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Metal distribution characteristic of MSWI bottom ash in view of metal recovery

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ABSTRACT

Bottom ash is the major by-product of municipal solid waste incineration (MSWI), and is often reused as an engineering material, such as road-base aggregate. However, some metals (especially aluminum) in bottom ash can react with water and generate gas that could cause expansion and failure of products containing the ash; these metals must be removed before the ash is utilized. The size distribution and the chemical speciation of metals in the bottom ash from two Chinese MSWI plants were examined in this study, and the recovery potential of metals from the ash was evaluated. The metal concentrations in these bottom ashes were lower than that generated in other developed countries. Specifically, the contents of Al, Fe, Cu and Zn were 18.9–29.2, 25.5–32.3, 0.7–1.0 and 1.6–2.5 g/kg, respectively. Moreover, 44.9–57.0 wt.% of Al and 55.6–75.4 wt.% of Fe were distributed in bottom ash particles smaller than 5 mm. Similarly, 46.6–79.7 wt.% of Cu and 42.9–74.2 wt.% of Zn were concentrated in particles smaller than 3 mm. The Fe in the bottom ash mainly existed as hematite, and its chemical speciation was considered to limit the recovery efficiency of magnetic separation.

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Introduction

Incineration is an important treatment technology in the sustainable management of municipal solid waste (MSW) and its use for this purpose is increasing. During the past 10 years in China, incineration technology has been developing rapidly. The China Statistical Yearbook showed that in 2014 there were 188 municipal solid waste incineration (MSWI) plants with a combined capacity of approximately 0.186 million tons/day, which means that about 30% of the collected MSW was incinerated (National Bureau of Statistics of China, 2015). Therefore, the annual production of MSWI bottom ash is estimated to reach more than 11 million metric tons in the next few years, from which large profits could result from

responsible reutilization of this material. The physical and chemical properties of bottom ash, especially its high proportion of calcium and silicon, make the use of bottom ash feasible as an engineering construction material. For example, bottom ash is mainly used for road construction in countries such as France, The Netherlands and Spain, while in Sweden and Norway landfill construction is the primary route for bottom ash utilization (ISWA-WGTT, 2006). Moreover, metal recovery from bottom ash was deemed to be a necessary process for increasing the stability of bottom ash and thereby improving its suitability as a construction material. The metals found in bottom ash, especially the aluminum, can generate hydrogen when they react with water, causing swelling and expansion of the bottom ash material and posing a safety problem in service

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Table 1 – Municipal solid waste composition in different countries and regions (wet mass%).

Region	Organic waste	Paper	Plastic	Glass	Metal	Textile	Others	Reference
USA	21.1	12.4	17.6	5.1	8.9	7.5	27.4	OECD (2007)
France	29.4	23.3	14.8	4.2	5.4	n.m.	22.9	Bayard et al. (2010)
Germany	30.0	24.0	13.0	10.0	1.0	n.m.	22.0	Muhle et al. (2010)
Italy	29.0	28.0	5.0	13.0	2.0	n.m.	23.0	OECD (2007)
UK	36.5	24.0	9.0	6.5	4.0	n.m.	20.0	Burnley (2007)
Japan	34.0	33.0	13.0	5.0	3.0	n.m.	12.0	OECD (2007)
Beijing City	66.2	10.9	13.1	1.0	0.4	1.2	7.2	Wang and Wang (2013)
Shanghai City	72.5	6.0	13.8	3.1	0.2	2.1	2.3	Zhang et al. (2010)
Shenzhen City	47.8	13.7	13.9	1.7	0.7	10.3	11.9	Luo (2006)
n.m.: not mentioned.								

(Pecqueur et al., 2001). Economically, scrap metal recovery from MSWI bottom ash also makes sense owing to the cost and availability of raw materials.

The percentage of metal in MSW shows significant differences across different regions and countries (Table 1). Generally, metal consumption has been strongly correlated to economic development, and has affected the quantity of metals discarded in MSW. Yet, in the MSW from most developed cities of China, such as Shanghai, Beijing and Shenzhen, the metal composition is several times less than that found in MSW from many developed countries. The quantity and diversity of metal species found in MSWI bottom ash reflects the complex composition of MSW itself. In addition, the morphology of metals in MSW governs their conversion into different chemical forms, such as elemental or oxidized states, in the bottom ash after thermal treatment. Table 2 lists the contents of both commonly found and scarce metals in bottom ash from different countries.

Considering metals to be a valuable resource, European countries have taken efforts to separate metals from bottom ash for several years. Among all metals, aluminum and iron are the major targets in recovery processes that use physical and mechanical methods. Based on the electrical and magnetic property of different materials, it is feasible to recover the ferrous and non-ferrous metal through magnetic and eddy current separators (ECS), respectively. Schmelzer (1995) designed

a set of processes to recover metals from MSWI bottom ash using magnets and achieved a 35.5% recovery rate for ferrous metal from input MSW. Muchová and Rem (2006) reported an advanced metal recovery process capable of recovery rates from MSWI bottom ash for ferrous and non-ferrous particles as high as 83% and 73%, respectively. Generally, the recovery efficiency of ferrous metal by magnetic separation has been significantly higher than that of non-ferrous metal by ECS. About 57%–83% of ferrous scraps can be recovered through magnetic separation while only about 30% of aluminum can be separated from bottom ash using commonly available technology (Grosso et al., 2011).

Due to limitations of technology and cost, most bottom ash currently generated in China is directly disposed of without pretreatment in landfills, in accord with Chinese Standard GB 16889–2008. Most studies in China that concern MSWI bottom ash have researched the use of this material; few have focused on metal recovery. Hu et al. (2011) investigated the distribution of different types of aluminum packaging waste through the thermal process and corresponded influence on the recovery rate by ECS. Huang (2013) used jigging and gravity separation to treat MSWI bottom ash. However, neither the accessibility of metal recovery through magnetic separation and ECS, nor the characteristic metal distribution in MSWI bottom ash from China, is clear.

Table 2 – Chemical composition of bottom ash from different countries (mass%).

Element	Netherlands ^a	Italy ^b	France ^c	Japan ^d	Korea ^e	China ^f
Na	1.14–2.05	1.87–2.27	2.69–4.70	1.71–1.88	2.30–2.70	4.00–7.60
Mg	0.90–1.74	1.73–4.34	1.27–2.02	1.31–2.00	n.m.	1.10–2.87
Al	3.35–4.05	4.01–4.76	3.37–6.92	7.42–8.81	3.00–4.10	n.m.
K	0.82–1.20	0.90–1.23	n.m.	0.71–1.24	1.50–1.90	1.40
Ca	7.17–10.49	16.7–23.8	11.42–16.58	17.62–23.86	18.00–21.00	1.50–8.60
Fe	3.87–11.97	7.19–7.21	3.37–6.91	3.61–5.52	1.50–3.00	2.24–2.90
Ti	n.m.	0.68–0.72	n.m.	0.87–0.98	n.m.	n.m.
Cu	0.17–0.74	0.19–0.36	0.12–0.17	0.17–0.25	0.25–0.53	0.03–0.12
Zn	0.32–0.56	0.22–0.37	0.21–0.43	0.31–0.33	0.31–0.38	0.03–0.33

n.m.: not mentioned.

