



Co-disposal of MSWI fly ash and Bayer red mud using an one-part geopolymeric system



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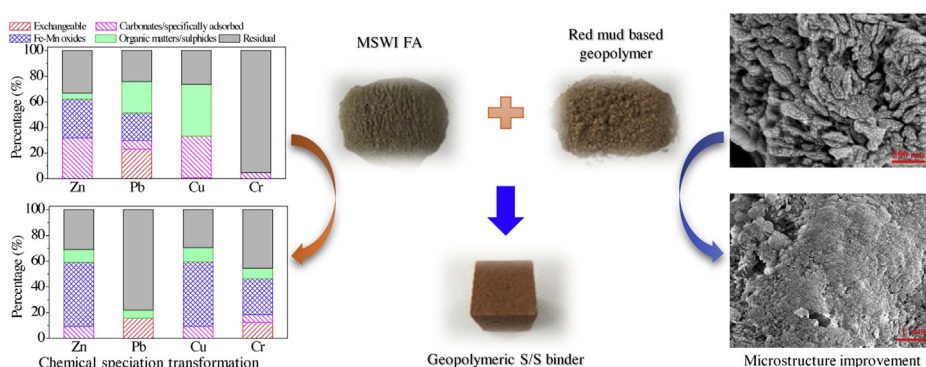
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HIGHLIGHTS

- The pretreated RM was firstly used as one-part geopolymeric S/S reagent for MSWI FA.
- MSWI FA contributes to improving 28 d strength of RM-based geopolymeric solid.
- The S/S effects for the heavy metals exhibit the following order: Pb > Cu > Zn > Cr.
- Main heavy metals transform into the inactive fractions difficult to leach out.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, Bayer red mud (RM) was pretreated through alkali–thermal activation process, and prepared as an one-part geopolymer precursor, which could be used as geopolymeric solidification/stabilization (S/S) reagent for municipal solid waste incineration fly ash (MSWI FA). Compressive strength test, modified TCLP leaching test and sequential extraction test were conducted to evaluate the effectiveness of the RM-based geopolymeric S/S reagent. The results show that the S/S effects for heavy metals of RM-based geopolymer exhibit the following order: Pb > Cu > Zn > Cr. Most of the Zn, Pb and Cu in the MSWI FA transform from the leachable fractions into the inactive fractions difficult or unavailable to leach out. In the geopolymeric S/S solid, the active aluminosilicates in MSWI FA are dissolved in the alkaline environment formed by pretreated RM and then participate in the geopolymerization, which increases the SiO₂/Al₂O₃ ratio and enhances the structural stability of geopolymeric S/S solid. MSWI FA offsets the strength deterioration of RM based one-part geopolymer and improves the immobilization efficiency for heavy metals in the geopolymer structure.

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1. Introduction

The quantity of municipal solid waste (MSW) generated in China reached 172 million tons in 2013 [1], which has increased by 16% in the past decade. Due to the rapid increase of MSW generation and land shortage for landfill disposal, incineration is becoming the prior choice of many cities for MSW treatment because of higher

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degree of volume reduction, risk minimization and energy recovery from MSW incineration. From 2003–2013, the number of MSW incineration plants increased from 47 to 166 in China, and the amount of incinerated MSW increased from 3.7 million tons to 46.3 million tons per year [1,2]. Although incineration could significantly reduce the waste volume by approximately 85–90% [3] and provide usable energy, it is still imperfect for MSW disposal. One of the main concerns for MSW incineration is the generation of potentially hazardous residues such as fly ash. The weight of fly ash from MSW incineration (MSWI FA) is up to 2–5 wt% of the original MSW [4]. MSWI FA is usually considered as a hazardous waste due to its high content of toxic substances (e.g., heavy metals, dioxins, and furans), and should be treated to reduce the potential leaching of contaminants prior to final disposal.

Methods to treat MSWI FA are mainly classified to three groups: separation, thermal treatment, and solidification/stabilization (S/S) [5]. Separation processes include washing [6,7], leaching [4,8], or electrochemical process [9,10]. In fact, they are pretreatment methods and not independent treatment processes, which are usually conducted for the purpose of immobilization or utilization in a more efficient way by removing the soluble salts, heavy metals, and other toxic substances. F. Colangelo et al. recovered the MSWI FA as road basement through optimally pre-washing [11]. Thermal treatment is usually applied for reuse of MSWI FA, and is mainly done by sintering [12,13], melting [14] or vitrification [15,16]. For example, MSWI FA could be converted to glass-ceramics with enhanced physical and mechanical properties after suitable thermal pretreatment [17–19]. S/S methods refer to technologies or processes that use additives (or binders) to physically and/or chemically immobilize hazardous constituents in wastes, soils and sludges [20]. Chemical stabilization [4] and cement solidification [21,22] are mainly utilized in the S/S methods. Addition of ordinary Portland cement (OPC) for solidification is the most popular approach applied in many countries.

In recent years, geopolymer technology has been utilized to immobilize MSWI FA due to its lower CO₂ emissions and better durability compared to OPC. Geopolymers are inorganic binders obtained by alkali activation of aluminosilicates through dissolution-polycondensation reactions [23]. Zheng et al. investigated the immobilization of heavy metals in MSWI FA by activating it with NaOH and Na₂SiO₃ solutions to synthesize MSWI FA based geopolymer [24,25]. It was found that water-wash pretreatment resulted in a higher strength of geopolymer and reduced the total leached fractions of heavy metals compared to the counterpart without water-wash [24]. Lancellotti et al. employed metakaolin as the main silica and alumina source to synthesize geopolymeric immobilizing agents for MSWI FA [26]. Some researchers activated the mixture of MSWI FA and coal fly ash with alkali solutions to prepare geopolymer to immobilize MSWI FA [27–29].

The purpose of this research was to immobilize MSWI FA using another type of solid waste—Bayer red mud (RM) through the geopolymer technology. RM is the residue of bauxite ores after digestion by caustic soda through the Bayer process to produce alumina. RM is a toxic industrial waste due to its high alkalinity with an average pH of 11.3 ± 1.0 [30], and its disposal is one of our most environmental concerns. Approximately 120 million tons of RM is being generated annually around the world [31], imposing a great burden on environment protection. In our previous work, the RM was pretreated through alkali–thermal activation and turned into a one-part geopolymer precursor, which could be used in a blending process by only adding water [32,33]. The RM pretreated through alkali–thermal activation could be recycled for cementitious materials, which reduced the pollution risks of land disposal to the environment. However the long-term strength of the one-part geopolymer deteriorated because of the unstable polymerization of Al–O and Si–O groups at the low SiO₂/Al₂O₃ molar

ratio of 1.41 [32,33]. Since SiO₂ and Al₂O₃ are the major compounds in MSWI FA, which could be considered as an aluminosilicate source for geopolymer. This research explored the co-disposal of MSWI FA and RM through geopolymer technology, in which the alkali–thermal activated RM worked as a geopolymeric S/S reagent for the heavy metals in MSWI FA, and MSWI FA participated to improve the property of RM-based one-part geopolymer.

