Chemical characteristics of ash formed from the combustion of shoe manufacturing waste in a 2.5 MW_{th} circulating fluidized bed combustor

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Abstract: The ash formation behaviour and associated compositional characteristics of the combustion of shoe manufacturing waste (SMW) in a 2.5MW$_{th}$ pilot-scale circulating fluidized bed combustor (CFBC) were investigated to better understand the combustion behaviour and to find effective management strategy for the disposal of the ash streams produced. The compositional characterisations for the ashes produced from the pilot demonstrations showed the presence of a variety of trace heavy metals both in the fly ash and bottom ash. A pronounced uneven partitioning behaviour was observed on the distribution of these heavy metals between the fly ash and bottom ash, and it was found that all the heavy metals except chromium were preferentially enriched in the fly ash, with the contents of lead and cadmium in the fly ash being over 11 and 6 times higher than in the bottom ash. Leaching tests demonstrated that the concentrations of most of the aforementioned metals present in the leachates from the fly ash and bottom ash could meet the permissible limits for landfill disposal but with lead as an exception with its concentration in the fly ash leachates being over 2 times higher than the limit. The total PCDD and PCDF contents both in the fly ash and bottom ash were also much below the legal limit. To further understand the ash behaviour, the slagging and fouling tendency during SMW combustion in the CFBC was examined by use of the characterisation of the ash mineralogy and the results indicated that the SMW ash likely had low tendencies for slagging and fouling. The best two valorization routes for the SMW bottom ash and fly ash were recommended, one being to use them to produce Colloidal Silica Medium to Obtain Safe inert (COSMOS) filler and the other being to use them as the raw materials in the cement industry.

Key words: shoe manufacturing waste; ash; heavy metals; PCDD and PCDF; Ash fusion temperature

Statement of Novelty

Shoe manufacturing waste (SMW), which usually consists of hard-to-separate rubbers, fabrics, and cellulose-based and wood materials at varying quantities, is usually classified as low-value organic waste with variable high ash and moisture content. Our previous research had demonstrated the feasibility of energy recovery from SMW using CFB combustion technology. This study focused on ash related issues during the combustion of SMW in a 2.5 MW_{th} circulating fluidized bed combustor. The characteristics of ashes determine their final application (e.g. deposal in a landfill, construction material， adsorbent or fertilizer). What’s more, the waste ash characteristics also influence ash sintering, agglomeration and slagging on combustion and heat exchange equipment. Therefore, a comprehensive understanding of characteristics of ashes produced during incineration process is necessary. This study aims to find effective management strategy for disposal of the ash streams produced. The compositional characterizations for the ash samples produced from the pilot demonstrations showed the presence of a variety of trace heavy metals both in the fly ash and bottom ash samples. A pronounced uneven partitioning behaviour was observed on the distribution of these heavy metals between the fly ash and bottom ash samples. The results of this study can be used to provide more useful information for the treatment and utilization of SMW ash and guide the operation of the SMW combustion plant to reduce the influences of ash sintering, agglomeration and slagging.

1. Introduction

The production of shoe manufacturing waste has emerged over recent years as an ever growing new class of solid industrial waste stream produced in large quantities, with the global market for footwear projected to reach US$430 billion by 2024 (http://www.strategyr.com/MarketResearch/Footwear_Market_Trends.asp) and the number of shoes produced to reach 40 billion pairs by 2025 led mainly by Asia-Pacific countries (http://www.indexbox.co.uk/store/world-footwear-market-report-analysis-and-forecast-to-2020), including China in particular where the growth in footwear industry increased by 10 times in the past 10 years [1, 2, 3]. Consequently, the disposal of shoe manufacturing waste (SMW) is of increasing environmental concern.

SMW, which usually consists of hard-to-separate rubbers, fabrics, and cellulose-based and wood materials at varying quantities [4-7], is usually classified as low-value organic waste with variable high ash and moisture content [5, 6] and is often disposed of in landfill [1, 8]. However, given the increasing environmental concerns of landfill and severe shortage of suitable landfill sites, finding alternative solid waste management strategies with potential socioeconomic benefits has received ever growing attention. Waste-to-energy conversion has been regarded as being the most techno-economically viable option as it can dramatically reduce the waste volume while facilitate the recovery of energy contained in the combustible organic matter [1, 9-12]. Circulating Fluidized bed (CFB) combustion is considered to be one of the best available technologies for waste incineration due to its great inherent fuel flexibility and high combustion efficiency [13] in addition to other advantages, such as the relatively low combustion temperatures and hence lower emissions levels of toxic particulate matter and gaseous pollutants of low NO_x and CO etc. [14-16].