^a Meima and Comans (1997).

^b Funari et al. (2015); Funari et al. (2016).

^c Dabo et al. (2009); Francois and Pierson (2009).

^d Shim et al. (2005); Wei et al. (2011).

^e Shim et al. (2005).

^f He et al. (2005); Yao et al. (2010).

Table 3 – Mass distribution of the MSWI bottom ashes (mass%).

Particle size	Samples			
	JS1	JS2	YQ1	YQ2
<1 mm	23.06	18.81	25.47	19.32
1–3 mm	6.04	19.29	12.55	15.53
3–5 mm	22.69	32.49	21.04	20.40
5–10 mm	20.03	14.77	16.87	16.02
10–20 mm	16.57	8.22	11.63	15.28
>20 mm	11.62	6.42	12.44	13.45
Median particle size (mm)	2.86	2.05	2.25	2.78

As is often noted, size reduction and screening are fundamental steps that must precede the metal separation process in order to improve the recovery rate. However, ECS has only been proved to be efficient for recovering the metals from bottom ash having a particle size of more than 2 mm. In addition, the increased oxidation level of non-ferrous metal in bottom ash can decrease the current force acting on the metals and reduce the efficiency of ECS (Biganzoli and Grosso, 2013). As with ECS, the recovery of ferrous metal by magnetic separation is also decided by the magnetic property of minerals. Paramagnetic

and ferromagnetic minerals such as iron and magnetite can be easily recovered using a weak magnetic field, while diamagnetic mineral such as hematite is difficult to recover using commonly available magnetic field separators. In other words, the distribution characteristics and morphology of metals in bottom ash govern their recovery and dictate the selection of a separation technique. The key objective of the research reported here was to verify the quantity and quality of metals found in bottom ash from typical MSW incinerators in China, and then give suggestions for the reutilization and recycling of this material.

1. Materials and methods

1.1. Sources of MSWI bottom ash

The MSWI bottom ashes were collected from two mass-burn incineration plants (A and B) in Shanghai, with MSW treatment capacities of 800–1000 tons/day and equipped with reciprocating mechanical grate incinerator. At both plants, the incineration temperature was about 850 °C and the residence time of the waste was 1.5–1.8 hr. Bottom ashes were first quenched with water and then stored in ash pits before being transported to landfills.

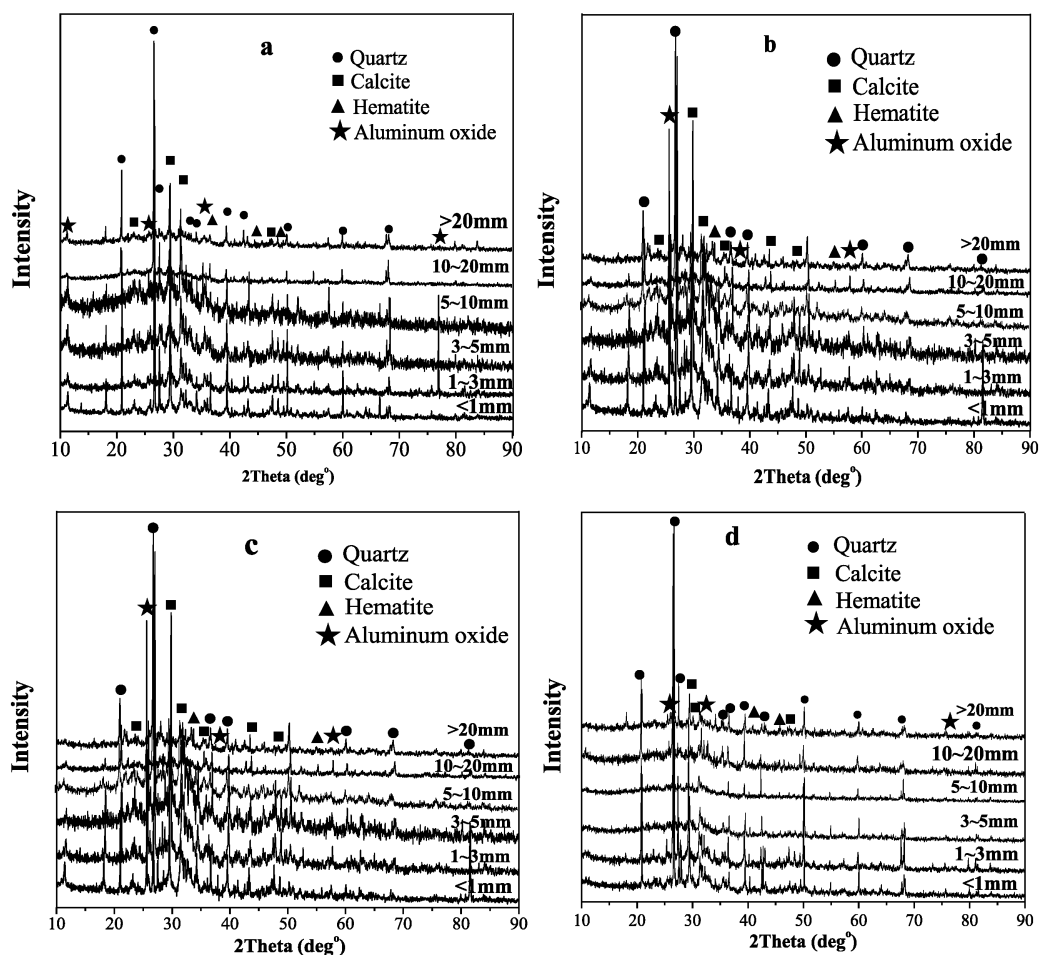


Fig. 1 – X-ray diffraction spectra of the municipal solid waste incineration (MSWI) bottom ashes A1 (a), B1 (b), A2 (c), B2 (d).

Table 4 – Chemical compositions of the MSWI bottom ashes (g/kg bottom ash).

