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Volatilization and leaching behavior of heavy metals in MSW incineration fly ash in a DC arc plasma furnace

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ABSTRACT

Three fly ash samples collected from different waste incinerators were vitrified using a direct current arc plasma furnace at 1250–1400 °C. The influence of water-wash extraction and wrapping pretreatment on the volatilization and leaching behavior of heavy metals was investigated. Results showed: After thermal arc plasma treatment, the volume reduction and weight loss of fly ash were in the range of 68.7–82.2% and 23.8–56.7%, respectively. The residual fractions (wt.%) of heavy metals in slag are in the following sequence: Cr < Ni < Cd < Pb < Cu < Zn. Water-washing could reduce the volatilization rate of heavy metals due to some volatile salts removed by washing, while wrapping of fly ash could most effectively resist heavy metals against volatilizing, especially for Zn and Ni. The possible CaO – Al$_2$O$_3$ – SiO$_2$ (CAS) ratio for successful melting of fly ash is suggested to be CaO in range of 20–48%, Al$_2$O$_3$ in range of 10–15%, and SiO$_2$ in range of 40–65%. Moreover, toxicity characteristic leaching procedure results showed that the leaching of heavy metals in slags was much lower than the standard limit of toxicity characteristic leaching procedure (TCLP).

1. Introduction

With economic development and accelerated urbanization, the generation of municipal solid waste (MSW) is continuously increasing at annual rate of about 8–10% in China. Incineration of MSW has become a top-priority technology choice in most cities in China, due to its volume reduction and power generation [1]. Besides, 61.67 million tons of MSW were disposed by incineration in 2015 [2], namely producing about 1.8 million tons of municipal solid waste incineration (MSWI) fly ash. The fly ash, defined as hazardous waste, contains quite a high level of heavy metals such as Zn, Cu, Pb, Cd, Ni, Cr. With a growing environmental concern on MSWI fly ash in China, the fly ash is not allow to landfill without treatment because of its potential risk to the environment, especially to groundwater and soil.

Generally, various treatment methods for eliminating the harmful impact of heavy metals of MSWI fly ash can be grouped into three catagories: (i) metal isolation using water-extraction and electro-dialytic; (ii) heat treatment, such as sintering, melting, or vaporization; and (iii) solidification/stabilization [3]. In China, most fly ash disposed by cement-based solidification, leading to 1.5–2 times of volume expansion, which probably raises a big burden on landfill sites.

Comparatively, melting can reduce the volume of fly ash by 80%, and destroy toxic organic compounds effectively [4]. However, the melting treatment, such as surface treatment, rotary kiln, and plasma, is an energy-intensive process.

Plasma melting is the most energy-intensive, demanding lots of electricity and generating non-toxic glassy slag after vitrifying incineration residues. Even though plasma melting is a high energetic process, thermal plasma furnaces were still widely studied to dispose hazardous materials as it produced glassy leaching-resistant slag, immobilizing the non-volatile heavy metals into an extremely stable glass matrix [4–6]. It finally eliminates the problems of the leaching of heavy metals into soil when the ash is buried. The molten materials with adequate physical properties can be used to make high quality materials with commercial value such as construction materials, artificial marble, permeable bricks, asphalt concrete, ornament and lightweight aggregate [5]. Undoubtedly, thermal vitrification technology is considered to be promising, but costly relatively. However, volatile components, acidic gases, heavy metals or other compounds would be unavoidable emitted with the flue gas and release into environment during the melting process [7–9]. The emission of volatile components leads to partial weight loss. It is a pity that very few studies focused on
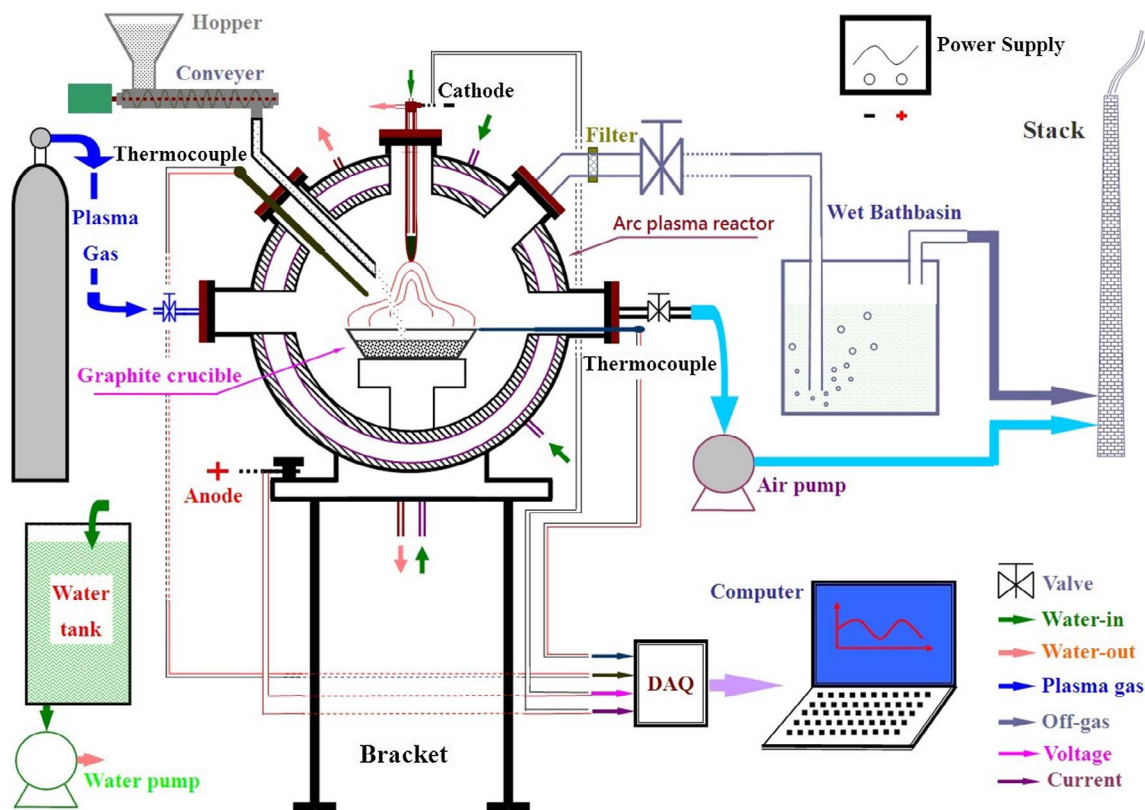

Fig. 1. Configuration of thermal DC arc plasma furnace system.