However, the waste-to-energy conversion of carbonaceous waste streams via combustion or incineration is never free of operational issues and environmental impacts and has to be subjected to a range of environmental legislations, which could be even more stringent than those for the combustion of conventional fuels [17]. There have been numerous investigations on the combustion behaviour and related environmental performance of various solid waste-derived carbonaceous fuels, and one of the most researched areas has been the fuel-induced operational problems and issues of waste combustion ash disposal, such as the ash formation and related slagging and fouling behaviour [19-26], the partitioning of heavy metals [27-32] and associated leaching behaviours of the ashes from the combustion of different wastes [15, 17, 19 , 26, 33-35], and the formation and entrapment of persistent organic pollutants (POP) in the ash streams [13, 17, 18, 36-39]. During the combustion of the waste and the formation of particular matter, the organic-metallic compounds were firstly released by pyrolysis and then devolatilized. As the temperature increased, part of the alkali and alkali-earth compounds and volatile trace elements diffused out of the fuel. Some volatile compounds then begin to form submicron particles and residual fly ash through nucleation, adsorption, condensation, and chemical reaction, resulting in a series of ash-related issues such as alkali-induced slagging, silicate melt-induced slagging (ash fusion), and agglomeration, which can reduce heat exchange efficiency and boil energy utilizing efficiency [26]. As a by-product of waste incineration, the waste ash always contains some hazardous matter such as toxic heavy metals and persistent organic pollutants (POP) including dioxins [13], which can pose a serious threat to the environment and human health [17,18]. Therefore, the ash must be carefully handled and more attention must be paid to its leaching behaviour. The characteristics of the ash determine its final application (e.g. deposal in a landfill, construction material， adsorbent or fertilizer) [13, 16， 17 and 19]. The waste ash characteristics also influence ash sintering, agglomeration and slagging on combustion and heat exchange equipment [20]. Therefore, it is necessary to have a comprehensive understanding of characteristics of ashes produced by the incineration process.

All of the above-mentioned previous studies focus on municipal solids waste (MSW) and biomass waste. While SMW is a mixture of many components, which is similar to the MSW waste to some extent, the shoe manufacturing waste, however, has no incombustible component with higher low heating value, which is a big difference from the MSW waste. Some components such as composite wood materials and cellulose-based materials of SMW belong to biomass and hence SMW ash has some similarity to biomass ash containing a large amount of K and Na which tends to result in alkali-induced slagging. In addition, using chromium sulphate to turn hides into leather during tanning process results in a relatively larger amount of chromium (Cr) in the leather [40]. SMW contains many kinds of leather and hence its combustion may lead to its ash with a high content of heavy metals. However, so far, there has been no investigation on the characteristics of the ash generated from the shoe manufacturing waste incineration. The study on the characteristics of SMW ash will be useful for its environmentally sound treatment and utilization.

The aim of this study is to examine the chemical characteristics of the ash derived from the combustion of SMW in a 2.5MWth pilot-scale circulating fluidized bed combustor. Various properties of different ash samples have been investigated, such as their chemical compositions, mineral phase, ash fusion and leaching behaviours and the presence of heavy metals and PCDD (polychlorinated dibenzo-p-dioxins) and PCDF (dibenzofurans). Further, the possible ways to utilize the SMW ash were discussed based on the ash characteristics. The results of this study can be used to provide more useful information for the treatment and utilization of SMW ash and guide the operation of the SMW combustion plant to reduce the influences of ash sintering, agglomeration and slagging.

2. Material and method

2.1 Fuel properties

The SMW used in this study is a mixture with different shapes and low density, which was obtained from a shoe manufactory in Wenzhou, Zhejiang province, China. The typical materials of the SMW include thick rubbers (A), thin cotton cloth (B), leather (C), composite fabric of rubber and cloth (D), hard woven fabric (E), soft rubber (F), Elastic leather (G), wood (H), plastic (I) and composite fabric of leather and hard shell (J). Due to the same fuel being used in this study as that in our previous work [41], the analysis conducted for the individual components identified in the waste and more details about the SWM can be seen in our previous work [41].

