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Thermal behaviour of ESP ash from municipal solid waste incinerators

Y. Yang [a,*], Y. Xiao [a], N. Wilson [a], J.H.L. Voncken [b]

[a] Department of Materials Science and Engineering, Delft University of Technology, Mekelweg 2, 2628 CD, Delft, Zuid Holland, The Netherlands
[b] Department of Geotechnology, Delft University of Technology, Stevinweg 1, 2628 CN, Delft, The Netherlands

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ABSTRACT

Stricter environmental regulations demand safer treatment and disposal of incinerator fly ashes. So far no sound technology or a process is available for a sustainable and ecological treatment of the waste incineration ashes, and only partial treatment is practised for temporary and short-term solutions. New processes and technology need to be developed for comprehensive utilization and detoxification of the municipal solid waste (MSW) incinerator residues. To explore the efficiency of thermal stabilisation and controlled vitrification, the thermal behaviour of electrostatic precipitator (ESP) ash was investigated under controlled conditions. The reaction stages are identified with the initial moisture removal, volatilisation, melting and slag formation. At the temperature higher than 1100 °C, the ESP ashes have a quicker weight loss, and the total weight loss reaches up to 52%, higher than the boiler ash. At 1400 °C a salt layer and a homogeneous glassy slag were formed. The effect of thermal treatment on the leaching characteristics of various elements in the ESP ash was evaluated with the availability-leaching test. The leaching values of the vitrified slag are significantly lowered than that of the original ash.

1. Introduction

Ash disposal and landfill are becoming an important environmental issue, especially for the region with limited disposal area. The air pollution control (APC) residues from MSW incinerators are classified as hazardous waste, including boiler ash, ESP ash and filter cake. The ESP ash is collected by an electrostatic precipitator as the second step after the boiler ash collection. The thermal behaviour of bottom ash and boiler ash has been investigated and published in the authors' previous work [1,2]. Nowadays, cement solidification is usually applied for the stabilisation treatment of the ESP ash. However, this technique is limited due to the high concentrations of chlorine compounds present in the forms of dioxins and alkali chlorides. By cementation or chemical treatment, it is difficult to destroy or stabilise dioxins [3], and alkali chlorides hinder hydration of cement. Even though cement solidification-landfill is considered to be the most convenient and inexpensive method of the fly ash disposal, for long-term sustainability the best method for the ash treatment is recycling and reuse. Landfill causes many environmental problems such as soil and groundwater pollution. The increasing tendency of the MSW incineration or waste-to-energy (WTE) processing requires appropriate option for the fly ash treatment, and the vitrification is one of the most promising solution among the various available technologies. It has the advantages of high destruction efficiency of organics and toxic compounds, excellent immobilisation of environmental harmful elements, and significant volume reduction. The disadvantage of the thermal processing is the high-energy cost.

In the literature, the leaching behaviour of the fly ash was widely investigated [4–8], and the effects of chloride additives and oxidation on the volatilisation of heavy metals during waste combustion were also studied [9–11]. Various techniques for the fly ash treatment were reported [12–15], including washing and chemical precipitation, stabilisation with additives and thermal processing. For the thermal treatment, the effort was focused on the immobilisation of heavy metals (Pb, Zn, Cu and Cd) and some other elements (Al, Cr) [16–18] as well as the environmental properties of the vitrified slag [6,19–23].

Previous studies show that Cu and Zn as heavy metals are present in a relatively high concentration in the ESP ash, and the concentrations of Pb and Cd are lower [4]. However the concentration of Pb and Cd in the eluate exceeds the legislation limits. Another study indicated that the leaching solution of fly-ash in water becomes more basic due to the alkaline nature of the fly ash, with a pH of approximately 9.9 [5]. Cd, Cu, Pb and Zn have a high acidic leachability. It was found that the redox potential is of insignificant influence on the leachability of the heavy metals. Heavy metal removal by volatilisation of the ESP ash is dependent on temperature and time. Zn exhibits a low grade of volatilisation if the compound with Zn is another element than chlorine [7]. Chlorine-compounds with heavy metals have relatively low boiling points and high vapour

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* Corresponding author. Tel.: +31 15 2782542; fax: +31 15 2786730.
E-mail addresses: Y.Yang@CiTG.TUDelft.NL, Y.Yang@ta.tudelft.nl, y.yang@tudelft.nl (Y. Yang).

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pressure. That is the reason why these metal chlorides are more volatile [10]. Previous experiments showed that in an inert environment the Cd-bearing salts volatilise more quickly than in an oxidized environment [11].

In the present research, the ESP ash taken from AVR, the largest waste incineration company in the Netherlands was characterised, thermal-treated and vitrified under controlled atmosphere. The thermal behaviour of the ash was investigated with differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). The vitrified products were analysed and examined with X-ray fluorescence (XRF) and X-ray diffraction (XRD). Leaching tests were conducted to determine the leaching availability of elements from the vitrified products, and compared to that from the original ash. The objective of the research is to provide necessary fundamental knowledge for the new route development of thermal processing and recycling of municipal solid waste incineration residues.

2. Experimental

2.1. ESP ash sampling

In the Netherlands about 80 kt/year fly ash is generated from 11 MSW incinerators with a total incinerated waste of more than 5500 kt in 2006 [24]. AVR in Rozenburg has 7 MSW incineration lines with a total incinerated waste of 1100 kt/year. Line 0 has a separate horizontal boiler from the combustion furnace consisting of reheaters, superheaters and economizers, and the ashes were collected separately. Lines 1–6 have the vertical boiler built within the combustion furnace, where the ashes are discharged and mixed with the bottom ash. In the line 0 the off-gas temperature decreases from the 1st superheater (OVO1) of 600–700 °C to the 2nd superheater (OVO4) of 500–600 °C, and drops to about 180 °C at the end of the economizer (ECO1). Line 0 has only one ESP, while lines 1–6 have 2 separate ESPs (EF-OLD and EF-NEW) in each line.