Table 1
Chemical composition (wt.%) of fly ashes by XRF.

(wt.%)	CaO	Cl	K_2O	Na_2O	SO_3	SiO_2	MgO	Fe_2O_3	ZnO	Al_2O_3
FA1	38.4	22.3	8.1	7.9	7.3	4.9	2.6	2.5	1.6	1.4
FA2	37.1	17.6	7.1	6.9	13.0	6.7	1.5	2.2	2.5	2.4
FA3	40.5	23.7	8.5	7.9	6.9	3.5	1.1	2.0	1.8	0.9

the effect of volatile components on the emitting of heavy metals during melting process, and how to prevent heavy metal from volatilizing. The study of wrapping fly ash by glass bottle has not reported in previous research. Moreover, problem of soluble salts drew attention of system analysis: washing fly ash removed 30% up to 95% of chlorine, and achieved high removal rates of 30.7–72.8% of Ca, Na, K, and Cl at liquid-to-solid rates (L/S) of 10, whereas Pb, Cd and some minor elements were removed by 10–30% [10–13]. It was mentioned stability and leaching properties of glassy slags would be improved because of more network structures in slag after washing process [5,14]. But the effect of water-washing on volatilization and leaching behavior of heavy metals was scarcely reported. It has once reported that addition of SiO_2 enhances the glassy amorphous phase to produce more

uniformly in slags [14,15], without any detailed interpretation. Many studies have been carried out on the toxicity of fly ash and leaching behavior of molten slag by different types of plasma furnaces.

The aim of this study was to assess the effect of pretreatment on volatilization and leaching behavior of heavy metals during thermal plasma melting fly ash, focusing on weight loss, volume reduction, residual fractions of target heavy metals and leaching behavior. In this paper, a 30-kW thermal direct current (DC) arc plasma furnace was used to vitrify MSWI fly ash with washed and wrapped pretreatment. The toxicity characteristic leaching behavior of heavy metals was explored using TCLP 1311 (US EPA 1311). The total content of target metals were analyzed by mixed acid extraction in microwave digestion system.

2. Materials and methods

2.1. Materials

The fly ashes (FA1-3) were collected from three MSWI plants in TJ (GPS: N39.17, E117.17), SZ (GPS: N23, E114), MC (GPS: N22.19, E113.55), respectively. These MSWI plants were selected as a
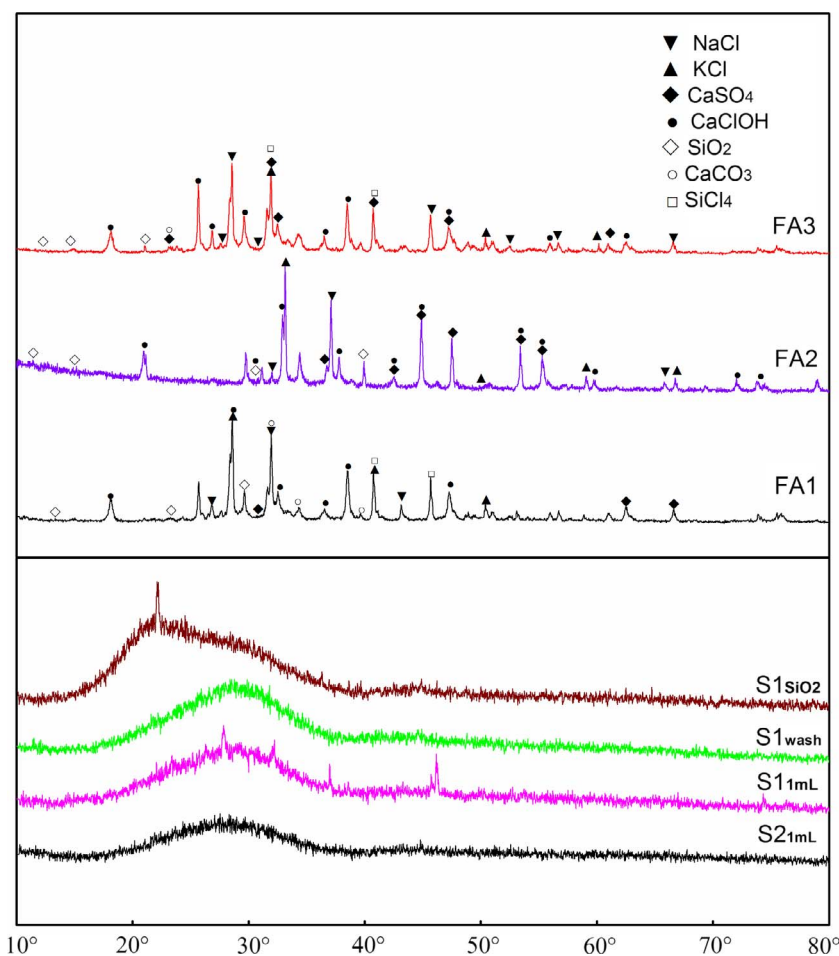
Table 2
The weight loss ratio of sample after melting (g).