Sample	Particle size	Na	Si	K	Ca	Ti	Mg	Al	Fe	LOI%
JS1	<1 mm	9.9	69.0	8.0	158	4.5	8.6	47.0	81.2	2.52
	1–3 mm	14.5	83.5	8.1	121	4.8	7.1	13.2	23.4	2.28
	3–5 mm	11.2	68.0	6.0	103	3.3	4.4	69.9	79.9	2.59
	5–10 mm	25.5	103	6.6	101	5.3	5.5	42.3	44.4	1.04
	10–20 mm	25.9	108	6.8	97.1	4.8	7.4	37.1	62.1	1.32
	>20 mm	15.4	111	8.7	86.5	2.7	6.6	80.6	32.9	1.13
JS2	<1 mm	9.0	53.3	7.3	150	3.5	8.0	29.2	50.0	1.40
	1–3 mm	12.5	62.9	7.8	121	3.2	6.8	29.3	60.1	1.75
	3–5 mm	16.1	72.7	7.1	105	2.6	6.2	47.1	102	1.77
	5–10 mm	19.6	91.3	7.2	82.7	2.1	4.9	23.5	33.5	1.76
	10–20 mm	18.1	104	9.5	82.4	2.4	6.3	27.5	20.7	1.73
	>20 mm	16.4	146	10.8	82.6	3.6	9.3	32.4	15.0	2.36
YQ1	<1 mm	9.6	678	7.2	133	2.8	8.6	48.4	68.8	5.45
	1–3 mm	12.5	728	6.6	101	2.4	6.9	22.3	35.1	4.80
	3–5 mm	17.5	914	6.7	95.8	2.8	6.3	33.7	58.5	4.40
	5–10 mm	32.8	134	6.9	84.8	2.1	7.8	28.0	34.8	1.70
	10–20 mm	26.8	144	7.7	79.4	2.4	5.9	24.7	37.2	3.18
	>20 mm	23.4	155	5.9	77.6	3.2	4.8	26.1	39.3	4.33
YQ2	<1 mm	12.3	89.0	9.5	117	3.0	6.4	41.3	53.5	4.75
	1–3 mm	14.1	92.4	8.8	115	2.7	8.9	36.8	34.9	4.00
	3–5 mm	43.0	187.	9.3	104	2.6	12.9	68.1	53.4	2.75
	5–10 mm	43.4	166.	6.3	91.1	1.5	9.1	28.0	17.5	1.75
	10–20 mm	28.0	156.	9.6	79.7	1.9	7.7	55.5	37.4	0.75
	>20 mm	24.9	183.	9.4	49.9	02.6	12.8	54.4	58.6	1.60

1.2. MSWI bottom ash sampling and preparation

1.2.1. Sampling

The fresh bottom ashes were collected from the ash pits in August 2013 and April 2014 from MSWI plant A (samples A1 and A2, respectively), and in December 2013 and March 2014 from MSWI plant B (samples B1 and B2, respectively). At each sampling, 50 kg of the ash was taken to the laboratory for analysis. Each 50 kg sample was generated by coning and quartering 200 kg of ash that was collected from different locations in the ash pits. The samples were air-dried for 1 to 2 days before being screened.

1.2.2. Sample preparation

A series of standard sieves for aggregate separation were used to divide the bottom ash into different particle-size fractions, i.e., >20 mm, 10–20 mm, 5–10 mm, 3–5 mm, 1–3 mm and <1 mm. The weight and moisture content of each particle size fraction were measured, from which the mass distribution of the bottom ash was calculated.

The particle size fractions less than 10 mm were directly ground into fine powders (<100 μm) using a ball mill. Metals were taken out from the particles sized >10 mm, and size reduced by cutting wire and drill. The leftovers were first broken into smaller particles by hammer crushing, and then ground using a ball mill into fine powders (<100 μm).

1.3. Analytical methods

Loss on ignition measurement was conducted in triplicate by heating bottom ash samples in a muffle oven at 600 $^{\circ}\text{C}$ for 2 hr. The weight loss of cooled samples after heating reflected

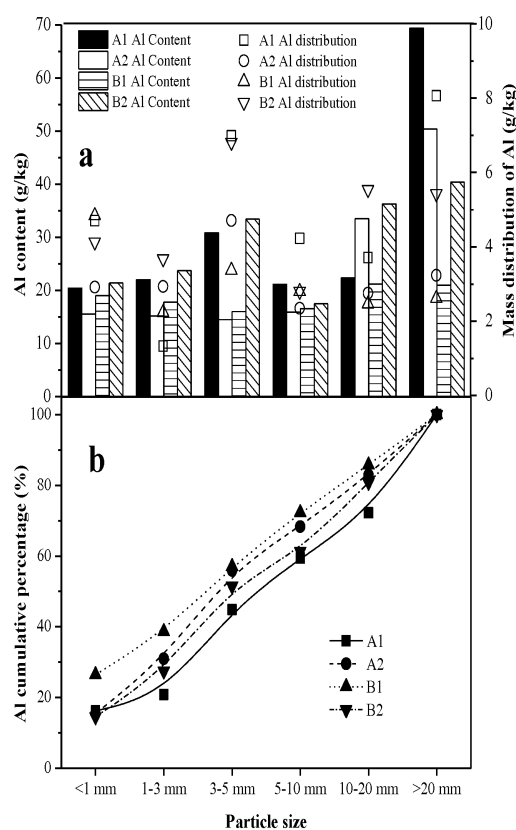


Fig. 2 – Content and distribution of Al in the MSWI bottom ashes (a) content and mass distribution of Al in the MSWI bottom ashes (b) cumulative percentage of Al in the MSWI bottom ashes.

the organic matter content. The density of bottom ash samples was measured using the pycnometer method.

The metal contents in the bottom ash samples in different particle size fractions were determined in triplicate. Major elements (>1 wt.%) such as calcium (Ca), silicon (Si), aluminum (Al), iron (Fe), magnesium (Mg), sodium (Na), potassium (K) and others were measured by X-ray fluorescence (XRF, S4 AXS Explorer, Bruker, Germany) after the samples were mixed with KBr and pressed into the pellets and trace elements such as copper (Cu), zinc (Zn) and others were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, 720ES, Agilent, USA) after HCl-HNO₃-HClO₄-HF acid digestion.

The mineralogical compositions of the milled bottom ashes were identified by X-ray diffraction (XRD, D8 Advance X, Bruker, Germany), with Cu K_α radiation at a scan speed of 0.2°/sec and the 2θ range of 10–90°.

The metal speciation in the bottom ash was determined according to a sequential extraction procedure (SEP), a modified version of the practical procedure developed by Tessier et al. (1979). After each step of extraction, the solution was centrifuged (at 3000 ×g for 20 min) and filtered before analysis. The residue of each step was washed using deionized water. The SEP produced six fractions as follows: Fraction 1 (F1, water soluble fraction) was obtained by combining 2.0 g of bottom ash with 20 mL of deionized water and shaking the mixture for 12 hr at room temperature. To obtain Fraction 2 (F2, exchangeable fraction), the residue

from the water soluble fraction was mixed with 16 mL of 1 mol/L magnesium chloride (MgCl₂) solution and shaken for 1 hr at room temperature. To obtain Fraction 3 (F3, bound to carbonate fraction), the residue from the exchangeable fraction were added 16 mL of 1 mol/L acetate sodium (CH₃COONa) and the mixture was shaken for 5 hr at room temperature. To obtain Fraction 4 (F4, bound to Fe-Mn oxides fraction), the residue from the bound to carbonate fraction was mixed with 20 mL of 0.04 mol/L hydroxylamine hydrochloride (NH₂OH·HCl) and heated at 96 ± 1 °C for 5 hr with intermittent agitation. To obtain Fraction 5 (F5, bound to organic matter fraction), the residue from the bound to Fe-Mn oxides fraction was combined with 6 mL of 0.02 mol/L HNO₃ and 10 mL of 30% hydrogen peroxide (H₂O₂) (pH adjusted to 2.0) and heated at 85 ± 1 °C for 2 hr with intermittent agitation. Then, an additional 6 mL of 30% H₂O₂ (pH adjusted to 2.0) was added and the mixture was heated again for 3 hr with intermittent agitation. After the sample cooled, 10 mL of 3.2 mol/L ammonium acetate (CH₃COONH₄) in 20% HNO₃ were added, and the mixture was shaken for 30 min. To obtain Fraction 6 (F6, residue fraction), the residue from the bound to organic matter fraction was determined by acid digestion as described.