The ashes were sampled from both the new line ESP (line 0, only 1 ESP) and old lines (2 ESPs in each line), as shown in Fig. 1. In addition, a mixture sample was taken after the 2nd ESP (EFNEW-L1/6) from all 6 lines (180 °C). The off gas temperature in the first ESP is over 90 °C higher than that in the 2nd ESP for lines 1–6. Table 1 shows the location, sample name and the gas temperature in the location and moisture content of all the fly ash samples. Furthermore, various boiler ashes have also been sampled and the research on the thermal and leaching behaviour have been published previously by the authors [2].

2.2. Thermal processing and vitrification

Three types of tests were conducted to investigate the thermal behaviour of the ESP ash: (1) DTA/TGA analysis in a small furnace (thermal balance), (2) TGA tests in a larger tube furnace, and (3) thermal treatment and vitrification tests in a larger chamber furnace. Thus the thermal behaviour of the ash samples in different sizes and under different furnace configurations could be compared.

2.2.1. DTA/TGA test in a small scale furnace

Thermal analysis with a Netzsch STA 409C thermal balance was conducted under nitrogen atmosphere with a flow rate of 3 l/h, for combined TGA and DTA tests. The ESP ash sample of 50 mg was charged in an alumina crucible. Alumina powder was used as reference material. The furnace was gas-tight, and was heated to 1400 °C with a rate of 10 °C/min, and equilibrated at 1400 °C for 1 h. The TGA and DTA curves were recorded for the thermal analysis.

2.2.2. TGA test in a larger tube furnace

Larger scale TGA tests were carried out in an electrical resistance tube furnace from room temperature to 1400 °C for the ESP ash sample of EFNEW-L1/6. About 12 g ESP ash (as loose powder or compressed into tablets with pressure of 3.5 bar/cm^2) was charged in an alsint crucible with outer diameter of 50 mm, inner diameter of 46 mm and height of 80 mm, and placed in the constant temperature zone of the furnace. Nitrogen gas with a flow rate of 20 l/h was supplied to prevent the sample from oxidation. The temperature of the furnace was measured with a Pt – PtRh10 thermocouple.

Under the same conditions as for the small-scale test, the sample was heated with a rate of 10 °C/min, and kept at 1400 °C for 1 h. The weight loss of the sample was recorded by using a balance mounted on the bottom of the furnace. After the experiment, the sample was left to cool down in the furnace under nitrogen atmosphere. The compositions of the heat treated and vitrified products were examined.

2.2.3. Heat treatment and vitrification in a chamber furnace

Larger samples of about 36 g of the ESP ash were melted in a Carbolite chamber furnace in alsint crucibles. The furnace was flushed with nitrogen gas with a flow rate of 80 l/h. The heating rate was set at 10 °C/min and the final temperature was controlled to be 900 °C for sintering and 1400 °C for vitrification for 1 h, respectively. After the test, the crucible was taken out of the furnace and quenched

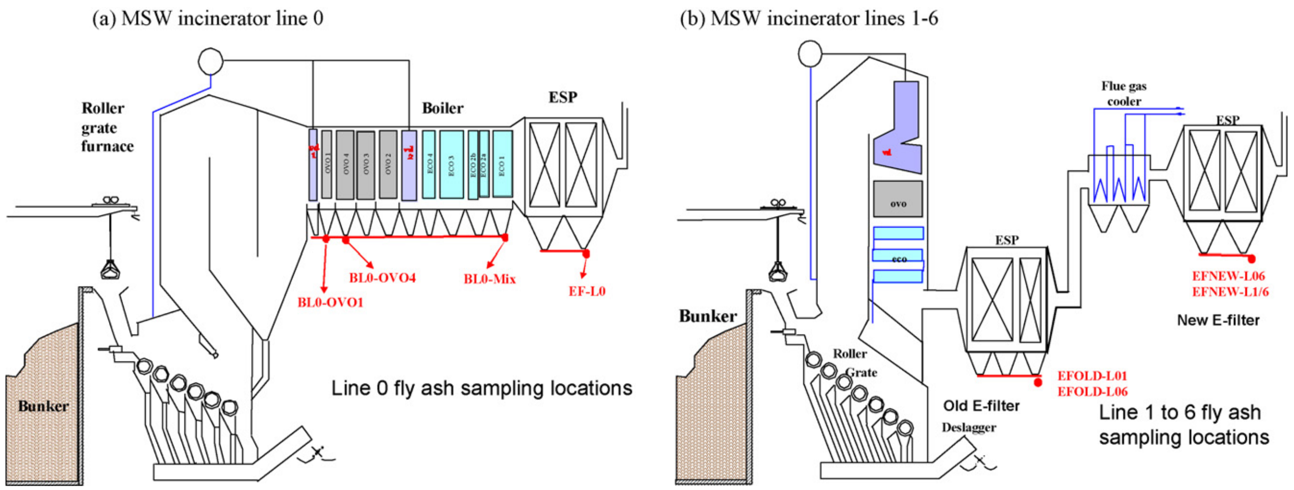

Fig. 1. Fly ash sampling locations: (a) line 0 is with a horizontal boiler and a single ESP (new) and (b) lines 1–6 are with vertical boilers, an old ESP and a new ESP in each installation. (a) MSW incinerator line 0 and (b) MSW incinerator lines 1–6.

Table 1
ESP ash samples from both the new line (line 0) and old lines (line 1–6).

Sample	Location	Gas temperature	Moisture (wt%)
EF-L0	ESP of line 0 (1 ESP only)	180	0.38
EFOLD-L01	Old/1st ESP, line 1	270 °C	0.5
EFOLD-L06	Old/1st ESP, line 6	330 °C	1.5
EFNEW-L06	New/2nd ESP, line 6	180 °C	3.5
EFNEW-L1/6	New/2nd ESP, line 1–6 mixture	180 °C	3.0

with nitrogen gas. The crucibles and the samples were weighed before and after the experiments and the total weight loss in the end of the heat treatment was determined. However, no weight loss curves were obtained because of the absence of the thermal balance in the chamber furnace.