Item	FA (a)	Silica additives (b)	Sum (c = a + b)	Slag (d)	Fly ash-Slag (e = d − b * (1 − r))	Weight loss (f = (1 − e/a) * 100%)
$FA1_{SiO2}$	18.90	26.25	45.15	36.16	11.34	40.0%
$FA1_{wash}$	16.99	18.16	35.15	30.11	12.95	23.8%
$FA1_{0.5\ ml}$	9.50	15.10	24.60	20.52	6.25	34.3%
$FA1_{1\ ml}$	15.60	18.20	33.80	23.97	6.77	56.7%
$FA1_{5\ ml}$	7.42	13.76	21.18	15.03	4.30	42.1%
$FA2_{1\ ml}$	15.25	18.13	33.38	26.03	8.90	41.7%
$FA3_{1\ ml}$	15.86	18.11	33.97	27.25	10.14	36.1%

Note: r was weight loss rate, 5.5% for SiO_2, 0.5 ml and 1 ml glass, and 22% for 5 ml glass bottles.

representative of the north, south and offshore of China. As waste characteristics were influenced by regions and people's living habits, it may also lead to different composition of fly ash. The waste incinerators in those three plants were martin grate furnace, SN type grate furnace and stoker furnace, respectively. Flue gas cleaning was performed by semi-dry absorption tower and activated carbon-fabric filter system. The flue gas was deacidified by spraying calcium hydroxide in semi-dry absorption tower, resulting in high calcium content in the samples. The fly ash was collected from semi-dry absorption tower and bag filter.

2.2. Thermal plasma system

The configuration of a thermal DC arc plasma furnace system was presented in Fig. 1. The thermal plasma system consisted of DC arc plasma furnace, power supply system, feed unit, working gas unit, cooling water unit and exhaust gas cleaning unit. The thermal plasma furnace, a stainless steel chamber, used by a 30 kW DC arc plasma, which is the core body of this plasma furnace. It was more steady and efficient than alternating current arc [6]. In this work, argon was used as carrier gas at a flow rate of 20 L min^{-1}, spiral to the furnace from both sides of the sight glass. The sample was in the graphite crucible with a graphite cover, and heated by the arc through the middle hole of graphite cover. The inorganic components of sample melted to form slag. The dioxins could decompose into small molecules by both ultraviolet radiation and heat from the arc [6,16,17]. The exhaust gas treated by gas cleaning devices.

2.3. Vitrification

The high calcium content leaded to low content of Si. To form good

glass crystal, proper ratio between CaO, SiO$_2$, Al$_2$O$_3$ is necessary [18–20]. Thus, addition of SiO$_2$ as agent is considered, and two different experiments designed. One is to add certain amount of SiO$_2$ (1.39 times of fly ash weigh) into FA1, ground, homogenized and finally sieved through a #50 sieve (namely FA1$_{SiO2}$), put into crucible for plasma treatment. The other is to fill fly ash into glass bottles with different volume (0.5 ml, 1 ml, 5 ml) for plasma treatment (namely FA1$_{0.5 ml}$, FA1$_{1 ml}$, FA1$_{5 ml}$, FA2$_{1 ml}$, FA3$_{1 ml}$). The slag products signed as S1$_{SiO2}$, S1$_{0.5 ml}$, S1$_{1 ml}$, S1$_{5 ml}$, S2$_{1 ml}$, S3$_{1 ml}$, respectively. All fly ash samples were dried in an oven at 105 °C till the weight not changed.

Moreover, to discuss the influence of soluble salts on stability and leaching behavior of heavy metal, FA1 washed by deionized water at L/S of 10 for 20 h for NaCl, KCl, etc. removal was carried out, named FA1$_{wash}$. After water washing, fly ash was dried at 105 °C till the weight not changed. Then FA1$_{wash}$ was added into 1 ml glass bottles for plasma melting, namely S1$_{wash}$.

The fly ash samples were vitrified at 1250–1400 °C for 25 min in the arc plasma furnace. Then the molten slag was air-cooling quenched in the furnace. The slag with dark appearance was vitreous and homogenous.

2.4. Analytical apparatus

The mineralogical investigations of fly ashes and glassy slags were determined by X-ray diffraction analysis (XRD) (D/MAX 2500) and scanning electron microscopy (SEM) (TDCLS4800) with EDX. The XRD investigations were conducted by a D/MAX 2500 using Cu Kα radiation between 2θ = 10° and 80° at a scanning speed of 5 °/min.

