasserzadeh, J. Swithenbank, Formation and elimination of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from municipal solid waste incinerators, *Combust. Sci. Technol.* 175 (2003) 103–124.
- [21] M.A. Fernández, L. Martínez, M. Segarra, J.C. García, F. Espiell, Behavior of heavy metals in the combustion gases of urban waste incinerators, *Environ. Sci. Technol.* 26 (1992) 1040–1047.
- [22] H. Belevi, H. Moench, Factors determining the element behavior in municipal solid waste incinerators. 1. Field studies, *Environ. Sci. Technol.* 34 (2000) 2501–2506.
- [23] D. Verhulst, A. Buekens, P.J. Spencer, G. Eriksson, Thermodynamic behavior of metal chlorides and sulfates under the conditions of incineration furnaces, *Environ. Sci. Technol.* 30 (1996) 50–56.
- [24] M.B. Chang, S.-R. Ku, Fates and partitioning of heavy metals in municipal solid waste incineration process, *Toxicol. Environ. Chem.* 67 (1998) 161–169.
- [25] D.J. Poole, Identification and control of metal pollutant spikes in municipal solid waste incinerators, PhD Thesis. University of Sheffield, Sheffield, UK, 2005.
- [26] S. Wang, L. Baxter, F. Fonseca, Biomass fly ash in concrete: SEM, EDX and ESEM analysis, *Fuel* 87 (2008) 372–379.
- [27] N. Saikia, S. Kato, T. Kojima, Compositions and leaching behaviours of combustion residues, *Fuel* 85 (2006) 264–271.
- [28] S. Jiménez, J. Ballester, Influence of operating conditions and the role of sulfur in the formation of aerosols from biomass combustion, *Combust. Flame* 140 (2005) 346–358.
- [29] J. Fernández, J. Renedo, A. Garea, J. Viguri, J.A. Irabien, Preparation and characterization of fly ash/hydrated lime sorbents for SO₂ removal, *Powder Technol.* 94 (1997) 133–139.