2.3. Leaching tests

The Dutch standard for availability test NEN 7341 was used to evaluate the immobilisation of inorganic compounds from high temperature vitrification [25]. The procedure was described in the previous publication [2]. The results of the leaching tests give maximum quantity of each inorganic element that can leach in an extreme circumstance.

2.4. Analysis

The ESP ash and the thermal treated or vitrified slag samples were analysed with XRF and XRD. The selected elements in the leachate from the leaching tests were determined with ICP-OES.

3. Results and discussion

Thermal behaviour of the various ESP ashes without pre-treatment has been investigated under laboratory conditions. The leaching behaviour of the ash before and after thermal treatment has been compared.

3.1. ESP ash characterization

The composition of the ash was determined with XRF and is given in Table 2. The sum of the analysed elements amounts to slightly over 80 wt% with XRF, due to the presence of non-detectable elements of C, N and O. The analyses show that Cl, K, Na, S, Ca, Zn and Si have the higher concentration in the ESP ash, followed by Pb, Fe, Al, Mg, etc. It contains significant amount of heavy metals such as Zn, Pb, Sn, Sb, Cu and Cd. In general, the ESP ash contains higher chlorine and heavy metals than that in the boiler ash [2].

Comparing Table 2 with Table 1 it can be observed that the off-gas temperature has direct effect on the contents of alkali salt and volatile heavy metals: the higher the temperature the lower the salt and heavy metal contents. On the contrary, the slag forming elements such as Si, Ca, Mg and Al increase with the off-gas temperature. The existing forms of the heavy metals present in the fly ash could not be identified, either due to the amorphous structure of the compounds, or due to the low concentrations of the compounds.

The phase constitution was analysed with XRD and EMPA for selected representative samples. Fig. 2 illustrates the XRD analyses for the mixture ESP ashes from the 2nd ESP of lines 1–6 (EFNEW-L1/6). Fig. 3 illustrates the morphology and mineralogy of the ESP ash (EFNEW-L1/6), and the compositions of the major ash particles were qualitatively analysed with the electron probe micro-analysis (EPMA). Other ESP ash samples have similar mineralogy, but relative amount of different minerals vary from sample to sample which is mainly influenced by the locations and local gas temperature. The XRD and EMPA analyses indicates that the ESP ash is a mixture of fine inorganic compounds, and the detected crystalline phases include chlorides, sulphates and oxides, for example NaCl, K_2ZnCl_4, $CaSO_4$, $K_3Na(SO_4)_2$, $Na_2Mg(SO_4)_2$, and $CaAl_2SiO_6$. In addition, it also contains certain amount of un-burnt and partially burnt organic waste, which cannot be determined with XRD and XRF.

3.2. Thermal behaviour of the ESP ash

Thermal treatment of ESP ashes were conducted in three different type of furnaces: (1) small scale thermal analysis (thermal balance, continuous DTA/TGA measurements), (2) larger scale vertical tube furnace (continuous weigh loss monitoring TGA tests), and (3) larger scale chamber furnace without continuous monitoring.

Before thermal treatment, all the ESP ash was dried in an oven at 105 °C for 48 h, and the moisture contents were determined. The moisture content varies from about 0.4% for the ESP ash from the line-0 (EF-L0), to 3.5% for the ash from the 2nd ESP of line-6 (EFNEW-L06), as is shown in Table 1.

3.2.1. DTA/TGA measurements in the thermal balance

Fig. 4 shows the DTA/TGA curves of the mixture ash powder from 2nd ESP of lines 1–6 (EFNEW-L1/6). Other ESP ashes have similar behaviour in general, but the height of thermal peaks and weight losses differ from sample to sample. Taking the mixture sample EFNEW-L1/6 as an example (shown in Fig. 4), with increasing temperature the ESP ash experiences several high temperature reactions, which can be approximately classified into 4 phases.

- The first phase of pore water evaporation starting from room temperature to about 250 °C. Apart from loss of moisture, possible loss of volatile elements may also occur.
- From 250 °C to about 700 °C, little activity can be observed from the DTA curve, with a slight weight loss most probably due to the volatilisation and destruction of various organic pollutants in the ash.
- When further increasing temperature, there are two major reaction regions in the range of 700–900 °C and 900–1200 °C,

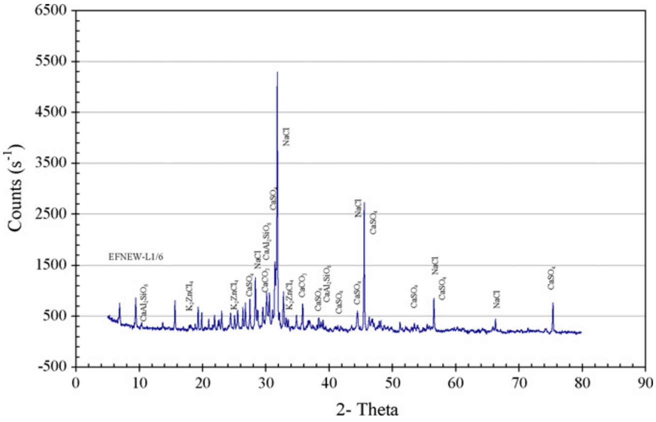

Fig. 2. The major crystalline phases identified with XRD analysis for the new ESP sample mixture of line 1–6 (EFNEW-L1/6).

Table 2
Concentrations of the elements in the original ESP ash samples.