2. Material and methods

2.1. Raw materials

The MSWI FA used in this study was obtained from a municipal waste incineration plant in Wuhan, China. The Bayer red mud was provided by an alumina plant of Chalco Co. in Zhengzhou, China. A class P II 42.5 ordinary Portland cement (OPC) from Huaxin Cement Co. Ltd. was selected as a control for comparing the effectiveness of S/S. Major elements of the raw materials were analyzed by an Axios Advanced X-Ray Fluorescence Spectrometer (XRF) (PANalytical B.V., Netherlands), and the results are presented in Table 1. The RM will release a higher content of alumina than silica to participate in the geopolymer gel network, which will lead to relatively higher early strength, but the lack of available silicon impedes further strength development [34]. The MSWI FA has a similar SiO₂ content as RM, but a much lower Al₂O₃ content than that of RM. The MSWI FA contains a large amount of chloride and sulphate salts, which may be detrimental to the durability of the solidified product.

To determine the content of trace elements, the samples were wet digested using a combination of HNO₃ + HClO₄ + HF acids [35]. The digested solutions were then filtered through 0.45-μm filter membranes and then analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Optima 8300DV, Perkin Elmer, USA). As shown in Table 1, Zn, Pb, Cu and Cr are the main heavy metals that have leaching risks identified in the raw materials. Other trace elements such as As, Sb and Se etc. present low contents and thus are not presented in Table 1. MSWI FA has high contents of Zn, Pb and Cu. The RM and OPC have much lower contents of Zn, Pb and Cu, which could be ignored in comparison with the MSWI FA. But relatively higher contents of Cr present in RM and OPC.

2.2. Pretreatment of RM and the S/S process

The RM was pretreated through an alkali–thermal activation process to obtain one-part geopolymer precursor reported in our previous studies [32,33]. RM samples were mixed with the addition of 10 wt% NaOH pellets (value based on Na₂O with respect to the mass of RM), and then calcined at 800 °C for 1 h in a muffle furnace. The alkali–thermal activated RM (named as RM-10N) was then grinded in a comminuter for 3 min to pass a 0.315-mm sieve.

For the purpose of S/S, the MSWI FA samples were mixed with alkali–thermal activated RM in the percentage of 40, 45, 50, 55, and 60 wt% with respect to the total solid amount. The solid mixtures were then mechanically blended with water with a water/solid ratio of 0.50 for 5 min to obtain homogeneous pastes by using a NJ-160 paste mixer. The pastes were then molded in steel molds (40 × 40 × 40 mm) and covered by plastic films and then cured at 20 ± 1 °C for 24 h. The binders were then demoulded and sealed in polyethylene zip-lock bags and cured again under the same condition. Afterwards, the compressive strength test and leaching test of the solids were performed after curing for 3, 7, 14 and 28 days. For comparison, the MSWI FA was also solidified with the addition of 40, 50, 60 wt% of OPC following the same blending and curing procedures.

Table 1
Chemical compositions of the raw materials.

Major components	Mass percentage (wt%)			Trace elements	Concentration (mg/kg)		
	MSWI FA	RM	OPC		MSWI FA	RM	OPC
SiO ₂	20.48	20.38	20.57	Zn	2683.93	21.57	115.59
Al ₂ O ₃	10.16	24.50	5.39	Pb	1377.12	91.99	70.13
CaO	27.44	12.86	58.76	Cu	756.15	114.56	82.94
Fe ₂ O ₃	4.25	9.48	2.90	Cr	93.76	168.48	105.30
K ₂ O	2.17	0.88	0.35				
Na ₂ O	3.15	11.46	0.23				
Cl	5.77	0.07	0.02				
SO ₃	4.45	0.67	2.36				
LOI*	12.91	15.40	4.02				

LOI*: Loss on ignition, mass loss at 1200 °C.

2.3. Leaching test

The S/S effect of the RM-based geopolymer and OPC was assessed by determining the leaching ratio of heavy metals through modified TCLP (toxicity characteristic leaching procedure) test. Since both MSWI FA and RM are alkaline, the leaching solutions might become alkaline during the leaching test, which would lead to precipitation of heavy metals. Therefore, the effects of initial leachant pH on the leachability of heavy metals in the MSWI FA were first studied. The NO. 2 leachant in the method of Chinese Ministry of Environmental Protection Standard HJ/T 300–2007 [36] was chosen in the subsequent leaching tests for the S/S solids. The HJ/T 300–2007 method is an extraction method with the same liquid/solid ratio (L/S) of 20 ml/g for 18 h, as that in the USEPA TCLP method [37], except that acetic acid solution of pH 2.64 ± 0.05 is used in the former method, slightly lower than the pH of latter method. After the leaching tests, samples were filtered through 0.45- μ m filter membranes, and then the concentrations of heavy metals were determined by ICP-OES. To calculate the leaching ratios of heavy metals in the S/S solids, the contents of heavy metals in the RM and OPC were also taken into account.

The leaching ratio of each heavy metal is calculated using Eq. (1):

$$\text{Leaching ratio} = \frac{\text{The mass of each heavy metal in leaching solution}}{\text{The total mass of each heavy metal in the starting solid}} \quad (1)$$

2.4. Chemical speciation analyses of heavy metals

The chemical speciation analyses of heavy metals in the MSWI FA samples and the geopolymeric S/S solids were carried out by sequential extraction according to the Tessier's method [38] for five metal categories: (1) exchangeable fraction, (2) bound to carbonates/specifically adsorbed, (3) bound to Fe–Mn oxides, (4) bound to organic matters and sulphides, and (5) residual fraction. The results of sequential extraction might not necessarily reflect the associations with the claimed phases, but rather represent the different leaching conditions within a landfill over time. The exchangeable fraction is immediately available under neutral conditions; the carbonates/specifically adsorbed fraction is potentially available under neutral conditions; the fractions of Fe–Mn oxides and organic matters and sulphides are potentially available under reducing conditions; and the residual fraction is unavailable for leaching [39].

2.5. Material characterization methods

The mineral phases of the raw materials and the geopolymeric S/S solids were investigated by the powder X-ray diffractometry (XRD) technique, using an Empyrean (PANalytical B.V., Holland) with Cu K α radiation and $\lambda = 1.5418 \text{ \AA}$, operated at 40 mA, 40 kV with a scanning rate of $0.2785^\circ/\text{s}$ for 2θ in the range from 10 to 75° .