2.2 The pilot-scale combustion facility and operating condition

Table 1 The parameters of the stable combustion state

Parameters	Description
Feed flow rate	400 kg/h
Primary air flow rate	1650 Nm^3/h
Second air flow rate	1800 Nm^3/h
Density phase temperature	About 850 °C
The bed temperature	About 900 °C
Furnace outlet temperature	About 800 °C
Bed material	The bottom ash derived from bituminous coal combustion (1-5 mm)
Experiment duration	About 4 h
O_2 in the flue gas	About 3 vol.%
CO in the flue gas	About 2290 ppm

The pilot-scale combustion facility used in this study has been described in previous literature [41-42]. It is a circling fluidized bed with a thermal input of 2.5 MW. In this study, the manufacturing waste is fed into the combustion facility from the inlet at 0.14 m above the air distributor. The primary air flow is supplied to combustor from the bottom of the bed, while the second air flow is supplied from two different locations at 3.048 m and 4.87 m above the bottom of the front and rear wall of the CFB combustor. The waste and the air are mixed and combusted in the bed while the exhaust gas flue flows out from the bed, goes through U-beam separator, upper heating surface, medium temperature cyclone, the low heat surface and bag filter, and is discharged to the atmosphere from stack. The combustion conditions under which the samples were collected from the bag filter in this study are summarised in Table 1.

2.3. Methodology for ash characterisation

An X-ray fluorescence (XRF) technique was used to investigate the chemical compositions of the fly ash and the bottom ash. X-ray diffraction (XRD) analysis was used to identify the main crystalline phases of the fly ash and bottom ash, which were selected randomly during the test. The concentration of Hg in the fly ash and the bottom ash was determined by a solid mercury analyzer (Hydra II C, Leeman, USA). The concentrations of heavy metal elements except for Hg in the fly ash and in the bottom ash were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) according to JY/T 015-1996 [43]. The carbon contents in the ash samples were measured by the loss of ignition (LOI) method [44]. The toxicity characteristic leaching procedure (TCLP) was carried out according to the Chinese national standard (GB5085.3-2007): at an ambient temperature of around 20 °C, 10 g samples of the crushed ash (<10 mm) were rotated at 30 rpm with 100 mL extraction liquid, which was a dilute solution with pH 3.20 ± 0.05 of sulfuric acid and nitric acid at a ratio of 2: 1, in a plastic bottle for 18 h [45]. PCDD and PCDF compounds in the fly ash were collected isokinetically before and after the bag filter, respectively, and were analysed by the high resolution gas chromatography (HRGC) (Thermo Trace GC) and high resolution mass spectrometry (HRMS) according to Chinese national standard method (HJ77.3-2008) [46]. Due to short experiment duration (4 h), the slagging performance was not observed in this study, therefore, the fusion temperatures of the SMW ash specifically generated in a muffle furnace at 815°C were used to predict the slagging tendency. 10 samples of the SMW were used to generate the muffle furnace ash and the obtained ash from all samples was mixed together (hereafter termed as SMW Ash-815) before the AFT analysis. The AFT analysis consisting of the initial deformation temperature (IDT), softening temperature (ST), hemispherical temperature (HT) and flow temperature (FT) was performed with the HR-5A computer ash-melting point tester based on the Chinese national standard (GB/T219-1996). Each ash cone with a specific geometry was heated at a rate of 15 °C/min up to 900 °C, and then the heating rate was changed to 5 °C/min [47]. All data obtained from the characterization analysis were those of the average values calculated from the analysis of triplicate samples.