Element	ESP ashes (wt%)				
	EF-L0	EFOLD-L01	EFOLD-L06	EFNEW-L06	EFNEW-L1/6
Na	7.58	15.5	6.99	12.5	13.4
K	8.18	12.5	7.01	14.6	14.0
Rb	0.02	0.03	0.02	0.04	0.04
Mg	1.28	0.83	0.97	0.52	0.64
Ca	21.05	11.3	19.6	8.65	7.87
Sr	0.08	0.04	0.07	0.04	0.04
Ba	0.17	0.10	0.16	0.091	0.10
Ti	1.59	0.67	2.29	0.57	0.54
Zr	0.04	0.02	0.04	0.01	0.01
Cr	0.10	0.05	0.11	0.06	0.05
Mo	0.03	0.03	0.02	0.04	0.04
Mn	0.09	0.09	0.13	0.06	0.07
Fe	1.91	0.82	2.78	1.65	2.25
Ni	0.01	0.03	0.03	0.02	0.02
Cu	0.22	0.25	0.22	0.41	0.41
Zn	3.80	4.94	3.89	6.69	6.52
Cd	0.06	0.14	0.06	0.20	0.19
Sn	0.32	0.45	0.32	0.67	0.63
Pb	0.99	1.47	1.10	2.76	2.73
Sb	0.32	0.32	0.24	0.39	0.42
Al	3.39	1.44	3.70	1.82	1.56
Si	8.79	3.66	10.7	4.30	3.97
P	0.79	0.49	0.63	0.44	0.44
S	4.65	5.83	6.35	9.88	10.8
F	0.89	0.39	0.58	0.38	0.42
Cl	15.12	23.4	11.2	16.5	15.7
Br	0.39	1.15	0.37	0.57	0.59

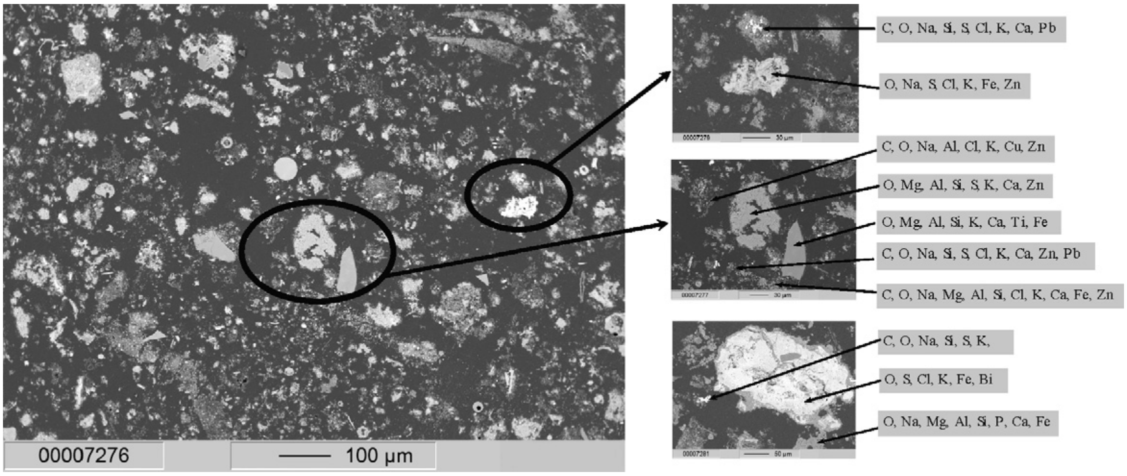

Fig. 3. Microstructure of the ESP ash EFNEW-L1/6.

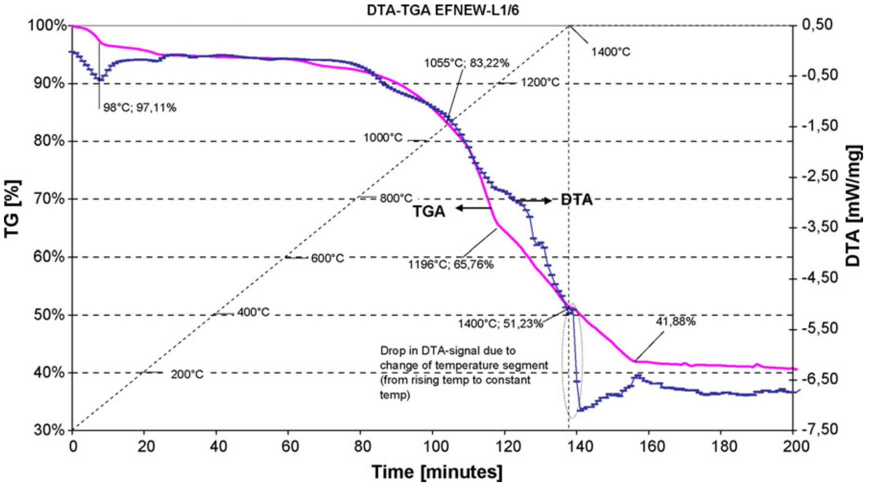

Fig. 4. DTA/TGA curves of the ESP ash under rising temperature (Netzsch STA 409C). Heating rate is indicated by the dashed line.

Table 3
Chemical composition of the mixed ESP ash (EFNEW-L1/6) before and after thermal treatment.