All glassy slag samples were weighed accurately to 40 mg, then extracted by an acid mixture of HNO$_3$, HClO$_4$ and HF (5:3:2, Volume) in
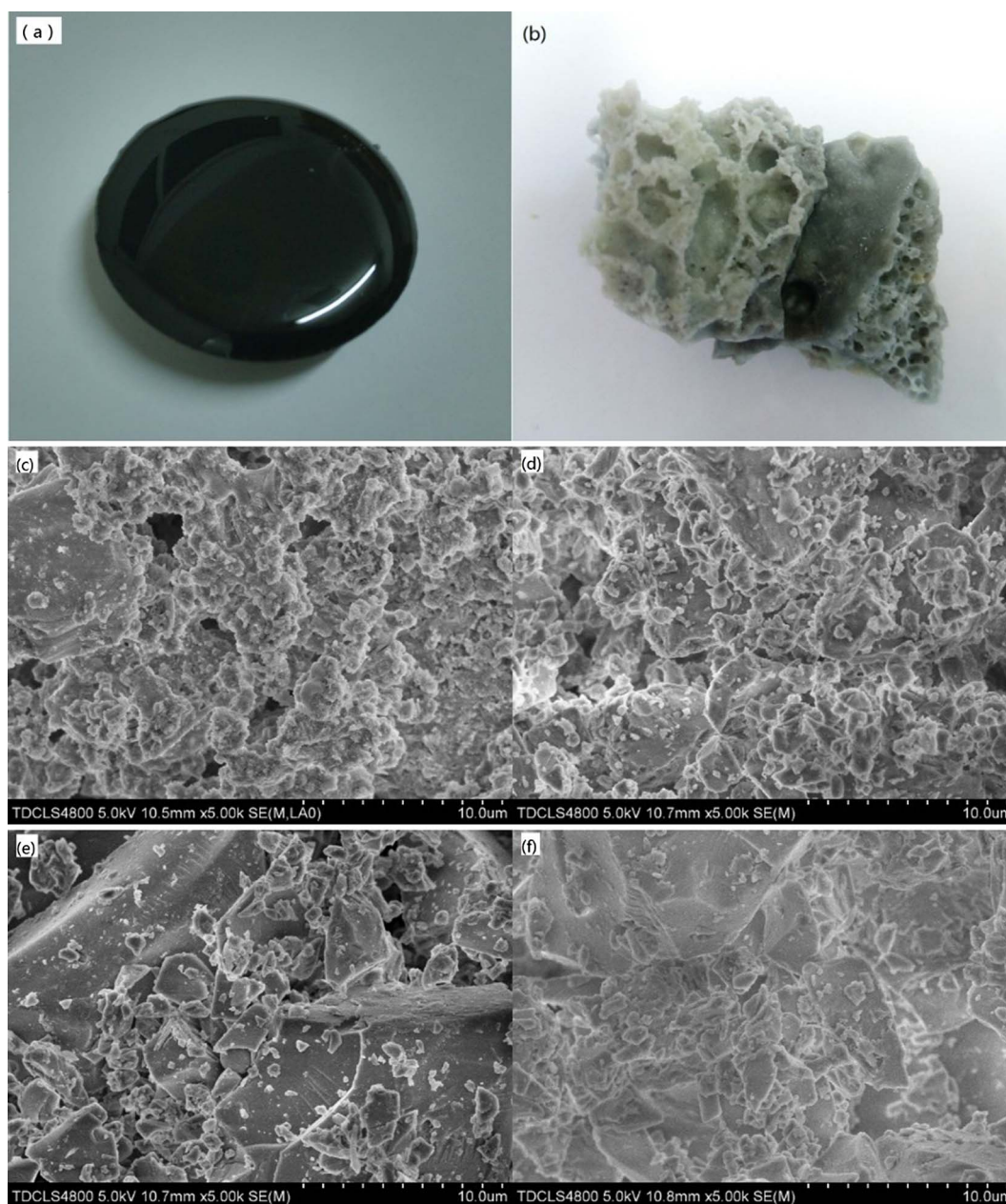
Fig. 3. Photograph of slag and SEM micrographs of fly ash and slag. (a) External appearance of $S1_{1\ ml}$; (b) External appearance of $S1_{SiO2}$; (c) SEM micrograph of FA1; (d) SEM micrograph of $S1_{SiO2}$;(e) SEM micrograph of $S1_{1\ ml}$; (f) SEM micrograph of $S1_{wash}$.

Table 3
The concentration of heavy metals in fly ashes and slags by microwave digestion.

Item	Test results (mg/kg)					
	Cr	Zn	Pb	Ni	Cu	Cd
FA1	615	10625	2041	204	988	190
FA2	467	19974	2834	140	922	185
FA3	580	11678	3228	118	1513	136.3
$S1_{SiO2}$	718.08	411.51	127.97	63.88	87.12	10.22
$S1_{wash}$	654.08	634.80	224.37	199.83	292.40	19.24
$S1_{0.5\ ml}$	2419.62	1452.12	445.97	259.92	154.90	45.62
$S1_{1\ ml}$	1765.51	1521.55	222.34	367.75	93.86	24.19
$S1_{5\ ml}$	1197.44	264.91	134.80	245.11	87.08	12.69
$S2_{1\ ml}$	1686.42	1052.45	2399.91	99.84	107.53	390.23
$S3_{1\ ml}$	1565.01	1405.15	693.23	122.71	146.43	87.26

microwave digestion system for 10 min. Eventually, all slags were soluble in the acids. Then the digested liquids were deacidified and analyzed by Agilent 7700X ICP-MS for the concentrations of target heavy metals (Cd, Cr, Pb, Cu, Zn, Ni).

The leaching behaviors of heavy metals in the fly ash and glassy slags were evaluated by toxicity characteristics leaching procedure (TCLP) according to US EPA method 1311. Acetic acid solution (pH = 2.88 ± 0.05) was used as the leaching liquid. The liquid-to-solid ratio was 20:1, and agitation time was 18 h with rotary tumbler at (30 ± 2) r/min. After extraction, the leachability analysis was examined by the Skyray ICP2060T for the target metals. Besides, the density of slag was measured by Archimedes's method.

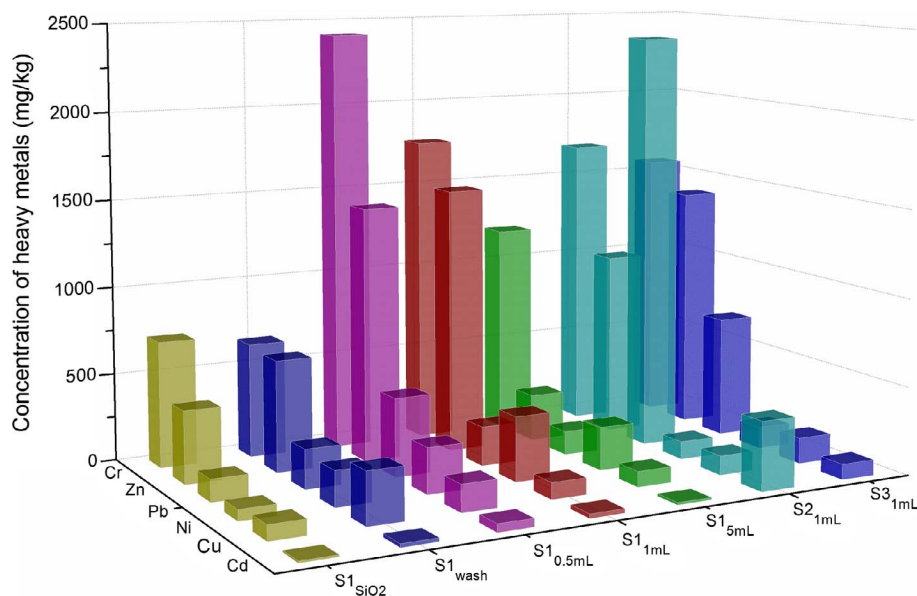The flue gas was determined by Laoying 3022, a comprehensive flue gas analyzer.