3. Results and discussion

3.1 Chemical compositions

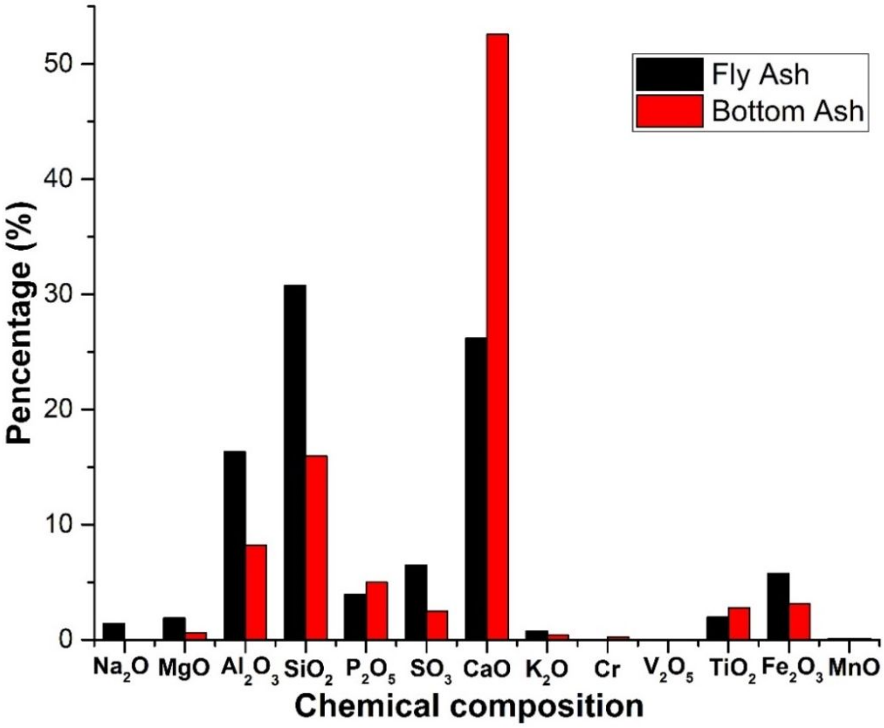

Fig.1 Chemical compositions of the fly ash and bottom ash

The chemical composition of the fly ash and bottom ash derived from SMW combustion can be seen in Fig.1. The three highest compositions in the two kinds of ash (fly ash and bottom ash) are the same: CaO, SiO_2 and Al_2O_3 (26.18%, 30.75% and 16.31% for fly ash; 52.57%, 15.96% and 8.21% for bottom ash), which agrees with the findings of other similar studies [19, 27]. The highest content in fly ash is SiO_2 while for bottom ash it is CaO. Generally, the SiO_2

in the incombustible composition with high melting point and boiling point such as ceramics and glass in the waste leads to high SiO_2 in the bottom ash. However, in this study, the SiO_2 was enriched in the fly ash, which was likely due to the organically-bound silicon in the waste being transformed to fly ash with the volatile matter release from the waste. The contents of K_2O and Na_2O in both ashes were lower than 1.5 wt%, which indicates that the chemical composition of the shoe manufacturing waste ashes was more similar to that of MSW than to that of biomass waste. In addition, these two ashes were considered unsuitable for being used as fertilizer due to the low contents of K, Na and P, which are the main nutrients needed for plant growing. Generally, a high content of Ca can result in an increase in the ash melting point, while high contents of Si and Al can decrease the ash melting point [24]. In this study, the ash melting point was influenced by both of these two factors. Therefore, the ash melting point is worth to be further studied.

A slagging index (SI) based on the fluxing and sintering oxides ratio is used to predict the ash melting point in this study. The SI was calculated as follows [22, 25]:

$$\mathrm{SI} = \frac{CaO+MgO+K_2O+Na_2O+Fe_2O_3+P_2O_5}{SiO_2+Al_2O_3+TiO_2} \qquad (1)$$

The SIs of the fly ash and bottom ash in this study were found to be 0.81 and 2.29, respectively. A SI index in the range of 0.75-2 means relatively low ash melting point leading to intensive slagging. Therefore, more attention must be paid to the potential slagging problem which may occur when this SMW is combusted in the CFB for a long period of operation.

3.2 XRD analysis

The results of the XRD analysis of two fly ashes and two bottom ashes are shown in Fig.2. The mineral phases identified in these four ashes were almost the same and the main mineralogical compounds were anhydrite, rutile, lime, pseudorutile, calcium vanadium oxide, mayenite, aluminum iron silicon, quartz, eskolaite, pigeonite and titanium oxide. The main difference between the fly ash and the bottom ash was that the peaks of SiO_2 of the bottom ash were stronger than those of the fly ash as the bottom ash contained more bed material (coal ash), which contained a larger fraction of SiO_2. Compared to the XRD analysis of the biomass bottom ash [48], the same mineralogical compounds of anhydrite and quartz were found in the biomass bottom ash and the SMW bottom/fly ash. However, other compounds identified in this study were not identified in the biomass ashes as the composition of the feedstock and the combustion conditions in this study were much different from those in the reference [48].