Elements	Cl	K	Na	S	Ca	Zn	Si	Pb	Fe	Al
EFNEW-L1/6 ash (%)	15.7	14.0	13.4	10.8	7.87	6.52	3.97	2.73	2.25	1.56
Treated at 900 °C (%)	13.6	14.4	11.0	11.5	10.3	5.83	4.45	1.25	3.47	2.06
Vitrified at 1400 °C[a] (%)	0.31	3.14	5.06	0.78	14.7	11.0	16.8	1.46	9.26	12.1

Elements	Mg	Sn	Br	Ti	P	Sb	F	Cu	Cd	Bi
EFNEW-L1/6 ash (%)	0.64	0.63	0.59	0.54	0.44	0.42	0.42	0.41	0.19	0.17
Treated at 900 °C (%)	0.76	0.66	0.46	0.64	0.50	0.43	0.66	0.38	0.15	0.13
Vitrified at 1400 °C[a] (%)	1.42	1.56	–	1.71	0.87	0.90	0.23	0.19	0.014	0.045

Elements	Ba	Mn	Cr	Rb	Mo	Sr	Ni	Zr	Ag	Se
EFNEW-L1/6 ash (%)	0.10	0.072	0.049	0.040	0.038	0.035	0.018	0.013	0.011	0.009
Treated at 900 °C (%)	0.11	0.089	0.055	0.041	0.041	0.041	0.019	0.016	0.012	–
Vitrified at 1400 °C[a] (%)	0.10	0.18	0.071	0.005	0.036	0.056	0.038	0.043	–	–

[a] Vitrified: the oxide slag only.

respectively. Up to 900 °C, there is significant weight loss of lead, chlorine, sodium, zinc, etc. as shown in Table 3 from the larger scale tube furnace tests.

- At further higher temperatures, there is a dramatic weight drop, with a loss of about 50 wt% at 1400 °C for FNEW-L1/6, which was largely due to the volatilisation of the un-burnt organic residues, the chlorine and sulphate compounds, and heavy metals. The total weight loss is about 60%. The salt components were melted and formed a salt layer on the surface, which may continue to evaporate under the present experimental conditions.

To identify the thermal behaviour difference among different ESP ashes, DTA/TGA continuous analyses were conducted for all other ash samples. Figs. 5 and 6 show the DTA and TGA curves of other ESP ash samples.

3.2.2. TGA tests in the tube furnace

Fig. 7 shows the effect of compactness on the thermal behaviour of the ESP ash in the tube furnace under inert atmosphere. Comparing the weight loss curves with that in Fig. 4 in the small-scale furnace, the trend of the weight change is similar, while the weight

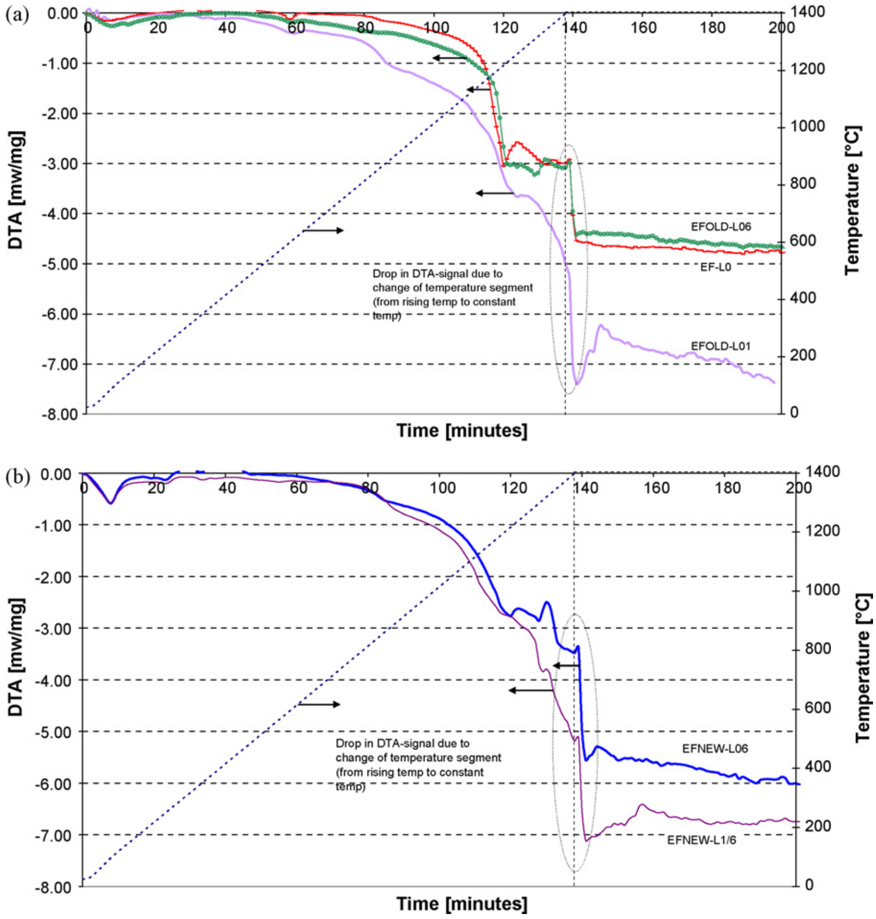

Fig. 5. Comparison of thermal behaviour of different ESP ashes: (a) DTA curves of ashes from 1st ESP (lines 1 and 6) and new line (line 0) and (b) DTA curves of ashes from 2nd ESPs (line 1 vs. line 1–6 mixture).

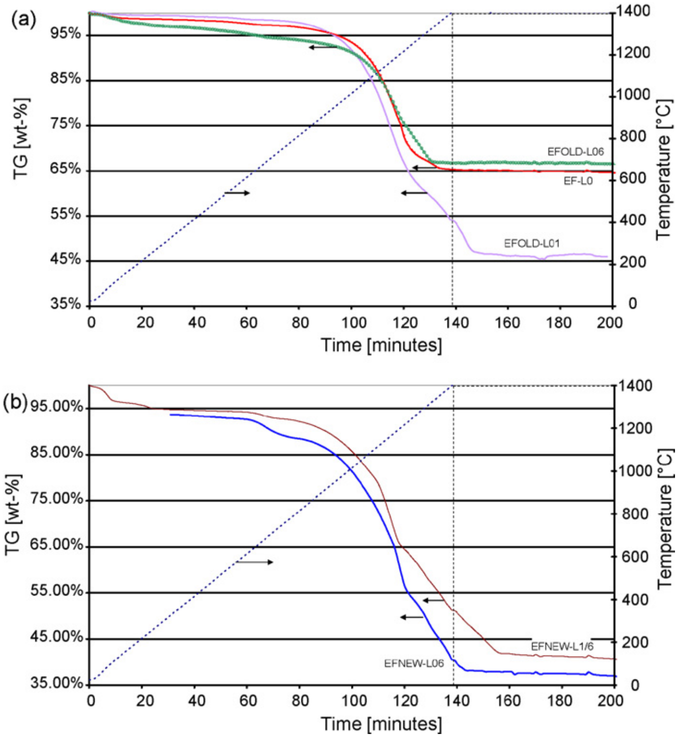

Fig. 6. Comparison of weight changes of different ESP ashes: (a) TGA curves of ashes from 1st ESP (lines 1 and 6) and new line (line 0) and (b) TGA curves of ashes from 2nd ESPs (line 1 vs. lines 1–6 mixture).