X-ray photoelectron spectra (XPS) were used to identify the chemical states of metals in different particle size fractions of bottom ash by their binding energy, with a relatively low detection limit (0.1 wt.%). The XPS were measured by a Perkin

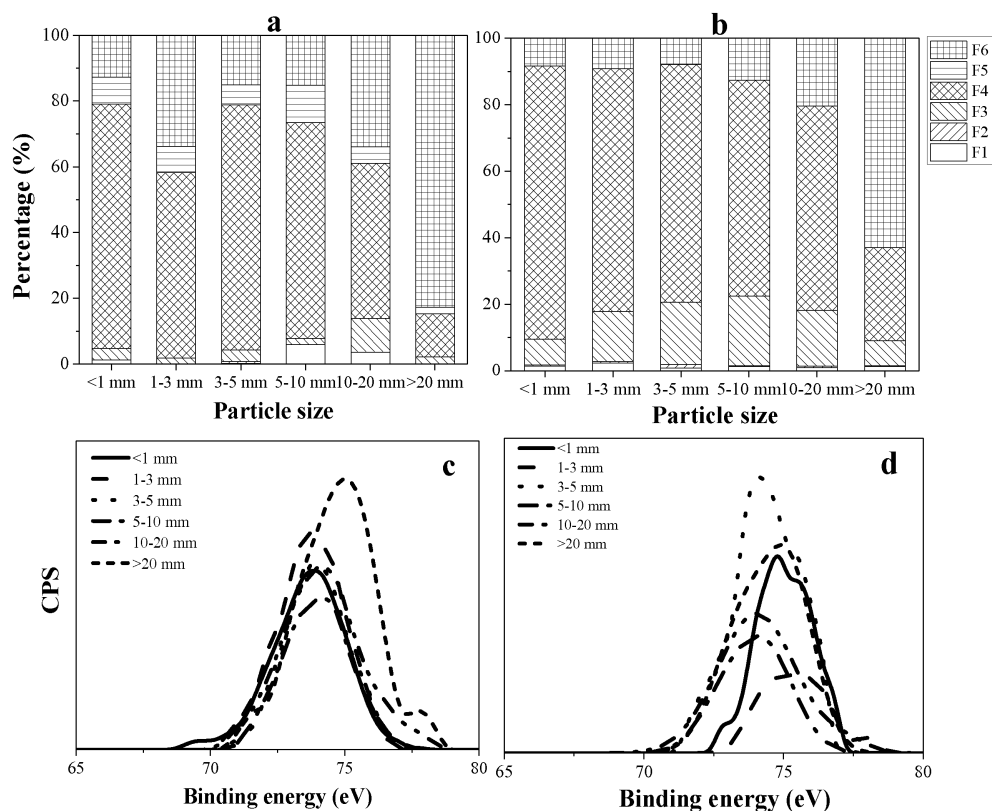


Fig. 3 – Metal speciation of Al in different MSWI bottom ash size particles (a) the fraction of Al in the bottom ashes from Plant A (b) the fraction of Al in the bottom ashes from Plant B (c) X-ray photoelectron spectra of Al in the bottom ashes from Plant A (d) X-ray photoelectron spectra of Al in the MSWI bottom ashes from Plant B.

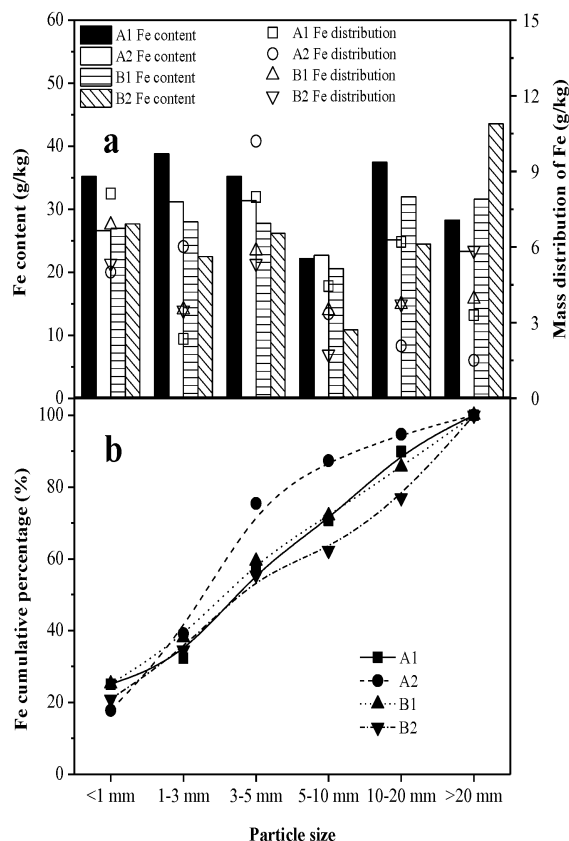


Fig. 4 – Content and distribution of Fe in the MSWI bottom ashes (a) content and mass distribution of Fe in the MSWI bottom ashes (b) cumulative percentage of Fe in the MSWI bottom ashes.

Elmer PHI 5000C ESCA System (USA) equipped with the Mg K α (1253.6 eV) anode and a hemisphere energy analyzer, which was operated at 14 keV and 20 mA. The pass energy was kept at 93.90 eV and all binding energies were calibrated by C1s line at 284.6 eV. The peak of binding energy in the XPS spectra was estimated using the software XPSPeak 4.1 (Kwok R., Hong Kong, China).

2. Results and discussion

2.1. General characterization of the MSWI bottom ashes

2.1.1. Mass distribution

The mass percentages of the particle size fractions of MSWI bottom ashes are shown in Table 3. Approximately 25% (by weight) of the bottom ash from these two facilities consisted of particles smaller than 1 mm and mainly composed of the grate siftings in the particle size range 0–250 μ m (Chang and Wey, 2007). Approximately 40 wt.% of the bottom ash was made up of particles larger than 5 mm. However approximately 60 wt.% of the ash was comprised of particles larger than 3 mm, which were particularly suited to metal recovery through magnetic separation and ECS. Only 6.42–13.45 wt.% of bottom ash was comprised of particles larger than 20 mm,

and these were mainly metallic and building particles. According to the particle size distribution of MSWI bottom ash, the median particle size was calculated to be in the range of 2.0–2.9 mm.