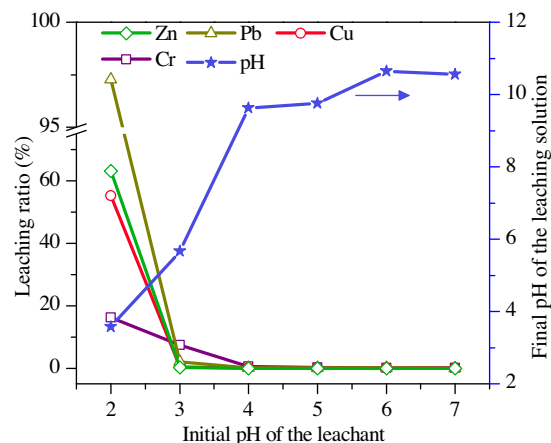


Fig. 1. Leaching ratios of heavy metals and final pHs of the leaching solutions from the MSWI FA leached with acetic acid solutions of different pHs at a L/S ratio of 20 ml/g.

The morphological analyses of the solids with fracture surfaces were conducted by the field emission scanning electron microscopy (FE-SEM) after coating with Au for 300 s, using a Sirion 200 (FEI Co., Netherlands).

3. Results and discussion

3.1. Leachability of heavy metals in raw materials

The influence of the initial leachant pH on the leaching ratio of Zn, Pb, Cu and Cr in MSWI FA is shown in Fig. 1. It is obvious that the leaching ratios of these four heavy metals decrease significantly to very low level as the initial leachant pH increases from 2.0–3.0. For the case of Pb, the leaching ratio decreases from 97.3% to 2% when the initial leachant pH increases from 2.0–3.0. The decrease of leaching ratio is supposed to be caused by the increase of final pH of the leaching solution, which increases dramatically with the increasing initial leachant pH. For initial leachant pHs ≥ 4 , the final solution pHs are all above 9.5 due to the alkaline nature of MSWI FA. It is known that an increase in pH of the leaching solution will dramatically decrease the leachability of heavy metals, because that insoluble hydroxides will form at higher pH [4].

The assessment of S/S effect would be interfered by the precipitation of heavy metals in the solution with high pH. RM is a solid waste with higher alkalinity than MSWI FA, and its alkalinity is increased after the alkali–thermal pretreatment. To reduce the influence of precipitation on the assessment of S/S effect, leachant with higher buffering capacity is needed for the leaching test in order to obtain lower final pH in the leaching solution. The NO. 2 leachant (pH 2.88 ± 0.05) in USEPA TCLP method is prepared by

diluting 5.7 ml glacial $\text{CH}_3\text{CH}_2\text{OOH}$ in 1 l of water. While, 17.25 ml glacial $\text{CH}_3\text{CH}_2\text{OOH}$ is needed to be added in 1 l of water for the case of NO. 2 leachant ($\text{pH } 2.64 \pm 0.05$) in HJ/T 300-2007 method. Thus the second one is a better candidate with much higher buffering capacity.

The concentrations of heavy metals in the leaching solution after the MSWI FA, RM, RM-10N, and OPC leached by the leachant at $\text{pH } 2.64 \pm 0.05$ with an L/S ratio of 20 ml/g are shown in Table 2. The concentration of Zn is the highest in the leaching solution from MSWI FA, followed by Cu, Pb and Cr.

The concentrations of heavy metals in the leaching solution from the raw RM sample are all lower than 1 mg/l, which indicates that the raw RM shows little heavy metal leaching risks. But the concentration and leaching ratio of Cr in the leaching solution from the RM-10N are increased significantly compared to that of the RM sample, which would give an additional contribution to the leachable Cr content of the S/S solid. It seems that the alkali-thermal pretreatment would cause significant chemical speciation transformation of Cr in the RM-10N sample. Cr is also the most leachable heavy metal in the OPC with a leaching ratio of 69.25%.

3.2. Compressive strength of the geopolymeric S/S solid

The compressive strengths of the geopolymeric S/S solids with different amounts of alkali-thermal activated RM are shown in

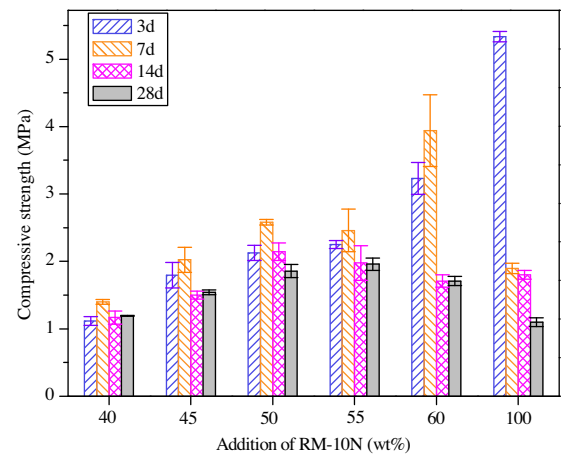


Fig. 2. Compressive strengths of geopolymeric S/S solids with different amounts of alkali-thermal activated RM (RM-10N).

Fig. 2. It was found in our previous studies that the RM pretreated through alkali-thermal activation would turn into a geopolymer precursor, which could be hardened after blended with water [32]. The solid with the addition of 100 wt% RM-10N shows the highest compressive strength of 5.3 MPa at the curing age of 3 days. But