Fig. 4. The concentration of heavy metals in the slags by microwave digestion.

Table 4
Residual fraction of heavy metals found in the slag after melting (wt.%).

	Cr	Ni	Cu	Zn	Cd	Pb
S1$_{SiO2}$	116.8%	31.3%	8.8%	3.9%	5.4%	6.3%
S1$_{wash}$	106.4%	98.0%	29.6%	6.0%	10.1%	11.0%
S1$_{0.5\ ml}$	393.4%	127.4%	15.7%	13.7%	24.0%	21.9%
S1$_{1\ ml}$	287.1%	180.3%	9.5%	14.3%	12.7%	10.9%
S1$_{5\ ml}$	194.7%	120.2%	8.8%	2.5%	6.7%	6.6%
S2$_{1\ ml}$	335.1%	87.7%	15.9%	7.0%	47.2%	24.5%
S3$_{1\ ml}$	290.8%	84.6%	7.1%	9.0%	286.3%	74.3%

3. Results and discussion

3.1. Characteristics of fly ashes and glassy slags

The chemical compositions of fly ash samples were summarized in Table 1. The results were shown in terms of weight percent of oxide. Major contents of three fly ashes are similar: $(38.5 \pm 2)\%$ CaO, $(20.5 \pm 3)\%$ Cl, 5–10% of K_2O, Na_2O, SO_3, SiO_2, and some components less than 5% of MgO, Fe_2O_3, ZnO, Al_2O_3. Due to less $Ca(OH)_2$ used in desulfurization of FA2, Ca content in FA2 was lower and SO_3 higher than that in FA1 and FA3. The chlorine was originated from incineration of polyvinyl chloride and kitchen waste (mainly NaCl and KCl) [21], and nearly 99% exists in soluble chloride salt [22]. The contents of SiO_2 and Al_2O_3 were only 3.5–6.7% and 0.9–2.4%, respectively. Furthermore, the total heavy metals and organic materials accounted for 3.80%, 4.96% and 3.43% of three fly ashes, calculated by difference, respectively.

After vitrification, the volume reduction ranges from 68.7% to 82.2%. Table 2 showed the weight reduction ranges from 23.8% to 56.7%, which is supposed to the chloride salts volatilization, such as NaCl, KCl, $ZnCl_2$, $PbCl_2$, etc.

As presented in Fig. 2, three original fly ashes had the same crystalline components, such as NaCl, KCl, $CaSO_4$, CaClOH, SiO_2 and $CaCO_3$. Among them, $CaSO_4$, NaCl and KCl were mainly contributed by fabric filter bags, while CaClOH was the byproduct in desulfuration process. Similar results have been reported in other studies [23]. The XRD pattern of slag was quite different from that of fly ash. There were no crystalline peaks in the slag pattern, which indicated the slags were amorphous and glassy. The result was similar to other researches [4,5,8,14].

The FA1 directly melting by plasma failed to form glassy slags. The

reason might be high CaO content and correspondingly high melting temperature over 2200 °C. Usually, the plasma furnace temperature kept around 1250–1400 °C, much lower than the target melting temperature. Thus, no glass slag was formed. For the FA1 mixed with SiO_2 sample, the melting temperature decreased to 1450 °C, and honeycomb structure was formed for S1$_{SiO2}$ (Fig. 3b). For the FA1 filled in the glass bottles or water-washing samples, perfect glass slag was formed. Fig. 3a showed the external appearance of S1$_{1\ ml}$ with a smooth surface and compact character, indicating good physical and mechanical properties. It can be used as glass-ceramics raw material and potential construction materials. Fig. 3c, d, e and f represented the SEM micrograph of FA1, S1$_{SiO2}$, S1$_{1\ ml}$ and S1$_{wash}$, respectively. Fly ash has various particle sizes distribution and a loose structure with a flocculent surface. Compared to fly ash, the microstructure of slag was homogeneous and compact. The microstructure of S1$_{wash}$ was the most compact, followed by S1$_{1\ ml}$, which indicated water-wash process had a significant effect on the microstructure and performance of vitreous slag [5]. Besides, the density of S1$_{1\ ml}$ was about 2.5 g cm^{-3}, measured by Archimedes method.