2.1.2. Mineralogy

The X-ray diffraction spectra that identify the mineralogy of the MSWI bottom ashes are shown in Fig. 1. Quartz (SiO_2) and calcite (CaCO_3) were the major components in the bottom ashes. The diffraction peak intensity of calcite increased as the particle size decreased, whereas the opposite relationship was exhibited by quartz. In addition, hematite (Fe_2O_3) and aluminum oxide (Al_2O_3) were also found in the bottom ashes, and were considered to be the result of oxidization through the thermal process which caused the economic losses of metals. Due to the detection limit of XRD, other minerals containing Cu and Zn could not be detected.

2.1.3. Chemical compositions

The major elemental composition of bottom ash except for recoverable metals is presented in Table 4. In terms of mass, the sequence of element content in the MSWI bottom ashes from high to low was as follows: Ca, Si > Na, K > Mg, Ti. Thus, calcium and silicon were the predominant elemental components and comprised 40 wt.% of the mass of bottom ash. The high content of calcium and silicon decided the application potential of bottom ash as an engineering construction material.

2.2. Metal distribution

2.2.1. Aluminum

Aluminum is typically one of the most abundant metals in the bottom ash of MSWI, and originates mainly from packaging such as beverage cans, foil containers, trays and thin sheet (Chimenos et al., 1999). As shown in Fig. 2, calculated through the Al content in every particle size fractions and mass distribution of bottom ash, the total weight of Al comprised 20 g/kg (18.9–29.2 g/kg bottom ash) of the bottom ash. The content of Al was highest in the particle size fraction greater than 20 mm (21.0–69.4 g/kg bottom ash), and less in the 10–20 mm fraction (21.2–36.3 g/kg bottom ash) and 3–5 mm fraction (14.5–30.8 g/kg bottom ash), similar to the results for bottom ash from Amsterdam reported by Hu et al. (2011). Considering the size distribution, the highest Al distributor was particles larger than 20 mm and thereafter, in particles 5–20 mm in size; these particles mainly originated from aluminum can scrap. Particles smaller than 3 mm contained 20.8–38.6 wt.% of the Al, and 44.9–57.0 wt.% of the Al was distributed in particles smaller than 5 mm.

The sequential fractionation of Al contained in different bottom ash particle size fractions is presented in Fig. 3a and b. The bound to Fe–Mn oxides fraction and the residual fraction were the dominant fractions of Al in all particle sizes, and ranged between 77.5–91.0 wt.% and 80.9–95.8 wt.% in the bottom ashes from plant A and B, respectively. According to the NIST XPS database (Naumkin et al., 2012), the binding energy of metallic Al and Al_2O_3 2p 3/2 XPS spectra was between 72.0–73.0 eV and 73.7–74.8 eV. As a result of peak fitting, the percentage of metallic Al in the total mass of Al from incineration plants A and B was 36.4 wt.% and 28.3 wt.%,

respectively, and increased as the particle size increased (Fig. 3c and d). The XRD, SEP and XPS analyses indicated that the main mineral compositions of Al were metallic Al and Al_2O_3 . The Al_2O_3 comprised 60–70 wt.% of the total amount of Al in the bottom ash, and this corresponded to the field results reported by Biganzoli and Grosso (2013), who found the similar oxidation level of Al in the bottom ash as well as the distribution of metallic Al which was concentrated in the ash particles larger than 3 mm.

Owing to the high performance of electrical conductivity, non-ferrous metal (especially Al) can be separated from a mixed waste stream by an ECS. However, even with the most advanced ECS technology available, the efficiency of an ECS is limited by the shape and size of metal scraps in the waste (Muchová and Rem, 2006; Ruan and Xu, 2012). Thus, an ECS has difficulty in recovering metals from bottom ash that are smaller than 3 mm, while the recovery rate of Al can be as high as 80% when with the metallic particles are larger than 5 mm. As shown in Fig. 2, almost half of the Al in the bottom ash from plants A and B was distributed in particles that were larger than 5 mm. Moreover, the concentration of metallic Al in bottom ash increased as the particle size increased. Hence, ECS is a feasible way by which to recover Al from the bottom ash investigated in this study.

2.2.2. Ferrous metals

As shown in Fig. 4a, a relatively low ferrous metal concentration (10.9–22.7 g/kg bottom ash) was found in the 5–10 mm particle size fraction of bottom ash; however, ferrous metal

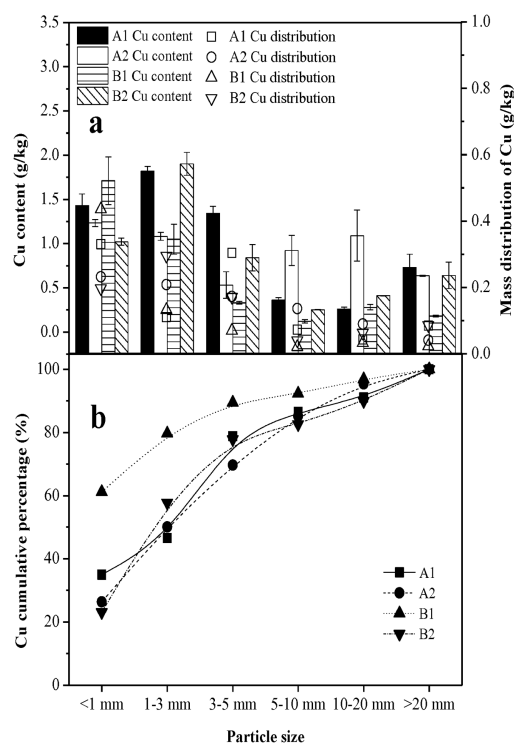


Fig. 6 – Content and distribution of Cu in the MSWI bottom ashes (a) content and mass distribution of Cu in the MSWI bottom ashes (b) cumulative percentage of Cu in the MSWI bottom ashes.