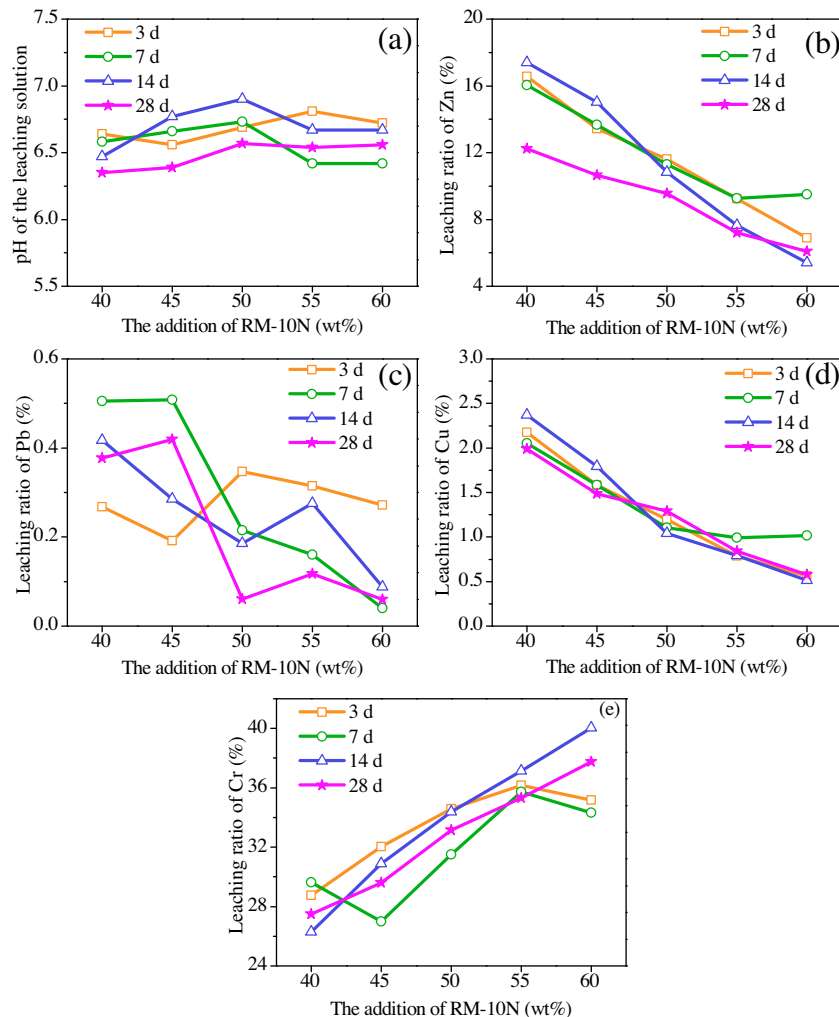


Fig. 3. Final pHs (a) and leaching ratios of Zn (b), Pb (c), Cu (d), Cr (e) in the leaching solutions from the geopolymeric S/S solids leached by a leachant at $\text{pH } 2.64 \pm 0.05$ with a L/S ratio of 20 ml/g.

Table 2
Concentrations and leaching ratios of heavy metals in the leaching solutions from the MSWI FA, RM, RM-10N, and OPC leached by the leachant at pH 2.64 ± 0.05 with a L/S ratio of 20 ml/g.

Materials	Concentrations (mg/l)				Leaching ratio (%)			
	Zn	Pb	Cu	Cr	Zn	Pb	Cu	Cr
MSWI FA	52.15	2.11	11.00	0.56	38.88	5.58	15.98	11.97
RM	n.d. ^a	0.78	0.06	0.37	0	16.95	1.13	4.43
RM-10N	n.d.	0.36	0.03	5.05	0	7.88	0.55	59.90
OPC	n.d.	n.d.	0.17	3.65	0	0	4.00	69.25

^a n.d.: Not detected. Detection limits: Zn, 0.3 $\mu\text{g/l}$; Pb 2 $\mu\text{g/l}$.

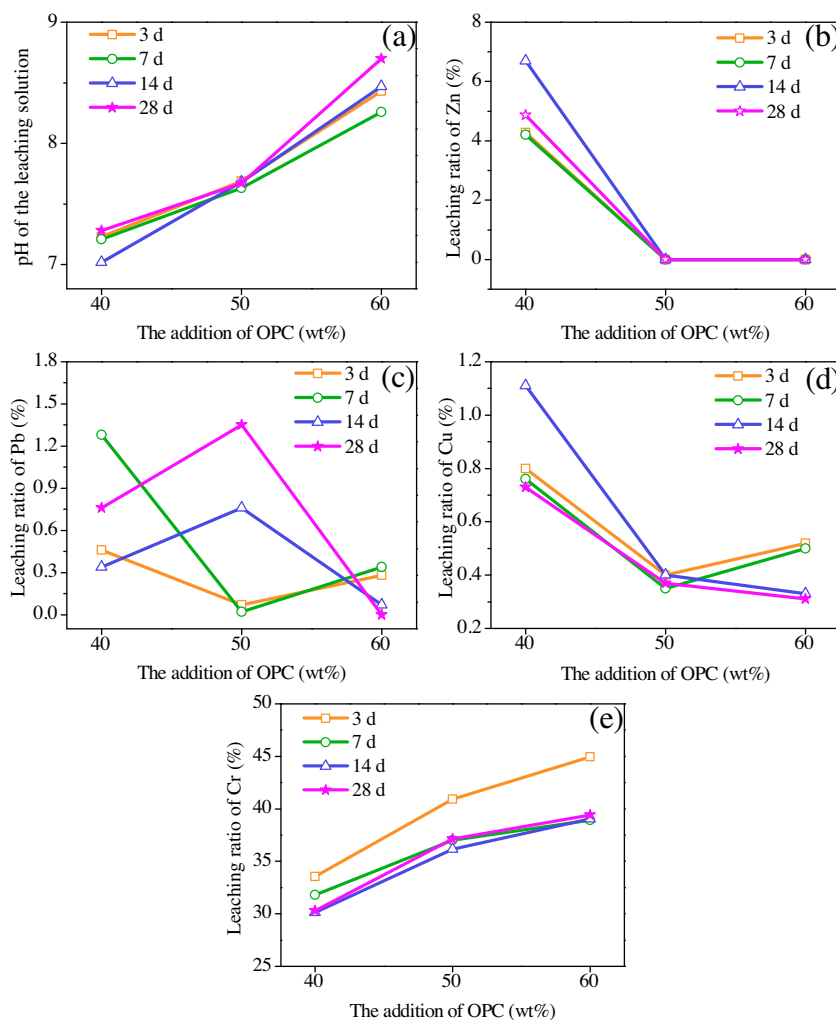


Fig. 4. Final pHs (a) and leaching ratios of Zn (b), Pb (c), Cu (d), Cr (e) in the leaching solutions from OPC S/S solids leached by a leachant at pH 2.64 ± 0.05 with a L/S ratio of 20 ml/g.

the compressive strength decreases continuously after that, and reaches the lowest value of 1.1 MPa at the curing age of 28 days. The compressive strengths of the geopolymeric S/S solids after curing for 3 and 7 days exhibit an increasing trend with increasing RM-10N addition from 40 to 60 wt%. But the compressive strengths at the curing age of 14 and 28 d increase when the addition of RM-10N increases from 40 to 50 wt%, and then decrease with the further increase of RM-10N addition from 55 to 100 wt%. Conclusively, the optimal addition dosage of the RM-10N for the S/S of MSWI FA is 50 wt%, considering both the early and long-term compressive strengths of the S/S solids.