3.2. Heavy metal volatilization

The concentrations of target heavy metals in fly ashes and slags, such as Cr, Zn, Pb, Ni, Cu and Cd, are described in Table 3 and Fig. 4. It can be seen that Cr and Ni were significantly enriched in slag. The residual fractions of Cr and Ni in glassy slags were approximately 1.3–3.4 times and 0.87–1.80 times of that in fly ash, respectively. It showed the thermal stability of Cr and Ni, which almost completely remained in slag after thermal plasma melting. However, the residual fractions of other target elements were extremely less, which indicated that they were largely volatilized. Two possibilities may be: the greater evaporation of heavy metal during vitrification, or incorporation of Si-O matrix. The former reduces the heavy metal content in slags, the latter increases resistance to HNO_3 so as not to be detected by microwave digestion method [22]. In this study, it is difficult to distinguish the reason either by evaporation or by incorporation into the Si-O matrix. Table 4, taking S1$_{0.5\ ml}$ as an example, proposes that the volatilization of heavy metals in slag presumably in the following sequence: Cr < Ni < Cd < Pb < Cu < Zn. Although in other slag samples the volatility order among heavy metals may change somehow, in general it compromise that Cr and Ni as low volatile metals, Cd and Pb as medium volatile metals, and Cu and Zn as easy volatile metals.
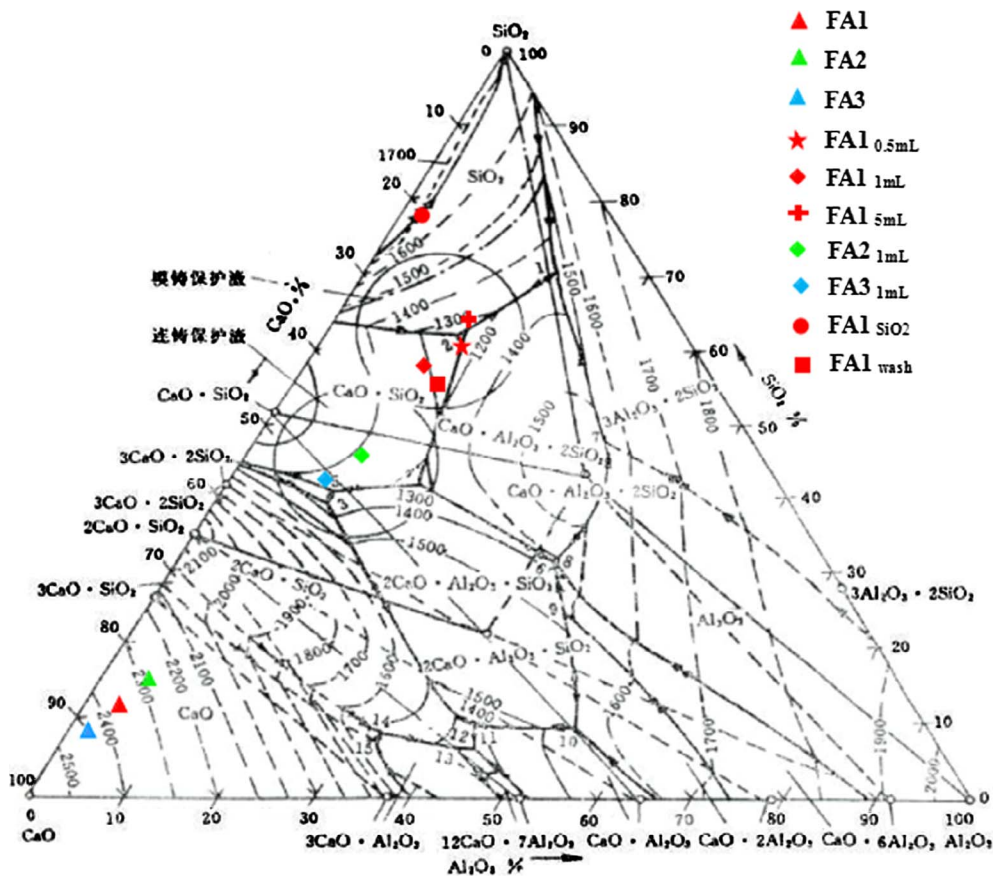
3.2.1. Wrapping influence

As shown in Fig. 4 and Table 3, the heavy metals concentrations in S1$_{SiO2}$ were lower than those in the slag from wrapped fly ash. Furthermore, the weight-loss ratio of FA1$_{SiO2}$ was 40.0% and weight-loss of FA1$_{1\ ml}$ was 34.28%, which indicated wrapping could effectively prevent heavy metals from volatilization and emission. Only through the molten glass membrane, the heavy metals could volatilize out theoretically. Especially, Cr and Ni in wrapper had a lower volatilization rate than other heavy metals.

The heavy metals of S1$_{1\ ml}$, S2$_{1\ ml}$ and S3$_{1\ ml}$ had similar residuals fractions respectively, which indicated physical barrier played a positive and effective role on solidifying heavy metals. However, 84.12–92.98% of Cu and Zn were emitted during plasma treatment process, since Cu and Zn are easy volatile element and escape easily. The Cl content of fly ash reached up to 17.6–23.7%, and glass membrane was difficult to restrain plenty of chlorine from volatilizing. It was interesting that other metals, which can form the chloride with low melting boiling point, had high residual fractions, taking Cr and Pb as an example. This is mainly due to the chemical reaction of Pb with SiO₂ and Al₂O₃ in the glass bottle to form Si-O-Al matrix so as to resistant Pb vaporization at high temperature. The equation can be shown [24]:

$$Al_2O_3 \cdot 2SiO_2 + PbCl_2 + H_2O = PbO \cdot Al_2O_3 \cdot 2SiO_2 + 2HCl.$$
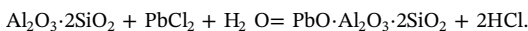
The increasing reason for Cr in slags results from the thermo-oxidization of the trivalent chromium Cr^{3+} to its hexavalent form Cr^{6+} [22].

3.2.2. Washing influence

A proportion of 23.25% fly ash (FA1$_{wash}$) was removed after washing process. As shown in Fig. 4, the components of heavy metals in S1$_{wash}$ were lower than those in S1$_{1\ ml}$, which may due to dissolution and removal of heavy metals after washing. As previous research reported [22], Cr was the most leachable element of less than 5.20%

getting removal in water extraction process, followed by Cd (0.77%), Pb (0.33%), Cu (0.05%), Zn (0.01%). The concentrations of Cr, Ni and Zn in S1$_{wash}$ were 37.05%, 54.34% and 41.72% of that in S1$_{1\ ml}$, respectively. The residual fractions of Cd and Pb were roughly similar in S1$_{wash}$ and S1$_{1\ ml}$. Cu content in S$_{wash}$ was 3.1 times of that in S1$_{1\ ml}$, which might incorporate into the Si-O matrix and enhance stability of Cu in the FA1$_{wash}$. Theoretically, the alkali chloride was leached after water-washing extraction, and the volatilization of heavy metal was inhibited [25]. In fact, some minor elements were removed by 10–30%, while the heavy metal content (Zn, Cr, Ni) in water-extracted fly ash was increased due to soluble salt leaching (Na, K, Cl, S) [26]. In addition, alkali metals and alkaline metal oxides, known as network modifiers, get removal of more than half during water washing process, which suppressed heavy metal evaporation during melting. In conclusion, washing extraction process could reduce the volatilization rate of heavy metals, either due to some volatile salts removed by washing, or by incorporate into the Si-O matrix in slags.