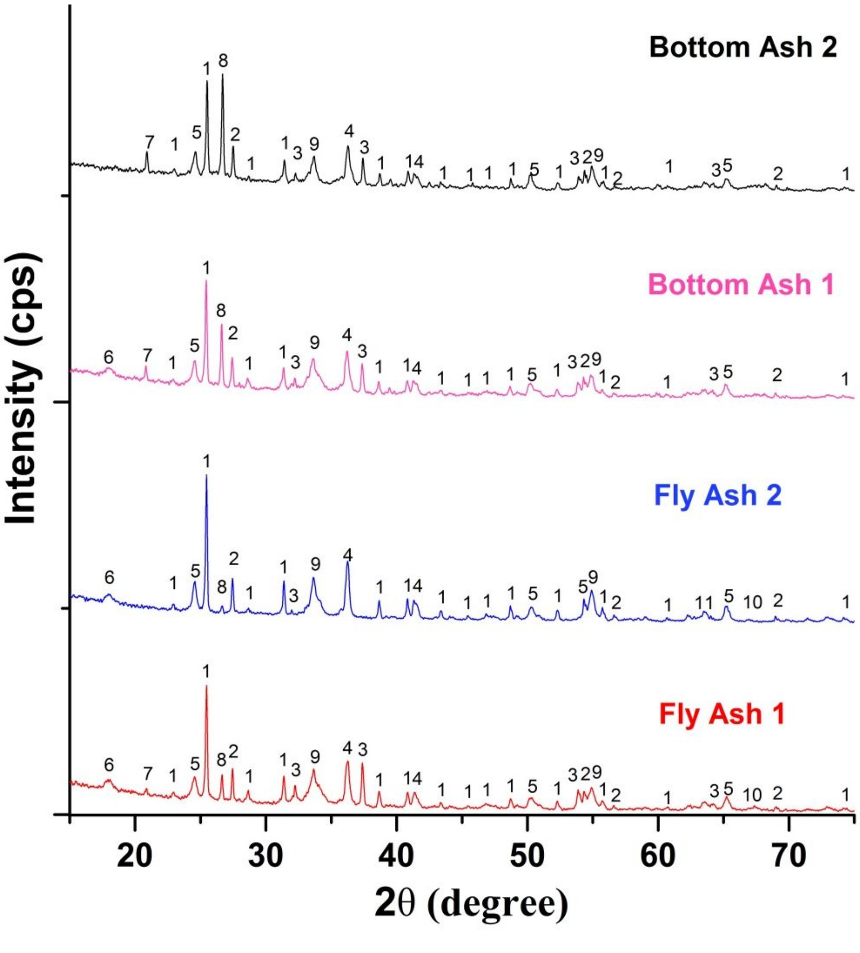

Fig. 2 XRD patterns of the bottom ashes and fly ashes.

1, Anhydrite, syn-$CaSO_4$; 2, Rutile, syn-TiO_2; 3, Lime, syn-CaO; 4, Pseudorutile-$Fe_2Ti_3O_9$; 5, Calcium Vanadium Oxide-CaV_2O_5; 6, Mayenite, syn-$Ca_{12}Al_2O_{33}$; 7, Aluminum iron silicon-Al_5FeSi; 8, Quartz, syn-SiO_2; 9, Eskolaite,syn-Cr_2O_3; 10, Pigeonite-(Fe, Mg, Ca) SiO_3; 11, Titanium Oxide-TiO

3.3 Heavy metal contents

The heavy metal contents in the ashes derived from SMW combustion are shown in Table 2. The heavy metal concentrations of the fly ash follow the following order: Zn > Ba > Cu > Pb > Cr > Ni > Cd, while for the bottom ash the order is Zn > Ba > Cu > Cr > Pb > Ni > Cd. The concentrations of As, Ag, Be, Se and Hg in both of the two ashes were below the detection limits. The heavy metal concentrations except for Cr in the fly ash were higher than those in the bottom ash. Cr was enriched in the bottom ash mainly due to the high melting and boiling points of Cr element and its compounds [28]. Some Cr might be entrained by convective transportation during the waste rapid pyrolysis and then be transformed into fly ash [29]. Among heavy metals measured in this study, Zn had the highest content with 0.356% in the fly ash and 0.169% in the bottom ash, which is similar to the composition of MSW ash [30]. Due to the high content of Zn, recovery of Zn as a second resource from these ashes may be a good choice to reuse these waste ashes. The method described by Schlumberger et al [31] can support this sustainable and economically viable treatment and utilization of these ashes. This method not only can produce high purity zinc, but also can reduce the concentration of the toxic heavy metals in the ash residues leading to these residues meeting the solid waste landfilling standards [32].

Table 2 heavy metal contents in the ashes derived from shoe manufacturing waste combustion

Heavy metal	Unit	Fly ash	Bottom ash
Zn	%	0.356	0.169
Pb	mg/kg	176.57	15.3
Cd	mg/kg	3.45	0.55
Cr	mg/kg	46.1	59.4
As	mg/kg	ND	ND
Ni	mg/kg	40.8	7.96
Ba	mg/kg	557	414
Cu	mg/kg	195	126
Ag	mg/kg	ND	ND
Be	mg/kg	ND	ND
Se	mg/kg	ND	ND
Hg	mg/kg	ND	ND