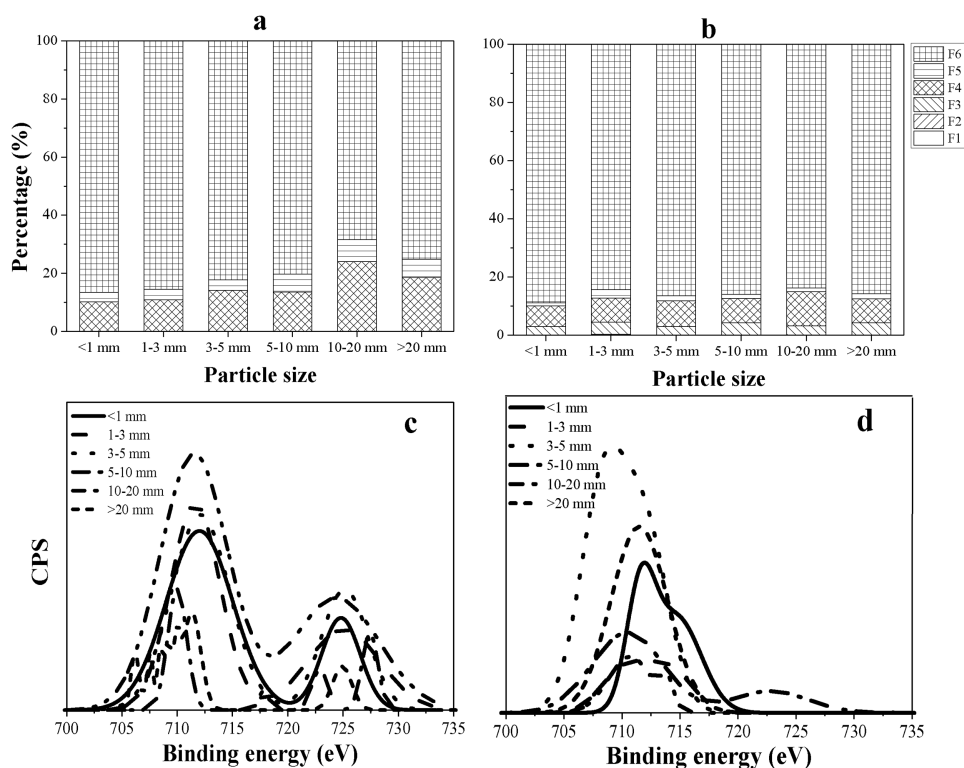


Fig. 5 – Metal speciation of Fe in different MSWI bottom ash size particles (a) the fraction of Fe in the bottom ashes from Plant A (b) the fraction of Fe in the bottom ashes from Plant B (c) X-ray photoelectron spectra of Fe in the bottom ashes from Plant A (d) X-ray photoelectron spectra of Fe in the MSWI bottom ashes from Plant B.

was evenly distributed among the other particle size fractions. The total content of Fe in different MSWI bottom ash samples was 25.5–32.3 g/kg bottom ash, but 32.3–39.2 wt.% of Fe was contained in particles smaller than 3 mm, while the cumulative mass percentage of Fe in particles smaller than 5 mm was 55.6–75.4 wt.% (Fig. 4b).

Considered as the most abundant recoverable metal in bottom ash, Fe is commonly separated from this waste using a magnet. In some cases, the recovery rate of Fe from MSWI bottom ash using magnetic separation is as high as 80%. However, the efficiency of magnetic separation is strongly influenced by the morphology of the ferrous metal. Similar to the speciation of Al in the bottom ashes, the distribution of ferrous metal in the bound to Fe–Mn oxides fraction and residual fraction accounted for 96.2, 88.6, 83.1, 94.2 and 89.1 wt.% for plant A bottom ash in particle size fractions of <1 mm, 1–3 mm, 3–5 mm, 5–10 mm, 10–20 mm and >20 mm, respectively; the comparable distribution of ferrous metal among these fractions in plant B ash was 92.8, 94.4, 94.5, 89.2, 90.6 and 85.1 wt.%, respectively (Fig. 5a and b). The XPS showed that the binding energies of Fe peaks were between 710 and 712 eV (Fig. 5c and d), which corresponded to the 2p_{3/2} XPS spectra of Fe₂O₃. The percentage of metallic Fe was

only in the range of 3.2–9.0 wt.%. This assessment was consistent with the XRD results showing that hematite was the primary mineral form of Fe in bottom ash (due to the oxidization during the thermal process). Diamagnetic mineral such as hematite is hard to separate using a magnetic density lower than 1 T; this restriction inhibits the effectiveness of magnetic separation using common magnet devices (De Boom et al., 2011).

2.2.3. Copper

Even though copper and zinc contents are lower than aluminum and ferrous metals in MSWI bottom ashes, their high economic value makes them worth recovering when they are present in this material. Previous research has shown that Cu and Zn are correlated with the input of bulky waste and the metals that remain in the bottom ash are mostly associated with the small particles (Chimenos et al., 1999; Jung et al., 2004). As shown in Fig. 6a, a total of 0.7–1.0 g/kg Cu was found in the bottom ash from plants A and B. Specifically, 46.6–79.7 wt.% of Cu occurred in the fine particles smaller than 3 mm, while 78.8–89.4 wt.% of Cu was distributed in particles smaller than 5 mm (Fig. 6b). This observation was consistent with previous research that