3.2.3. The influence of CaO – Al₂O₃ – SiO₂ (CAS) ternary phase on heavy metal stabilization

Melting point of fly ash, whose composition is listed in Tables 1 and 2, is influenced by the occurrence of slagging oxides (CaO, SiO₂, Al₂O₃, MgO, etc.) [27]. By calculating the percentage representation of oxides of metals with oxygen infinity (CaO, SiO₂, Al₂O₃) per 100%, taking FA1 as an example, the ratio among CaO:SiO₂:Al₂O₃ is 85.9: 11.0: 3.1. By using the thermal phase diagram of the system CaO – Al₂O₃ – SiO₂, it is clear that the ash melting point of FA1, FA2, and FA3 is around 2200–2500 °C (Fig. 5), which is quite high energy consuming and unavoidably failure operation to get melt and produce glassy slag.

In terms of energy, it is necessary to choose a suitable fluxing agent to decrease the ash melting point as low as possible. Various quantity of SiO₂, either in the form of direct addition or in the form of glass bottles (60% SiO₂, 15% Al₂O₃) as the fluxing agent designed to add to fly ash.
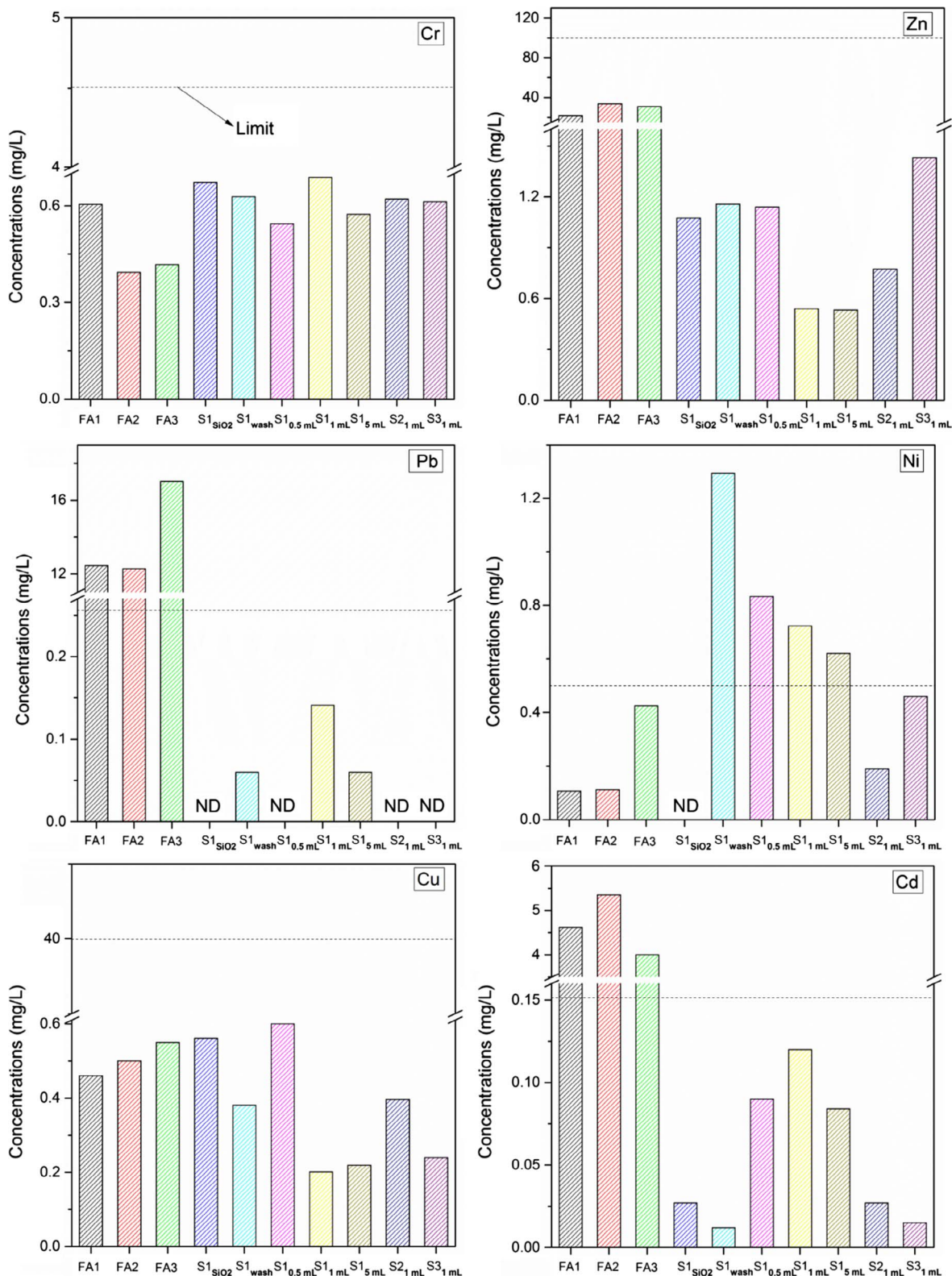
Fig. 6. The leaching test results of fly ash and slag using US EPA Method 1311 (ND – not detected; the horizontal dotted line means corresponding standard limits of GB16889-2008 in China).