3.4 TCLP

The concentrations of different heavy metals in the leachates from the fly ash and bottom ash are described in Table 3. In the fly ash, the two highest concentrations of trace metals were Zn and Ba, with 3.53 mg/L and 3.14 mg/L, respectively. The leaching of other metals followed the order of Ni (0.65 mg/L) > Pb (0.63 mg/L) > Cu (0.19 mg/L) > Cr (0.055 mg/L). The concentrations of other heavy metals were below 0.05 mg/L. While in the bottom ash, the highest leaching was for Ba (2.92 mg/L) and followed by Zn (0.065 mg/L) and Cr (0.053 mg/L). The concentrations of other heavy metals in the leachate were all below 0.05 mg/L. It is interesting to note that the highest content in the leachates from the bottom ash was Ba while the highest content in the bottom ash was Zn, maybe. This was likely due to low extractable fractions of Zn in bottom ash [33] and hence a larger fraction of Zn and its compounds were retained in the residue. The concentration of each heavy metal in leachate from the fly ash was higher than that from the bottom ash, which agrees with the results of Verma et al. [34] and is due to more refractory occurrence modes of these elements in the bottom ash than in the fly ash [35]. According to the Chinese standard for hazardous waste identification [49], all the concentrations of related heavy metals in the leachates from the fly ash and the bottom ash were found to be below the legal limits, and therefore, the fly ash and bottom ash can be considered as ‘non-hazardous waste’. However, according to the standard for pollution control of the landfill site of MSW in China [50], the concentrations of Pb and Ni in the fly ash were found to exceed the legal limits, whereas for the bottom ash they were below the limits. Therefore, the bottom ash produced from the SMW combustion of this study could be directly disposed in a landfill but the fly ash could not be dealt with in the same way. It is worth noting the leaching buffer solutions used in above two standards are different: the solution used in the first standard is sulfuric and nitric acids, however, in the second standard it is acetic acid. The results of this study were obtained by using sulfuric and nitric acids and despite of this deviation from the second standard in terms of the solution used, the results obtained in this study are still expected to provide useful information and guidance on the treatment and utilization of these ashes.

Table 3 Concentrations of different heavy metals in the leachates from fly ash and bottom ash

Heavy metal	Unit	Fly ash	Bottom ash	Limits for hazardous waste-Identification [48]	Limits for landfilling [49]
Zn	mg/L	3.53	0.065	100	100
Pb	mg/L	0.63	<0.05	5	0.25
Cd	mg/L	<0.01	<0.01	1	0.15
Cr	mg/L	0.055	0.053	15	4.5
As	mg/L	<0.05	<0.05	5	0.3
Ni	mg/L	0.65	<0.01	5	0.5
Ba	mg/L	3.14	2.92	100	25
Cu	mg/L	0.19	<0.01	100	40
Ag	mg/L	<0.05	<0.05	5	-
Be	mg/L	<0.01	<0.01	0.02	0.02
Se	mg/L	<0.05	<0.05	1	0.1
Hg	mg/L	<0.01	<0.01	0.1	0.05