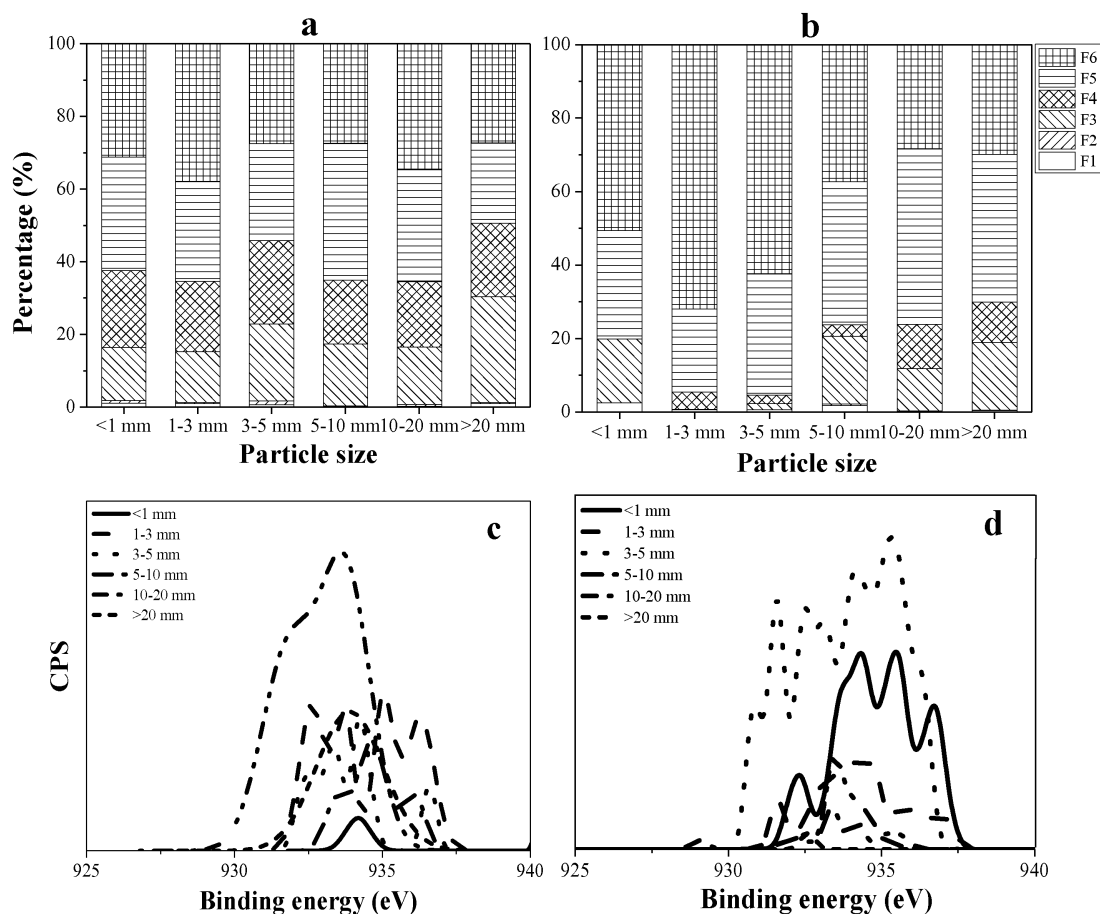


Fig. 7 – Metal speciation of Cu in different MSWI bottom ash size particles (a) the fraction of Cu in the bottom ashes from Plant A (b) the fraction of Cu in the bottom ashes from Plant B (c) X-ray photoelectron spectra of Cu in the bottom ashes from Plant A (d) X-ray photoelectron spectra of Cu in the MSWI bottom ashes from Plant B.

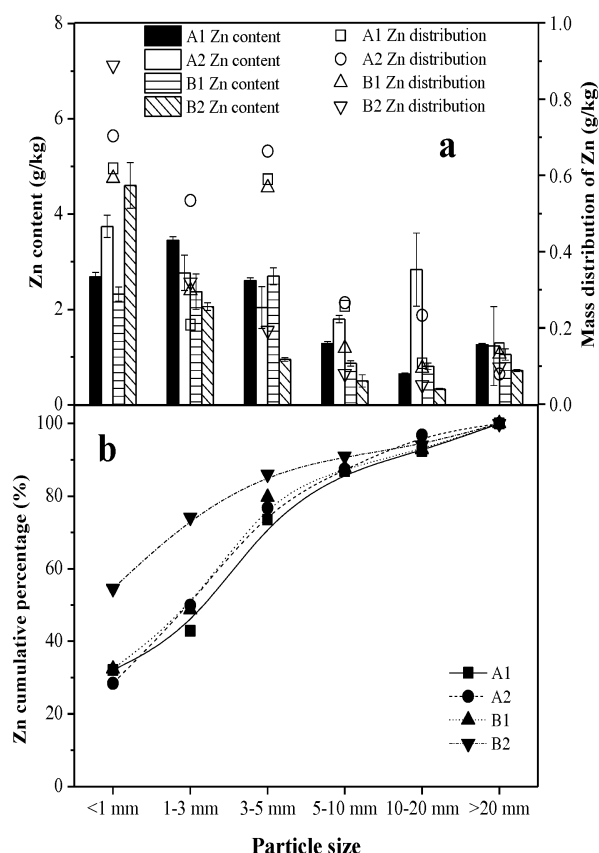


Fig. 8 – Content and distribution of Zn in the MSWI bottom ashes (a) content and mass distribution of Zn in the MSWI bottom ashes (b) cumulative percentage of Zn in the MSWI bottom ashes.

found heavy metals (especially Cu and Zn) were concentrated in fine particle size fractions of bottom ash because these metals were inclined to form the pure solid melt in small particles during the thermal process (Chimenos et al., 1999; Yao et al., 2010).

Because Cu can combine with organic matter and generate strong ligands, such as humic-acid-bound Cu and fulvic-acid-bound Cu (McGrath, 1996), the mass percentage of Cu that was found in the bound to organic matter fraction was higher than that for other species (Fig. 7a and b). As shown in Fig. 7, Cu in the bound to organic matter fraction was in the ranges 22.1–37.7 wt.% and 22.7–47.8 wt.% for the bottom ash from incineration plant A and B, respectively. The mass percentages of Cu in the Fe–Mn oxides fraction and residual fraction were evenly distributed among all particle sizes of ash from plant A, but increased as the size of particles decreased in the bottom ash from plant B. Owing to the complex composition of Cu in the MSWI bottom ashes, the binding energy of Cu peaks was between 930 and 937 eV and exhibited a multi-peak response (Fig. 7c and d). Moreover, the binding energy of metallic Cu 2p_{3/2} spectra was in the range of 932–933 eV which accounted for only about 12.4–14.0 wt.% of the total Cu, as most of Cu in the bottom ash was still in an oxidized form or complexed with organic matter. Hence, both the mass content analysis and speciation of Cu in the

bottom ash indicated that even though 50% of Cu should be in the range of particle sizes available for ECS recovery, further processing and refinement is needed to improve the value of products. Better-targeted techniques, such as gravity separation combined with flotation, could be efficient means by which to recover Cu from the fine ash particles.

2.2.4. Zinc

The total content of zinc in the different MSWI bottom ash samples was 1.6–2.5 g/kg. Similar to the mass distribution of Cu in bottom ash, 42.9–74.2 wt.% of Zn was found in particles smaller than 3 mm, and 73.5–86.1 wt.% of Zn was stored in the bottom ash particles smaller than 5 mm (Fig. 8a and b). Fig. 9a and b shows the distribution of Zn fractions, and indicates that the bound to carbonate fraction of Zn was the dominant component in the bottom ashes, accounting for 42.8–63.7 wt.% in different particles from plant A and 40.0–74.0 wt.% in those from plant B. Importantly, metallic Zn (binding energy between 1021 and 1022 eV) comprised only 6.2% and 8.5% of the total mass of Zn in ash from plant A and B, respectively, and was only distributed in the particles larger than 3 mm (Fig. 9c and d). Therefore, as with Cu, ECS is not a suitable way by which to recover Zn from bottom ash. Rather, an acid leaching process can be an effective method to treat the crude separation products based on the high proportion of Zn in the bound to carbonate fraction in the bottom ashes (Chiang et al., 2008).

2.3. Metal recovery potential analysis

The metal content of MSWI bottom ash from China is relatively low compared to that of bottom ash from other countries (Table 2). For instance, the ash from plants A and B in this study contained 18.9–29.2 g/kg Al, which was approximately half the content in bottom ash from countries such as The Netherlands, France, Italy, Japan and Korea. Nevertheless, the quantity of MSW incinerated in China is more than 53 million tons, while the quantity incinerated in The Netherlands, France, Italy, Japan, and the United States is 4, 12, 5, 41 and 32 million tons, respectively (Eurostat, 2009a, b; Shekdar, 2009; USEPA, 2014). Thus, even though the bottom ash in China has a lower metal content than that of other developed countries, the huge quantity of bottom ash produced in China makes recovering the metals from bottom ash a worthwhile economic endeavor, as well as a sensible environmental requirement to improve material utilization.