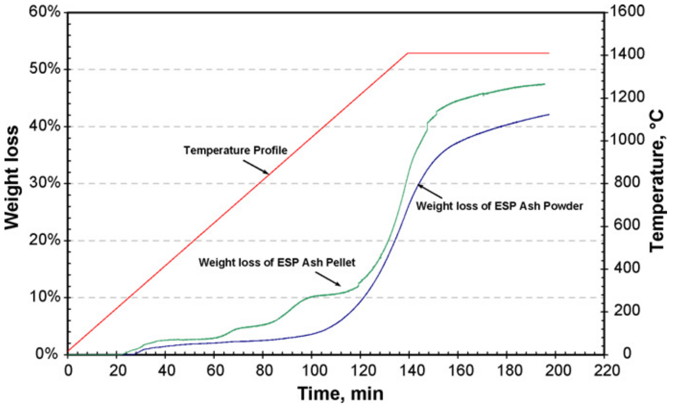

Fig. 7. Thermal behaviour of the ESP ash under rising temperature (tube furnace).

loss tends to be somewhat higher in the smaller furnace. On average, the melting tests conducted in the chamber furnace gives a comparable weight loss with that in the tube furnace. The total weight loss is about 42% for the loose powder, and 48% for the ash tablets in the tube furnace. It seems that the particles interfacial reactions play substantial role during the thermal treatment of the ESP ash.

From the observation of the tests from chamber furnace, at 600 °C the ash has sintered. A salt layer was formed at 1200 °C, but the ash was not yet melted. At 1300 °C, the ash started to melt, which can also be seen from the DTA peaks at about 1300 °C in Figs. 4 and 5. At 1400 °C, the ESP ash has vitrified, and molten salt and slag layers have formed, as can be seen in Fig. 8.

Table 3 shows the chemical compositions of the mixed ESP ash before and after thermal treatment. According to the composition changes, it can be seen that high volatile elements or compounds containing such as Cl, Br, S, Cd, Na, K, F, and Pb have higher mass loss in the tested ash sample. In addition, calcium bounded as $CaSO_4$ has also relatively high mass loss. The elements such as Al, Si and Fe, etc. have enriched in the vitrified slag phase due to the reduced total mass of the ash. In addition, the slightly dissolution of the alumina crucible also contributes to the significant increase of Al element in the vitrified slag. Chemical compositions of the ashes after thermal treatment are the direct XRF analyses without compensation due to the sample weight loss. For estimation of accurate loss of the individual element, the sample weight loss needs to be taken into account.

3.3. *Achieved immobilisation*

The average results of the ICP–OES analysis of the leachate are listed in Table 4. The immobilisation efficiency defined in Eq. (1) was calculated for each element. In general, it can be concluded that all leaching values of slag are significantly lower than those of the original ash.

$$\eta_i = \frac{\text{Leaching value of element } i \text{ in the ESP ash} \\ - \text{Leaching value of element } i \text{ in the vitrified oxide slag}}{\text{Leaching value of element } i \text{ in the ESP ash}} \qquad (1)$$

Here η_i represents the immobilisation efficiency of element *i* after vitrification. The standard leaching tests were based on 16 g dried samples, which were finely ground and screened into less than 125 μm [2]. It should be emphasized that this calculation was based on an equal mass. The contribution of the volatilisation of the volatile elements during the thermal treatment was not taken into account. Considering the weight loss of the ash samples during vitrification, the effect of volatilisation can be quite significant, especially for the volatile elements like heavy metals.

The conditions for maximum immobilisation may be different for different elements. Through vitrification, the achieved immobilisation efficiency as evaluated with the Dutch NEN 7341 test are over 90% for K, Na, Cd, Zn, Cu and Pb; 80–90% for Ca and Sr; 70–80% for Mn, Mg and B; and 40–60% for Al, Sn and Sb. Silicon has very low immobilisation efficiency of only 12.8% similar to Ti and Ba,

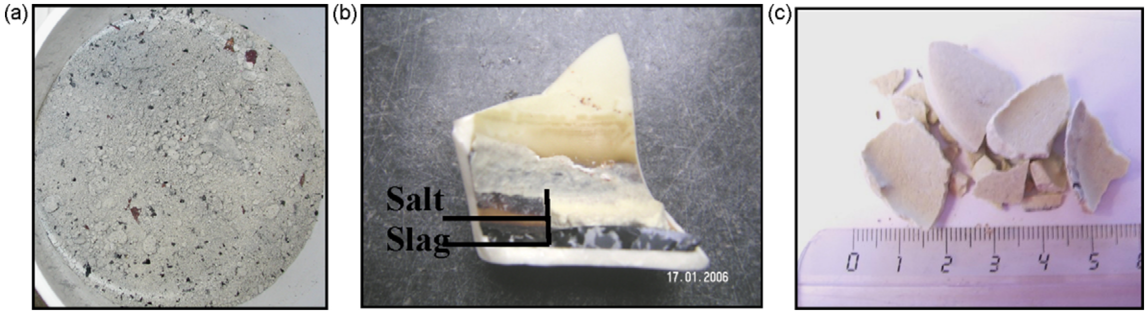

Fig. 8. ESP ash (EFNEW-L1/6) before and after thermal treatment: (a) ash tablets, (b) vitrified ash, and (c) the salt phase.