The early compressive strength of the S/S solid is mainly attributed to the dissolution-polycondensation reactions of alkali-thermal activated RM in water. But deterioration problem

of the long-term strength exists in the one-part geopolymer based on RM, which has been found in our previous studies [32,33]. The strength deterioration with further curing is a consequence of the depolymerization or re-dissolution of the aluminosilicate resulting from the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the formulation [33]. It had been found that by adding silica rich materials, such as silica fume, to improve the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the geopolymer formulation, the long-term strength would increase significantly [33]. In this research, the 28 d compressive strength is also slightly improved by MSWI FA, although the improvement effect is far behind silica fume. It is supposed that the dissolved aluminosilicate from MSWI FA could improve the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and enhance the stability of geopolymer gels, which could offset the strength deterioration. This means that the MSWI FA acts not only as a S/S target, but also an

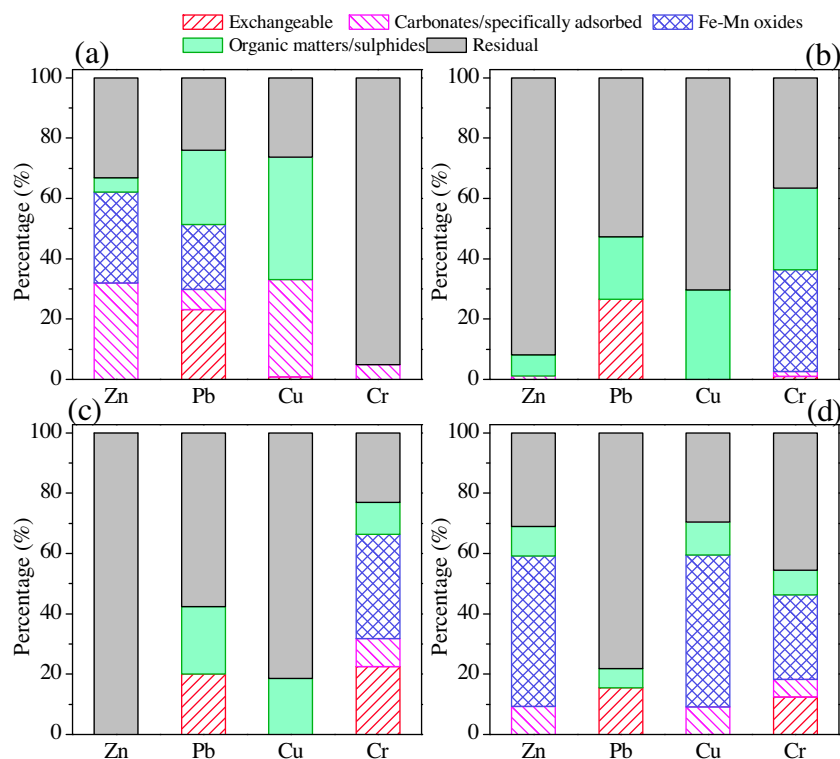


Fig. 5. Chemical speciations of Zn, Pb, Cu, Cr in MSWI FA (a), RM (b), RM-10 N (c), and geopolymetric S/S solid with 50 wt% RM-10 N at the curing age for 28 days (d).

aluminosilicate source for geopolymerization. Although the compressive strengths of the geopolymetric S/S solids are poor, with the values at 28 days in the range 1–2 MPa, it is still relatively easy to meet the mechanical requirements for landfill disposal. For instance, the UK landfill waste acceptance criteria for monolithic waste demands a minimum compressive strength of 1 MPa after 28 days curing [40]. Moreover, the performance of RM as a S/S reagent for heavy metals is acceptable, which is a new utilization approach for RM.

3.3. S/S effects for heavy metals

The leaching test results of the MSWI FA and the alkali-thermal activated RM mixed geopolymetric S/S solids are shown in Fig. 3. The final pHs of the leaching solutions are in the range of 6.4–6.9, as shown in Fig. 3(a), which are higher than that of the raw MSWI FA under the same conditions, and Fig. 3(a) shows no significant changes of pHs with the increasing RM-10 N addition. The leaching solutions of the solids cured for 28 d exhibit relatively lower pHs, which might result from the consumption of OH^- ions by the dissolution of aluminosilicates from the MSWI FA with the development of geopolymerization of the S/S solids. As shown in Figs. 3(b)–(d), the leaching ratios of Zn, Pb, and Cu decrease with the increasing RM-10 N addition, indicating that the S/S effects for Zn, Pb, and Cu improves with the increase of RM-10 N addition. But the leaching ratio of Cr increases with the increasing RM-10 N addition, due to the higher content of leachable Cr in the alkali-thermal activated RM, which is consistent with the result of Table 2. Although the solids cured for 28 d have lower pHs, most of the leaching ratios of these four heavy metals are relatively lower, which indicates that the geopolymetric S/S solids cured for 28 d have better encapsulation effects on heavy metals. According to the leaching ratios of heavy metals, the S/S effects for the four heavy metals in the geopolymetric S/S solids exhibit the following order: Pb > Cu > Zn > Cr. The three dominant heavy metals (Zn, Cu, and Pb) with relatively higher

concentrations in the leaching solution from MSWI FA, as presented in Table 2, are all well solidified in the geopolymetric S/S solids. Fortunately, Cr concentration in the leaching solution from MSWI FA is the lowest, as shown in Table 2, although S/S effect for Cr in the S/S solid is the poorest among the four heavy metals.

The S/S effect of OPC, the control group, are shown in Fig. 4. The final pH of the leaching solutions increases significantly with the increasing amount of OPC, which might be caused by the formation of large amount of $\text{Ca}(\text{OH})_2$ in the hydration products of OPC. In Fig. 4(a), the leaching solutions of the OPC S/S solids show alkaline characteristics, with the pH in the range of 7.0–8.7, higher than that of the RM-based geopolymetric S/S solids, as shown in Fig. 3(a). The higher pH is beneficial to the precipitation of heavy metals to form insoluble hydroxides, which would increase the S/S effect. On the other hand, no significant correlations between the curing age of OPC S/S solids and leaching ratios of the heavy metals are found. In most cases of cement S/S systems, the dominant fixation mechanism for heavy metals is through chemical precipitation of low solubility species, especially of hydroxides [41]. It was reported that the leaching behaviors of heavy metals in the S/S waste materials were mainly controlled by the alkaline nature and acid buffering capacity of the S/S matrix [42]. Therefore, in the OPC S/S solids, the precipitation reaction controlled by pH shows a significant effect on the S/S effect than the encapsulation reaction that controlled by the hydration products of OPC. The leaching ratios of the four heavy metals with the increasing OPC addition show similar trends as that of the RM-based geopolymetric S/S solids. Neither RM-based geopolymer nor OPC shows an outstanding S/S effect for Cr. The leaching ratio of Cr increases with the increasing OPC addition due to the higher content of leachable Cr in OPC. Because the total content of leachable Cr is low, less dissolved Cr would precipitate as hydroxide, which leads to the low S/S effect for Cr. In general, the S/S effects for the four heavy metals of the RM-based geopolymer with an amount of 50–60 wt% is close to that of 50–60 wt% OPC. Table 3 shows the leaching concentrations of the four heavy met-

Table 3

Leaching concentrations of heavy metals from S/S solids with 50 wt% of reagents at the curing age of 28 d.

Leaching concentration (mg/l)	Zn	Pb	Cu	Cr
Limit value ^a	100	0.25	40	4.5
Geopolymeric S/S solid	6.45	0.02	0.28	2.08
OPC S/S solid	0.24	0.14	0.08	1.85

^a Limit value in GB 16889-2008: Standard for pollution control on the landfill site of municipal solid waste [40].

als from the two S/S solids with 50 wt% of reagents compared with the limit values for the landfill disposal of MSWI FA in the Chinese national standard GB 16889-2008 [43]. Both the two S/S solids of MSWI FA achieved the immobilization objective for Zn, Pb, Cu and Cr, according to the Chinese Regulations.