According to the Chinese national “12th Five Year Plan” for environmental protection (incineration ratio reaches to 35% at the end of 2015), the annual amount of MSW incineration is 53.3 million tons, which will generate more than 13 million tons of bottom ash. Then the total amounts of Al, Fe, Cu, Zn in the MSWI bottom ash could be calculated as in the range of 0.24–0.38, 0.33–0.42, 0.009–0.013, 0.021–0.033 million tons respectively and the recoverable metals in the bottom ash based on the metal recovery in the published reports are shown in Fig. 10. Currently, the recovery of as high as 80% Al and 70% other non-ferrous metals (Cu and Zn mainly) was available for bottom ash particles sized more than 3 mm by advanced ECS technology while the recovery was around 30% for Al and 35% for

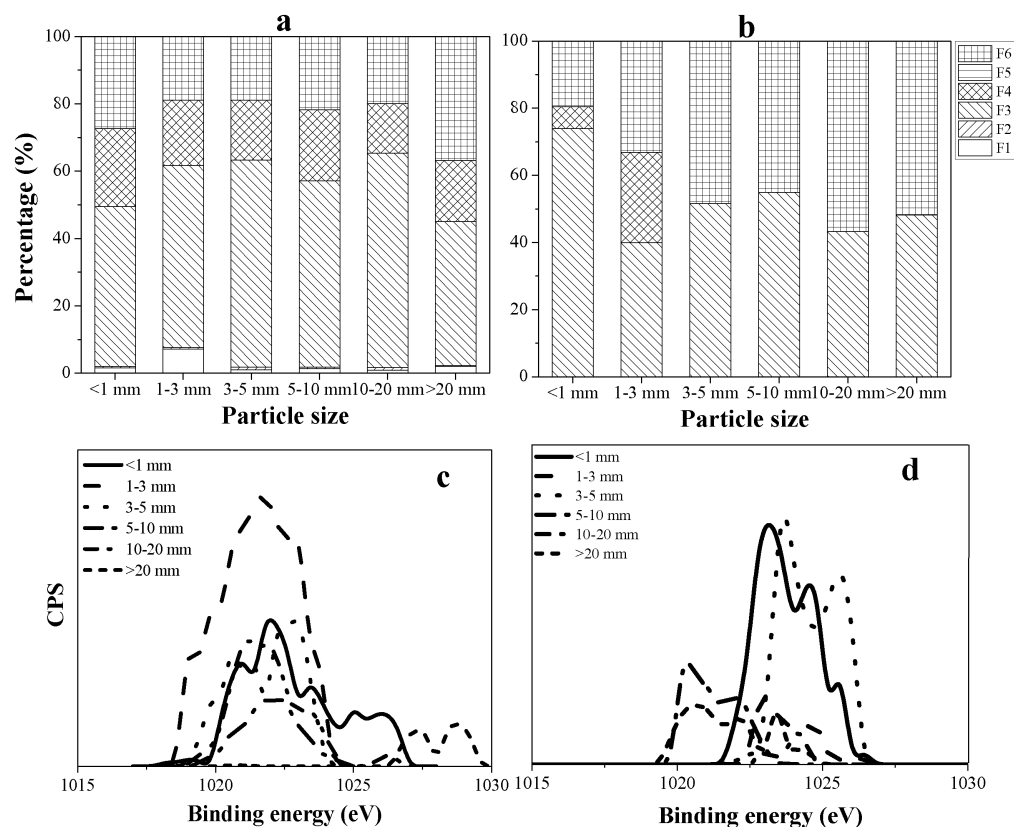


Fig. 9 – Metal speciation of Zn in different MSWI bottom ash size particles (a) the fraction of Zn in the bottom ashes from Plant A (b) the fraction of Zn in the bottom ashes from Plant B (c) X-ray photoelectron spectra of Zn in the bottom ashes from Plant A (d) X-ray photoelectron spectra of Zn in the MSWI bottom ashes from Plant B.

non-ferrous metals in traditional way based on the previous researches (Berkhout et al., 2011; Grosso et al., 2011; Muchová and Rem, 2006). However, considering the predominant distribution of Cu and Zn in very small bottom ash particles, the effectiveness of ECS as a recovery technique was limited. Other recovery methods, such as gravity separation, flotation and acid leaching could be attempted to separate Cu in the bound to organic fractions and Zn in the bound to carbonate fractions from the fine bottom ash particles. Totally, the recoverable amounts of Al, Cu and Zn in the MSWI bottom ash were estimated to be 36–170, 2.3–6.8, 7.1–27 thousand tons per year. For Fe, the reported magnetic recovery varied from 57% to 80% equaled 190–340 thousand tons Fe could be recovered from bottom ash. However, the majority of Fe in our research was found in the form of hematite, which is a diamagnetic mineral that is difficult to be recovered using common magnetic separation equipment (Lamers, 2008). Hence, it is better to recover Fe from MSW prior to incineration to avoid the metal oxidation. Alternatively, more advanced magnets capable of generating a higher magnetic density could be used to recover Fe from bottom ash.

3. Conclusion

The content and speciation of ferrous and non-ferrous metals, i.e. Fe, Al, Cu, and Zn, in bottom ash from MSWI were

determined and the main conclusions were as follows. (1) The mass fractions of Al, Fe, Cu and Zn in the MSWI bottom ashes were in the range of 18.9–29.2 g/kg, 25.5–32.3 g/kg, 0.7–1.0 g/kg and 1.6–2.5 g/kg, respectively, which were lower than those in MSWI bottom ash from developed countries; (2) 44.9–57.0 wt.% of Al and 55.6–75.4 wt.% of Fe were distributed in bottom ash particles that were smaller than 5 mm, likewise, 46.6–79.7 wt.% of Cu and 42.9–74.2 wt.% of Zn were concentrated in the fine ash particles smaller than 3 mm; (3) Al and Fe were

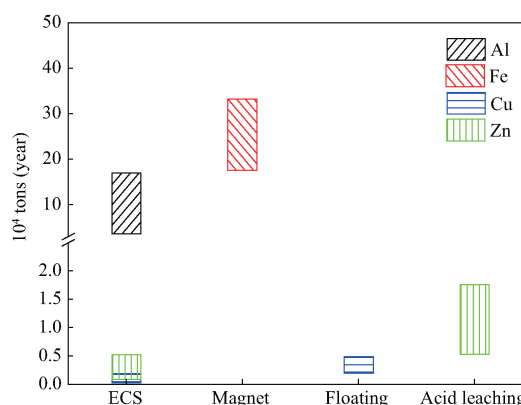


Fig. 10 – Recoverable metals from MSWI bottom ash in the year of 2015.

predominantly found in the bound to Fe–Mn oxides fraction and residual fraction, respectively, while the bound to organic matter fraction and bound to carbonate fraction were dominant components of Cu and Zn; (4) owing to the distribution characteristics of Cu and Zn in the MSWI bottom ash, the methods other than ECS, such as gravity separation, floating and acid leaching were suggested to be used to recover the metals from fine particles. More advanced magnets capable of generating a higher magnetic density was better used to recover Fe (mainly in the form of hematite) from bottom ash. The recoverable Al, Cu, Zn in the annually produced bottom ash were estimated to be 36–170, 2.3–6.8, 7.1–27 thousand tons respectively.

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