Table 4
The average leaching availability of ESP ash EFNEW-L1/6 and the vitrified oxide slag (1400 °C), and the achieved immobilisation efficiency.

Elements	Availability (mg/kg ds)		Immobilisation efficiency (%)	Immobilisation efficiency (%)	
	EFNEW-L1/6 ash	Vitrified slag		Boiler ash [2]	Bottom ash [1]
K	78,989	2129	97.3	92.0	NA
Na	70,396	2220	96.8	95.2	95.2
Ca	32,403	5046	84.4	91.4	98.3
Zn	16,253	1514	90.7	95.7	97.5
Mg	2319	693	70.1	50.9	87.8
Si	1967	1716	12.8	87.5	92.0
Al	1408	635	54.9	83.6	95.5
Cu	1192	35	97.1	92.9	>98.6
Cd	761	6	99.2	>71.9	>96.7
Pb	667	23	96.6	>78.7	80.4
Mn	131	38	71.0	79.2	97.8
Sr	79	9	88.6	>96.4	>96.5
Sb	64	38	40.6	>58.8	NA
Sn	51	27	47.1	>82.8	NA
B	36	9	75.0	77.0	>92.3
Ba	26	22	15.4	52.8	92.7
Ti	6	<5	16.7	25.1	NA

possibly caused by the dissolution of other elements in the silicate which breaks the bond of the silicate network structure, as the formation of $(MgFe)_2SiO_4$ and $ZnAl_2O_4$. The low leaching value of the silicon in the original ash sample is due to the stable silicate form of the silicon present in the ESP ash, for example as $Ca_2Al_2SiO_6$. The low silicon immobilisation efficiency in the mixed ESP ash may also be contributed by the high concentration of alkaline metals of K and Na in the vitrified slag, which causes the silicate component being more vulnerable to acidic leaching conditions. Compared to the boiler ash and bottom ash, the immobilisation efficiency is generally higher for the bottom ash, and lower for the ESP ash, and somewhere in between for the boiler ash for most of the elements.

In general, the reduced availability of the metallic elements is mainly due to the silicate phase formation. However, other mechanisms may be possible. It can be seen that the ESP ash contains much lower silicon (ca. 4–10%), compared to the boiler ash (12–20%) [2] and bottom ash (26.7%) [1]. Due to the high presence of the alkaline metals such as Na and K, the silicate network at low silicon presence may not be the main fixing mechanism for the immobilisation. By introducing additives with high silica content such as polluted sand and by removing the chlorides salt (NaCl and KCl) through a pre-washing, it is theoretically possible to control the leachability, and further to control a selective volatilisation of the interested components.

During melting, heavy metals to certain extent went to the gas phase, and formed secondary flue dust, while SiO_2 as the main components for slag formation has formed a glassy structured matrix. According to Refs. [5,6], leaching of metal ions decreases as the concentration of SiO_2 increases and it is most effective for Cr, Cd and Pb. In the present study, EFNEW-L1/6 contains 3.97 wt% of Si, and BL0-OVO1 contains 15.5 wt% Si reported previously [2], the immobilisation efficiency of Cd is 99.2% for EFNEW-L1/6, and >71.9 for BL0-OVO1. The conclusion cannot be simply obtained, due to the detection limit of the leaching solution for the boiler ash [2]. In addition, the formation of the separated salt layer in the vitrified product can also lead to an inaccurate judgment, because only the vitrified slag part was used for the immobilisation evaluation. In addition, during vitrification of fly ash with proper addition of glass-forming agent [7,8] such as silica content of over 35 wt%, and keeping the alkaline chloride low (5–15 wt%), the relatively stable slag products can be used in safer landfill and even in construction industry. In the present experimental study, the maximum available leaching values have been obtained for both ESP ash and the vitrified slag. To verify whether the vitrified ESP ash can be safely landfilled or used, further experimental work need be carried out.

3.4. *Phase identification of the ashes before and after treatment*

To understand the mineralogical changes, some of the ash samples before and after thermal treatment and vitrification were analysed with XRD. Fig. 9 shows the XRD analysis for the mixture ESP ash of line 1–6 (EFNEW-L1/6) after vitrification at 1400 °C. The XRD analysis of the original ESP ash sample is already shown in Fig. 2 for comparison. Table 5 lists all the identified compounds according to the further analyses of the XRD results for the same ESP ash samples before and after thermal treatment.

It can be seen that after the vitrification at 1400 °C all the sulphate compounds ($CaSO_4$ and $K_3Na(SO_4)_2$), and chlorides (NaCl and $KZnCl_3$) have disappeared completely. This is because of their high volatility at the vitrification temperatures. The main identified compounds are the silicates and aluminates such as Gahnite ($ZnAl_2O_4$) which is a spinel and very stable phase, Nepheline ($NaAlSiO_4$), Gehlenite ($Ca_2Al_2SiO_7$) and Ringwoodite ($(Mg, Fe)SiO_4$). However, thermal treatment at 900 °C can remove the sulphates and chlorides, but only small amount of silicate phases were identified such as Ca_2SiO_4 and $KFeSi_3O_8$. XRD analyses of other ESP ash samples (EFOLD-L01, EFOLD-L06, EFNEW-L06 and EF-L0) all indicate that sulphates, chlorides and free quartz are the main mineral phases, and they remain in the ash even after a

Table 5
Phase identification of original ESP ash and the sample after thermal treatment at 900 °C and 1400 °C.