As shown in Table 1, the MSWI FA contains many chlorides (5.77 wt%) and sulphates (4.45 wt%). Soluble salts in MSWI FA, such as chlorides and sulphates, are detrimental to the strength and durability of S/S solids [24]. In addition, the MSWI FA also has 12.91 wt% of LOI, implying the existence of a few of organic matters, which can affect the leachability and mechanical properties of the S/S solids. In some researches on material recovery of MSWI FA, pre-washing was usually proceeded to remove soluble salts, organic matters and heavy metals [11,24]. In our further research on the durability of one-part geopolymeric S/S solid, the leaching behaviors of chlorides, sulphates and organic matters in the S/S solid in the long-term curing will be studied in depth.

3.4. Chemical speciation transformation of heavy metals

The distributions of heavy metal speciation in the raw MSWI FA, raw RM, RM-10 N and geopolymeric S/S solid with 50 wt% RM-10 N at the curing age of 28 d are shown in Fig. 5. In the MSWI FA (Fig. 5(a)), most of Zn is mainly distributed in the carbonates/specifically adsorbed fraction, the Fe–Mn oxides fraction and the residual fraction; Pb is distributed uniformly in the other four fractions, except 6.6 wt% in the carbonates/specifically adsorbed fraction; Cu is mainly distributed in the carbonates/specifically adsorbed fraction, the organic matters/sulphides fraction and the residual fraction; and most of Cr exists in the residual fraction. The heavy metals in the exchangeable fraction and the carbonates/specifically adsorbed fraction would be released into the environment if they are attacked by acidic fluids such as landfill leachate [41]. Therefore, Zn, Pb and Cu are the three dominant heavy metal contaminants in the MSWI FA. It has been shown in Table 2 that the leaching concentration of Cr in the raw RM are increased significantly after the alkali–thermal activation. The sequential extraction tests show that part of Cr in the raw RM transforms into the exchangeable fraction and the carbonates/specifically adsorbed fraction, improving the leachability of Cr. The contents of hexavalent Cr in the solid samples and leaching solutions were also measured. The results show that 42.2% of Cr in the raw RM and all of Cr in the RM-10 N are in the hexavalent form, implying that the Cr(III) in raw RM is oxidized to Cr(VI) during the alkali–thermal activation. The Cr in leaching solutions of the geopolymeric S/S solids and the OPC S/S solid are all in the hexavalent form. Cr(VI) can not be precipitated directly as insoluble hydroxides like Cr(III), thus the S/S effects for Cr of the two S/S reagents are not as good as the other three heavy metals.

In the geopolymeric S/S solids (Fig. 5(d)), most of Zn and Cu in the carbonates/specifically adsorbed fraction transform into the Fe–Mn oxides fraction. In terms of Pb in the S/S solid (Fig. 5(d)), the amounts in the exchangeable fraction and the organic matters/sulphides fraction decrease, and the carbonates/specifically adsorbed fraction and Fe–Mn oxides fraction disappear, along with

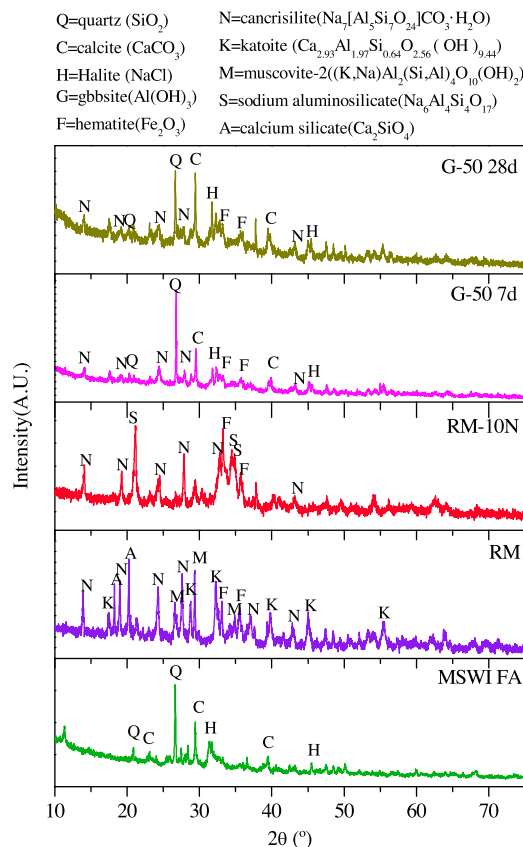


Fig. 6. The XRD patterns of the MSWI FA, RM, RM-10 N and geopolymeric solidified solid with 50 wt% RM-10 N (G-50) at the curing age of 7 and 28 days.

an increase in the residual fraction. The chemical speciation transformations of Zn, Pb and Cu indicate the outstanding encapsulation effect of the RM-based geopolymer. In consideration of the mixture ratio of MSWI FA and RM-10 N, the Cr seems to have no significant chemical speciation transformation in the geopolymeric S/S solid. A plausible reason is that the encapsulation reaction of Cr is restricted by the low degree of precipitation of Cr in the hexavalent form.

3.5. Material characterization

Fig. 6 shows the XRD patterns of the raw MSWI FA, raw RM, RM-10 and geopolymeric S/S solid with 50 wt% RM-10 N at the curing age of 7 and 28 days. The main crystalline phase of the raw MSWI FA is quartz, along with calcite and halite. The crystalline phases of the raw RM mainly consist of gibbsite, hematite, nancrisilite, muscovite-2, and katoite. The gibbsite, muscovite-2 and katoite in the raw RM decompose after alkali–thermal activation. Two new mineral phases, calcium silicate and sodium aluminosilicate, are formed in the RM-10 N. Both calcium silicate and sodium aluminosilicate disappear in the geopolymeric S/S solid, contributing to the formation of alkaline environment and hardening of the solid. But no new crystalline phases are formed in the geopolymeric S/S solid, implying the formation of some amorphous phases. The intensity of the main characteristic peak of quartz in the solid cured for 7d increases significantly. It is inferred that some new crystalline silicon oxide is formed due to the dehydration of H_3SiO_4^- monomers formed from the dissolution of MSWI FA in the high alkaline environment. The H_3SiO_4^- monomers that have not yet participated in the geopolymerization process might dehydrate during the specimen preparation for XRD test.