3.5 PCDD and PCDF in the fly ash

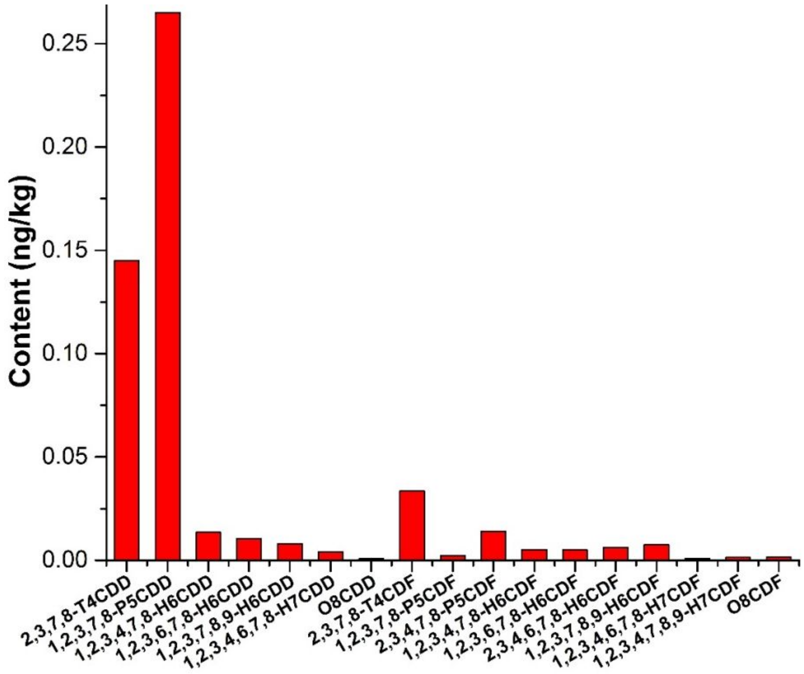

Fig. 3 PCDD and PCDF distributions in the fly ash

PCDD/Fs are serious cancer hazards to people. They can cause reproductive and developmental problems and harm the immune system of human body and hormone regulation [36]. Waste incineration usually produces hazardous PCDD/Fs. Therefore, the PCDD/Fs formation in the process of SMW combustion must be investigated. The PCDD and PCDF distributions in the fly ash are shown in Fig 3. The main PCDD and PCDF contents in the fly ash were 2,3,7,8-T4CDD and 1,2,3,7,8-P5CDD, with 0.145 ng/kg and 0.265 ng/kg, respectively. The limit for the total PCDD and PCDF contents in the ash specified by the standard for pollution control of the landfill site of MSW [50] is 3 ug TEQ/kg. The total PCDD and PCDF of the fly ash in this study was found to be 0.524 ng TEQ/kg, which is far below the legal limit in China. Freire et al. [17] investigated the properties of the fly ash and bottom ash collected from three Portuguese industrial biomass thermal plants. Their results indicated that PCDD and PCDF contents in the fly ash were much higher than those in the bottom ash, and the same conclusion was reported by Sjaak and Koppejan [37]. Therefore, the total PCDD and PCDF contents in the bottom ash were expected to be much lower than those in the fly ash. In this study, the total PCDD and PCDF contents in fly ash were far below the legal limit, therefore, the total PCDD and PCDF contents in the bottom ash should be far below the legal limit, which means the bottom ash can also be directly disposed in a landfill. PCDD/Fs formation mechanisms are complicated and the measurement of PCDD/Fs is difficult, therefore, a universally accepted formation mechanisms have yet to be obtained [38]. Generally, there are three possible ways to form PCDD/Fs: the condensation of Chlorophenol (CP) and chlorobenzenes (CBz), the chlorination of polycyclic aromatic hydrocarbons (PAHs), and the de novo reactions of fly ash. High contents of Cl in G and I (exceed 10% as shown in Table 1) should lead to PCDD and PCDF formation but the low percentages of G and I in the mixture of the shoe manufacturing waste could result in low PCDD and PCDF contents in the fly ash. In addition, $CuCl_2$ is the most effective catalyst for PCDDs / PCDFs formation [38, 39] and carbon content exceeding 5% in the fly ash inhibits PCDDs / PCDFs formation [38]. Therefore, the very low Cu content (195 mg/kg in Table 2) and high carbon content (10.7% in Table 4) of the fly ash might have led to the low PCDD and PCDF contents in the fly ash in this study.

Table 4 Carbon content and ash fusion temperature

Item	Unit	Fly ash	SMW Ash-815
Carbon content	%	10.7	2.3
IDT	℃		1006
ST	℃		1238
HT	℃		1243
FT	℃		1320

3.6 Ash fusion temperature

Due to short experiment duration (4 h), the slagging performance was not observed in this study. The fusion temperatures of the SMW Ash-815 were used to predict the slagging tendency, instead. Using the slagging factor (Fs), slagging index (SI) described in section 3.1 and Fe_2O_3/CaO ratio can give a good prediction of the slagging tendency. The Fs can be calculated by the following equation [22, 23]:

$$\mathrm{Fs} = \frac{\mathrm{HT}+4\ \mathrm{IDT}}{5} \qquad (2)$$

where HT is hemispheric temperature and IDT is initial deformation temperature.

Although the ash behaviours and deposition tendency mainly depend on the complex conditions in boilers and related heat transfer surfaces, these empirical indices combined with some pilot plant tests are widely used as a reference for decision making [33]. For Fs, if it is over 1340℃, the slagging tendency is low; when Fs is ranging from 1250℃ to 1340℃, from 1150℃ to 1250 ℃ and below 1150℃, the slagging tendency is medium, high and severe, respectively. The slagging tendency is low when the Fe_2O_3/CaO ratio is over 3.0 or below 0.31 and it is medium/high when the Fe_2O_3/CaO ratio is ranging from 0.31 to 3.0 [22, 23].

Values of Fs, SI and Fe_2O_3/CaO ratio and the relative slagging tendency of the SMW Ash-815 are presented in Table 6. The results showed that the slagging tendencies resulting from the SMW Ash-815 were considered to be severe, low and low according to the values of Fs, SI and Fe_2O_3/CaO ratio, respectively. This indicates the ash produced during SMW combustion of this study probably had low slagging tendency.