EFNEW-L1/6	Chemical formula	20 °C	900 °C	1400 °C
Sulphates	$CaSO_4$	+	+	
	$K_3Na(SO_4)_2$	+	+	
	KNaSO4			
	$Na_{21}Mg(SO_4)_2$	+		
	$Ca_4Al_6O_{12}SO_4$			
	$Na_6Ca_4F_2(SO_4)_6$			
Chlorides	NaCl	++	++	
	KCl		++	
	K_2ZnCl_4	+		
Oxides/silicates	$ZnAl_2O_4$			+++
	Ca_2SiO_4		+	
	$CaAl_2SiO_6$	+		
	$Ca_2Al_2SiO_7$			++
	$KFeSi_3O_8$		+	
	$(Mg,Fe)_2SiO_4$			++
	$NaAlSiO_4$			+++
Rest	$Ca_{10}(SiO_4)_3(SO_4)_3(OH,F,Cl)_2$		+	

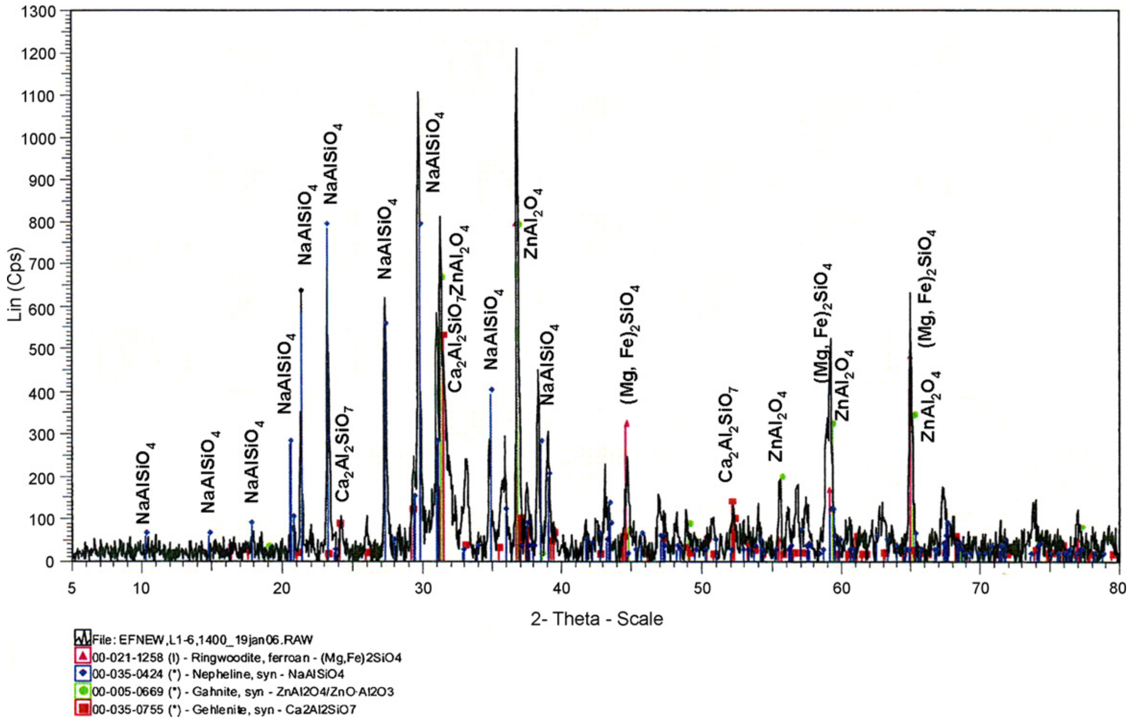

Fig. 9. XRD patterns of the mixture ESP ash sample (EFNEW-L1/6) after vitrification at 1400 °C.

thermal treatment at 900 °C. It is certain that silicate phases could only form above the melting temperature of the major mineral components. However, one needs to keep in mind that some silicate phases are amorphous and may not be detected with XRD.

Direct vitrification of the waste incineration residues [1,2] has been reported by the authors for boiler ashes and bottom ashes. The thermal behaviour of these ashes depends very much on the mineral compositions of the ashes. ESP ashes have highest volatile compounds of sulphates and chlorides, but much less silica. This leads to higher weight loss and reduced immobilisation efficiency for certain elements compared to the bottom ash and boiler ash. The leaching behaviour of the elements in the ESP ash, before and after vitrification shows similar behaviour as the boiler and bottom ashes, with the exception of the original concentration. According to the availability tests it was found that calcium, magnesium, potassium and sodium are the most available elements for acid leaching, but after vitrification at 1400 °C these elements have reached a high immobilisation efficiency.

4. Conclusions

During the vitrification of the fly ash generated in the MSW incineration, heavy metal immobilisation can be achieved. However significant amount of secondary flue dust are generated. According to the present experimental study for thermal treatment of the ESP ash, the following conclusions are obtained.

- The ESP ash is a relatively homogeneous fine powder, and it consists mainly of chlorides (NaCl, K_2ZnCl_4, and KCl in some ESP ashes), silica (SiO_2), and sulphates ($CaSO_4$, Na_2SO_4). The silicon content is significantly lower than that in the boiler and bottom ashes, and this will have some major effect on the immobilisation efficiency.
- Based on the results of the DTA and TGA tests, various reaction stages are identified during thermal treatment of the ashes, including the initial water removal, volatilisation, melting and silicate slag formation.
- Higher weight loss were observed after thermal treatment and vitrification compared to boiler ash and bottom ashes. Ash volatilisation could be a problem during vitrification, which will lead to a secondary emission and requires further treatment. However, chlorides have not completely volatilised within an hour at 1400 °C. Water pre-washing before thermal treatment and vitrification will be an option to remove the chlorides salt and to reduce the secondary flue dust formation.
- At the vitrification temperatures of 1400 °C, two molten layers were formed: a salt melt on top and a homogeneous glassy slag on the bottom. Addition of high silica bearing minerals may reduce the chloride salt layer formation and increase the overall immobilisation efficiency of the ash.
- The availability-leaching test was conducted following the Dutch standard NEN 7341. The leaching values of the vitrified slag are significantly lower than those of its original ash for most of the elements.

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