The SEM images of the fracture surface of geopolymer solids cured for 28 d are shown in Fig. 7. In the solid produced from

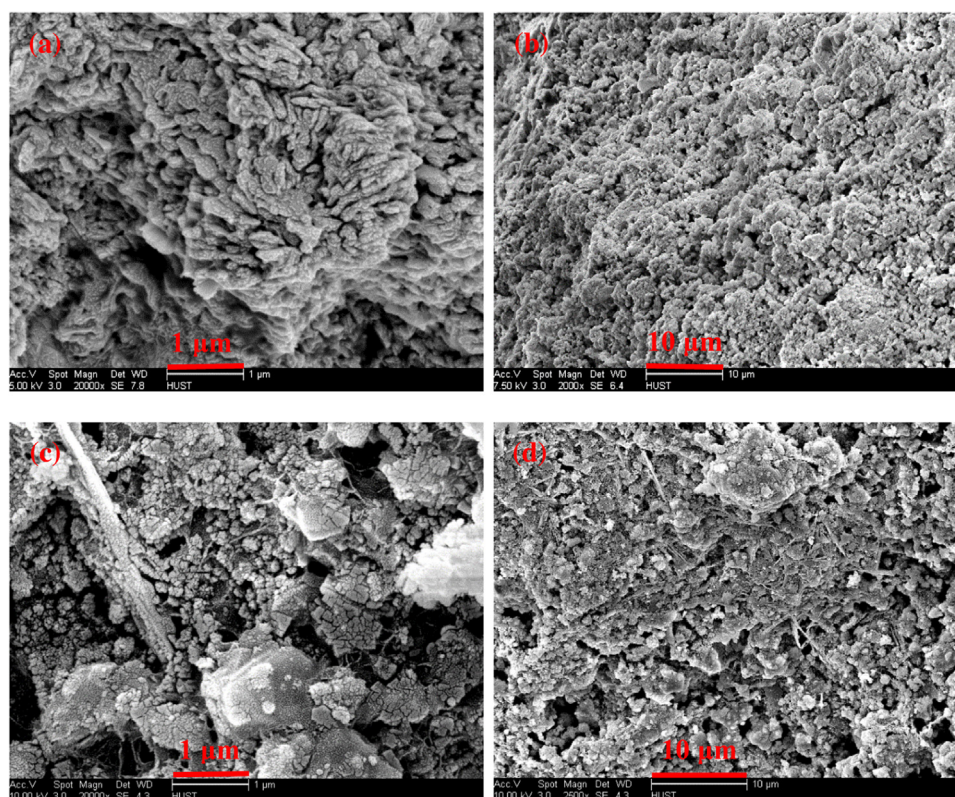


Fig. 7. The SEM images of the fracture surface of the solids at the curing age of 28 days: (a), (b); G-100 and (c), (d) G-50.

100 wt% RM-10 N (G-100), the microstructure consists of a large amount small RM particles, which aggregate together incompactly. With the addition of 50 wt% RM-10 N in geopolymeric S/S solid, smaller particles are formed in the solid, which seem to be the nanosized geopolymeric micelles [44]. Some blocks are formed through the polymerization of the nanosized particles. Although the microstructure of G-50 seems to have more pores among the framework formed by geopolymer products, the structure is more stable than the adhesive aggregation of RM particles in G-100. The transformation of microstructure indicates that MSWI FA could contribute to an aluminosilicate source for geopolymerization of RM-based one-part geopolymer, and then improve the structural stability of geopolymeric S/S solid, thus enhancing the immobilization efficiency for heavy metals in the geopolymer structure.

4. Conclusions

In this work, the MSWI FA is successfully co-disposed with Bayer red mud. The one-part geopolymer prepared from alkali-thermal activated RM implements the S/S of the MSWI FA. The S/S effect of the RM-based geopolymer with an amount of 50–60 wt% is close to that of 50–60 wt% OPC. The S/S effects for the heavy metals in the RM-based geopolymer exhibit the following order: $Pb > Cu > Zn > Cr$. The three dominant heavy metal contaminants (Zn, Cu, and Pb) in the MSWI FA are all well solidified in the geopolymeric S/S solids. After S/S by the RM-based geopolymer, most of the chemical speciations of the three dominant heavy metals (Zn, Pb and Cu) in the MSWI FA transform from the leachable fractions into the fractions that are difficult or unavailable to leach out. In the geopolymeric S/S solids, the MSWI FA acts not only as a S/S target, but also an aluminosilicate source for geopolymerization. The participation of MSWI FA offsets the strength deterioration of one-part geopolymer based on RM. The active aluminosilicates in MSWI FA are dissolved in the alkaline environment formed by pretreated

RM and then participate in the geopolymerization, which enhances the structural stability of geopolymeric S/S solid, and improves the immobilization efficiency of heavy metals in the geopolymer structure.

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References

- [1] National Bureau of Statistics of China, China Statistical Yearbook 2014, China Statistical Press, Beijing, 2014.
- [2] National Bureau of Statistics of China, China Statistical Yearbook 2004, China Statistical Press, Beijing, 2004.
- [3] Ole Hjelm, Disposal strategies for municipal solid waste incineration residues, *J. Hazard. Mater.* 47 (1996) 345–368.
- [4] Youcai Zhao, Lijie Song, Guojian Li, Chemical stabilization of MSW incinerator fly ashes, *J. Hazard. Mater.* 95 (2002) 47–63.
- [5] Charles H.K. Lam, W.M. Alvin Ip, John Patrick Barford, Gordon McKay, Use of incineration MSW ash: a review, *Sustainability* 2 (2010) 1943–1968.
- [6] Carl S. Kirby, J. Donald Rimstidt, Interaction of municipal solid waste ash with water, *Environ. Sci. Technol.* 28 (1994) 443–451.
- [7] T. Mangialardi, Disposal of MSWI fly ash through a combined washing-immobilisation process, *J. Hazard. Mater.* 98 (2003) 225–240.
- [8] Kyung-jin Hong, Shuzo Tokunaga, Toshio Kajiuchi, Extraction of heavy metals from MSW incinerator fly ashes by chelating agents, *J. Hazard. Mater.* 75 (2000) 57–73.
- [9] Céila Ferreira, Pernille Jensen, Lisbeth Ottosen, Alexandra Ribeiro, Removal of selected heavy metals from MSW fly ash by the electrochemical process, *Eng. Geol.* 77 (2005) 339–347.