Table 6 Ash index value (Fs, SI and Fe_2O_3/CaO ratio) and slagging tendency

	Fs (℃)	Tendency	SI	Tendency	Fe_2O_3/CaO ratio	Tendency
SMW Ash-815	1053.4	severe	2.29	low	0.059	low

3.7 Suggestion for ash valorization

There are many studies focusing on the potential utilization of biomass ashes and MSW incineration (MSWI) ashes. Based on the composition, mineral phase and classification of biomass ash, biomass ash can be used for soil amendment or fertilisation, construction material production, adsorbents, ceramics and other materials and mineral plus synthesis [51-52]. However, the main use of MSWI ashes is to recover secondary raw materials and products. These ashes can be used as the raw materials for the production of lightweight aggregates, glass-ceramics and cement, as well as for the recovery of zinc, rare metals and salts [53]. The main difference between biomass ash and MSWI ash is that the MSWI ash contains a large amount of hazardous metal components while the biomass ash contains a large amount of nutrient substance supporting plant growth. This difference means that the biomass ash can, while MSWI ash cannot, be used for soil amendment or fertilisation and that the MSWI ash can, while the biomass cannot, be used to recover metals. The characteristics of the SMW fly ash and bottom ash discussed above indicate that these two ashes are quite different from the biomass ash and biomass char [54-55], and they cannot be used for soil amendment or fertilisation due to the relative higher hazardous metal contents in their leaching liquids. Although the bottom ash in this study can be directly disposed in a landfill, using this waste as a secondary raw material instead of as a refuse to be disposed in a landfill is a more environmental-friendly and sustainable way to face the challenges of resource depletion and land shortage. Due to the higher contents of CaO and SiO_2 (Fig.1 and Fig. 2) and being very similar to MSWI ash, the best valorization route recommended for the SMW bottom ash and fly ash may be to use them to produce Colloidal Silica Medium to Obtain Safe inert (COSMOS), which can be a substitute for conventional fillers in polypropylene (PP) composites [56].

However, further investigation is needed for the realization of this valorization route. As found in this study (Fig.1), both the SMW bottom ash and fly ash contain significant amounts of Ca-, Si-, Al-, and Fe-bearing phases, potentially they can also be used as the raw materials for the cement industry. There are two main ways to utilize the ash in the cement industry as explained by Quina et al. [53]: one is the production of blended cement and the other is the co-processing of residues in the cement kiln to produce cement clinker.

4. Conclusions

This study has investigated the ash formation behaviour and the compositional characteristics of the fly ash and bottom ash of show manufacturing waste combustion in a 2.5MWth pilot-scale circulating fluidized bed combustor. The following conclusions have been deduced:

- The three highest compositions in the fly ash and bottom ash were found to be the same: CaO, SiO_2 and Al_2O_3, with 26.18 wt %, 30.75 wt % and 16.31 wt % for the fly ash; 52.57 wt %, 15.96 wt % and 8.21 wt % for the bottom ash, while K_2O and Na_2O were lower than 1.5 wt% in both ashes. The concentrations of heavy metals except Cr in the fly ash were higher than those in the bottom ash, which was attributed to the high melting and boiling points of the Cr element and its compounds and other heavy metals being easily volatilized during the waste combustion, and the concentrations of As, Ag, Be, Se and Hg in both ashes were below the detection limits.
- Recovery of Zn as a second resource from these ashes may be a good choice to deal with these waste ashes due to the high Zn contents in these two ashes (0.356 wt % in the fly ash and 0.169 wt % in the bottom ash).
- According to the results of leaching behaviours of these two ashes, the bottom ash in this study can be directly disposed in a landfill as they meet all the requirements of the Chinese national standard (GB 16889-2008). However, this is not the case for the fly

ash due to the concentrations of Ni (0.65 mg/L) and Pb (0.63 mg/L) in the leachate exceeding the legal limits (0.5 mg/L for Ni and 0.25 mg/L for Pb). The total PCDD and PCDF contents in the fly ash were found to be much lower than the legal limits and the total PCDD and PCDF contents were also expected to be much lower than the legal limits.

- The ash produced from SMW combustion is likely to have a low slagging tendency.
- The two best valorization routes for the SMW bottom ash and fly ash have been recommended, one being to use them to produce COSMOS as a substitute for conventional fillers in polypropylene (PP) composites and the other being to use them as the raw materials for the cement industry.

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