Taking FA1$_{SiO2}$ as an example, pure SiO$_2$ addition decreased the melting point to approximate 1600 °C (Fig. 5), but still higher than the plasma furnace temperature of 1250–1400 °C. Therefore, FA1$_{SiO2}$ did not form perfect glass slag, as shown in Fig. 3b. For the fly ash filled in the glass bottles and water-washing samples, with both SiO$_2$ and Al$_2$O$_3$ addition, the melting temperature decreased to approximately 1200–1300 °C (Fig. 5), and the perfect glass slag was formed (Fig. 3a). To assure a failure-free operation of ply ash vitrification, the temperature was set 50–100 °C higher than the theoretical melting temperature. And the possible CAS ratio for successful melting is suggested to be CaO
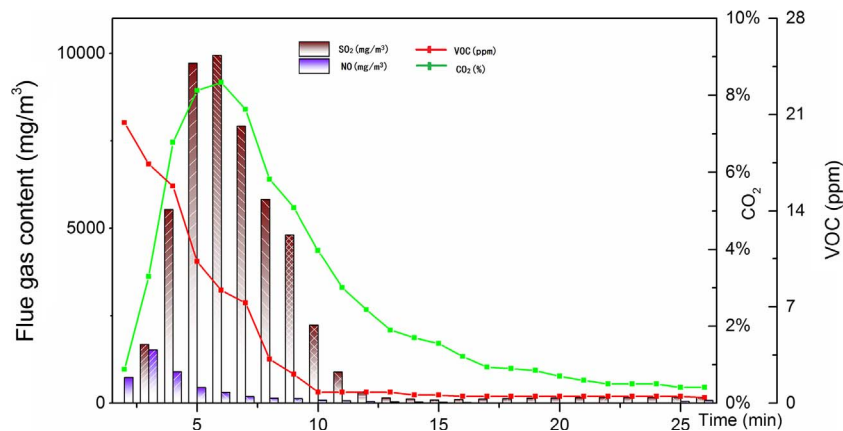
in range of 20–48%, Al$_2$O$_3$ in range of 10–15%, and SiO$_2$ in range of 40–65%. In the future study, adding a moderate amount of Al$_2$O$_3$ to adjust the ratio of CaO, SiO$_2$ and Al$_2$O$_3$, reducing the melting point and forming better glass slag, will be considered.

3.3. Toxicity characteristic leaching procedure results

Fig. 6 presents the heavy metal TCLP result of fly ash samples and slags using US EPA Method 1311. In previous studies, EPA TCLP regulatory levels were used to evaluate Cr, Pb and Cd. In this work, it is found all heavy metal leachabilities were far less than the TCLP limit. Furthermore, Chinese regulatory limits of national standard GB 16889-2008 for landfill requirements [28] were adopted as supplementary. Note should be given that the HJ299-2007 method should be followed for GB 16889-2008.

As shown in Fig. 6, Pb and Cd in the original fly ash exceeded the limits, while the others were below the limits. After vitrification, the heavy metals except for Ni were all below the limits for GB 16889-2008. The leaching amounts of Cr, Pb and Cd in slags were ranged from 0.544 mg/L to 0.688 mg/L, 0.012 mg/L to 0.12 mg/L, and 0 to 0.141 mg/L, respectively. For Zn, its leaching concentration varied from 0.531 mg/L to 1.431 mg/L. The leaching amounts of Zn, Cd and Pb were 3.3%, 1.15% and 0.03% of original fly ash on average. For Cu, the range of leaching concentration was 0.201–0.561 mg/L. For Ni, most slags had a TCLP leaching amount more than 0.5 mg/L of the regulatory limit, except for S2$_{1\ ml}$ and S3$_{1\ ml}$. It was caused by high residual fraction and strict standard of Ni. Furthermore, TCLP result of fly ashes showed that Zn in original fly ash had the strongest leachability, followed by Pb and Cd.

As a whole, the leaching values of Zn and Cu in slags were two orders of magnitude lower than the regulatory limits: about 0.95% and 0.93% of leaching standard, respectively. For Cr and Pb, the leaching amounts were nearly one order of magnitude lower than the limits: about 13.78% and 14.85% of leaching standard, respectively. For Cd, its leaching amount was equal to 35.48% of the standard of on average. No matter what kind of pretreatment has been adopted, the vitrification slag produced by plasma shows very low leaching rate, which proves the plasma technology is quite promising.

From Fig. 6, it is known all heavy metal leachabilities were far less than the TCLP limit. The result indicates that the thermal plasma melting is a good treatment method to treat fly ash. From the point of reducing the melting point, we know that wrapping the fly ash with glass bottle can minimize the melting point (Fig. 5), and obtain the perfect glass slag, which could be utilized as construction materials such as road-fill and concrete aggregate. The washing pretreatment method may cause higher running cost and potential ecological risk [10,19]. In summary, in the three treatment methods, the fly ash be wrapped with glass bottle is the best method.

3.4. Flue gas

Fig. 7 describes flue gas emissions of FA1$_{1\ ml}$ during vitrification process. As can be seen, the emission of SO$_2$ and CO$_2$ reached the highest concentration in the 6th minute simultaneously, namely 9941 mg/m^3 and 8.33% of exhaust emission, respectively. The SO$_2$ decompose mainly from CuSO$_4$ and other sulfates. Volatile organic compounds (VOC) and NO achieved their maximum output in the 1st and the 3rd minute, respectively, namely 22.9 ppm and 1520 mg/m^3. SO$_2$, VOC and NO no longer existed after 11 min. The emission concentration of CO$_2$ was under 1% in the 17th minutes. Fig. 7 also suggested, exhaust emission concentration basically completed melting process in the 11th minutes. Moreover, CO had a high concentration, more than 14575 mg/m^3 from beginning to end, and NO$_2$ was not detected.

4. Conclusions

Three kinds of MSWI fly ashes, from the northern, southern and offshore China, were vitrified in a plasma furnace, to investigate the volatilization and leaching behavior of heavy metals. Following conclusions could be made:

(1) After thermal arc plasma treatment, the volume reduction and weight loss of fly ash were in the range of 68.7–82.2% and 23.8–56.7%, respectively. The leaching amount of heavy metals in slags was much lower than the standard of TCLP and GB16889-2008 of China.

(2) Glass bottle wrapping had the best resistance of heavy metals to emit. The residual fractions (wt.%) of heavy metals in slag are in the following sequence: Cr < Ni < Cd < Pb < Cu < Zn.

(3) Washing extraction process could reduce the volatilization rate of heavy metals, either due to some volatile salts removed by washing, or by incorporate heavy metal into the Si-O matrix in slags. However, washing pretreatment is not suggested as an extraction step due to higher running cost and potential ecological risk.

(4) The possible CAS ratio for successful melting of fly ash is suggested to be CaO in range of 20–48%, Al$_2$O$_3$ in range of 10–15%, and SiO$_2$ in range of 40–65%.

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