- [10] Anne Juul Pedersen, Lisbeth M. Ottosen, Arne Villumsen, Electrodialytic removal of heavy metals from municipal solid waste incineration fly ash using ammonium citrate as assisting agent, *J. Hazard. Mater.* 122 (2005) 103–109.
- [11] F. Colangelo, R. Cioffi, F. Montagnaro, L. Santoro, Soluble salt removal from MSWI fly ash and its stabilization for safer disposal and recovery as road basement material, *Waste Manag.* 32 (2012) 1179–1185.
- [12] Ming-Yen Wey, Kuang-Yu Liu, Tsung-Hsun Tsai, Jing-Tong Chou, Thermal treatment of the fly ash from municipal solid waste incinerator with rotary kiln, *J. Hazard. Mater.* 137 (2006) 981–989.
- [13] T. Mangialardi, Sintering of MSW fly ash for reuse as a concrete aggregate, *J. Hazard. Mater.* 87 (2001) 225–239.
- [14] Katsunori Nishida, Yoshikazu Nagayoshi, Hitoshi Ota, Hidekazu Nagasawa, Melting and stone production using MSW incinerated ash, *Waste Manag.* 21 (2001) 443–449.
- [15] Shin-ichi Sakai, Masakatsu Hiraoka, Municipal solid waste incinerator residue recycling by thermal processes, *Waste Manag.* 20 (2000) 249–258.
- [16] Young Jun Park, Jong Heo, Vitrification of fly ash from municipal solid waste incinerator, *J. Hazard. Mater.* 91 (2002) 83–93.
- [17] Jiakuan Yang, Bo Xiao, Aldo R. Boccacini, Preparation of low melting temperature glass–ceramics from municipal waste incineration fly ash, *Fuel* 88 (2009) 1275–1280.
- [18] Guangren Qian, Yu Song, Cangang Zhang, Yuqin Xia, Houhu Zhang, Pengcheong Chui, Diopside-based glass–ceramics from MSW fly ash and bottom ash, *Waste Manag.* 26 (2006) 1462–1467.
- [19] Young Jun Park, Jong Heo, Conversion to glass–ceramics from glasses made by MSW incinerator fly ash for recycling, *Ceram. Int.* 28 (2002) 689–694.
- [20] Carlton C. Wiles, Municipal solid waste combustion ash: state-of-the-knowledge, *J. Hazard. Mater.* 47 (1996) 325–344.
- [21] Haobo Hou, Xinghua He, Shujing Zhu, Dajie Zhang, The cement solidification of municipal solid waste incineration fly ash, *J. Wuhan Univ. Technol. Mater. Sci. Ed.* 21 (2006) 137–140.
- [22] A. Poletti, R. Pomi, P. Sirini, F. Testa, Properties of Portland cement–stabilised MSWI fly ashes, *J. Hazard. Mater.* 88 (2001) 123–138.
- [23] Aurélie Favier, Guillaume Habert, Nicolas Roussel, Jean-Baptiste d'Espinose de Lacaillerie, a multinuclear static NMR study of geopolymerisation, *Cem. Concr. Res.* 75 (2015) 104–109.
- [24] Lei Zheng, Chengwen Wang, Wei Wang, Yunchun Shi, Xingbao Gao, Immobilization of MSWI fly ash through geopolymerization: effects of water-wash, *Waste Manag.* 31 (2011) 311–317.
- [25] Lei Zheng, Wei Wang, Yunchun Shi, The effects of alkaline dosage and Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymer, *Chemosphere* 79 (2010) 665–671.
- [26] Isabella Lancellotti, Elie Kamseu, Marco Michelazzi, Luisa Barbieri, Anna Corradi, Cristina Leonelli, Chemical stability of geopolymers containing municipal solid waste incinerator fly ash, *Waste Manag.* 30 (2010) 673–679.
- [27] Y. Luna Galiano, C. Fernández Pereira, J. Vale, Stabilization/solidification of a municipal solid waste incineration residue using fly ash-based geopolymers, *J. Hazard. Mater.* 185 (2011) 373–381.
- [28] E. Ivan Diaz-Loya, Erez N. Allouche, Sven Eklund, Anupam R. Joshi, Kunal Kupwade-Patil, Toxicity mitigation and solidification of municipal solid waste incinerator fly ash using alkaline activated coal ash, *Waste Manag.* 32 (2012) 1521–1527.
- [29] Claudio Ferone, Francesco Colangelo, Francesco Messina, Luciano Santoro, Raffaele Cioffi, Recycling of pre-washed municipal solid waste incinerator fly ash in the manufacturing of low temperature setting geopolymer materials, *Materials* 6 (2013) 3420–3437.
- [30] M. Gräfe, G. Power, C. Klauber, Bauxite residue issues: III. Alkalinity and associated chemistry, *Hydrometallurgy* 108 (2011) 60–79.
- [31] G. Power, M. Gräfe, C. Klauber, Bauxite residue issues: I. Current management, disposal and storage practices, *Hydrometallurgy* 108 (2011) 33–45.
- [32] Xinyuan Ke, Susan A. Bernal, John L. Provis, Jiakuan Yang, One-part geopolymers based on thermally treated red mud/NaOH blends, *J. Am. Ceram. Soc.* 98 (2014) 5–11.
- [33] Nan Ye, Jiakuan Yang, Sha Liang, Yong Hu, Jingping Hu, Bo Xiao, Qifei Huang, Synthesis and strength optimization of one-part geopolymer based on red mud, *Constr. Build. Mater.* 111 (2016) 317–325.
- [34] A. Hajimohammadi, J.L. Provis, J.S.J. van Deventer, Effect of alumina release rate on the mechanism of geopolymer gel formation, *Chem. Mater.* 22 (2010) 5199–5208.
- [35] C.J. Pickford, G. Rossi, Determination of lead in atmospheric particulates using an automated atomic-absorption spectrophotometric system with electrothermal atomisation, *Analyst* 103 (1978) 341–345.
- [36] Chinese Ministry of Environmental Protection, Method HJ/T 300–2007: Solid Waste-extraction Procedure for Leaching Toxicity–acetic Acid Buffer Solution Method, China Environment Science Press, Beijing, China, 2007.
- [37] USEPA, Method 1311: Toxicity characteristic leaching procedure (TCLP), in SW-846: Test methods for evaluating solid wastes, Physical/chemical methods, US Government Printing Office, Washington, DC, USA, 1990.
- [38] Andre Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851.
- [39] A. John Chandler, T.T. Eighmy, O. Hjelmar, D.S. Kosson, S.E. Sawell, J. Vehlouw, H.A. Van der Sloot, J. Hartlén, Municipal Solid Waste Incinerator Residues, Elsevier, 1997.
- [40] Environment Agency of UK, Waste Acceptance at Landfills, Environment Agency, Bristol, 2010.
- [41] Q.Y. Chen, M. Tyrer, C.D. Hills, X.M. Yang, P. Carey, Immobilisation of heavy metal in cement-based solidification/stabilisation: a review, *Waste Manag.* 29 (2009) 390–403.
- [42] X.D. Li, C.S. Poon, H. Sun, I.M.C. Lo, D.W. Kirk, Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials, *J. Hazard. Mater.* 82 (2001) 215–230.
- [43] Chinese Ministry of Environmental Protection, GB 16889–2008: Standard for Pollution Control on the Landfill Site of Municipal Solid Waste, China Environment Science Press, Beijing, 2008.
- [44] J. Davidovits, Geopolymer Chemistry and Applications, Geopolymer Institute, Saint-Quentin, 2011.