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Hydraulic activity of municipal solid waste incinerator fly-ash-slag-blended eco-cement

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Abstract

The melting of municipal solid waste incinerator (MSWI) fly ash can produce an extremely stable glassy slag that exhibits pozzolanicity if activated. Such slag, therefore, could be recovered in more valuable form as a cement replacement than as a roadbed aggregate. This study investigates the hydraulic activity, compressive strength development, composition variation, and heavy metal leachability of such fly-ash-slag-blended cement (FASBC). The results indicate that FASBC pastes, with cement replacement ratios of less than 20%, show a smaller early strength but a larger later strength at the age of 28 days. It was found that early cement hydration, followed by the breakdown and dissolving of the slag, enhanced the formation of calcium silicate hydrates (C-S-H), which contributes to the later strength. The XRD and ^{29}Si MAS/NMR results also indicate that, after 28 days, both the hydration degree and the average length of the linear polysilicate anions would increase with an increasing cement replacement ratio, implying an increased strength development. On the other hand, the targeted heavy metal leaching concentrations in the synthetic slag and the FASBC paste were significantly low, thus clearing the EPA's regulatory thresholds. These factors suggest the feasibility and safety of using MSWI fly ash slag in blended cement. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: MSWI fly ash; Melting; Slag-blended cement; Hydraulic activity; Heavy metal leachability

1. Introduction

The disposal of municipal solid waste incinerator (MSWI) ashes, in particular, of the heavy-metal-containing fly ash, has become a continuous and significant issue facing society, both environmentally and economically. In general, these hazardous fly ashes have to be detoxified, or stored in expensive security landfills. However, in response to a zero-emission goal in a sustainable waste disposal solution, MSWI fly ash processed by melting has offered not only an alternative to detoxification, but also the possibility of its being recycled as construction material (mainly fine aggregates). During the ash-melting process, heavy metals and inorganic components in the ash are bound up molecularly in a glassy matrix, resulting in a chemically stable and physically durable product that is normally nontoxic in the natural environment. However, in the alkaline environment of ordinary Portland cement, the fly-ash-derived slag is, in fact, chemically active and exhibits self-cementing properties when pulverized and activated by the cement [1–3]. That is, the pulverized slag is a latent hydraulic material and could thus be recycled as a cement replacement to make blends [4], or an eco-cement. In other words, the melting of MSWI fly ash to make slag-blended cement could not only resolve both detoxification and disposal problems, but also provide the means to recover the ashes as construction material. However, MSWI fly ash is often classified as hazardous, and in order to provide physical property analyses and a safety evaluation of masonry units made from the ash-blended cement, the hydraulic activity and the heavy metal leachability of the blends must be known. This means that the study of the hydraulic activity and heavy metal leachability of the vitrified slag powder in an alkaline environment as provided by the cement.

The work presented here is concerned with the preparation of slag-blended cement (referred to as SBC or eco-cement), using slag from the melting of MSWI fly ash. The hydraulic activity, compressive strength development, microstructure

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Table 1
Major components and heavy metal contents in MSWI fly ash

Major components (%)										Heavy metal contents (mg/kg)				
SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	TiO_2	P_2O_5	SO_3	Pb	Cd	Cr	Cu	Zn
34.3	16.6	4.3	3.6	5.3	3.0	1.6	4.2	3.9	8.8	1393.4	47.5	326.0	1048.3	6240.3

variations, and the heavy metal leachability of the fly-ash-slag-blended cement (FASBC) pastes are all studied.

2. Materials and methods

2.1. Preparation of MSWI fly ash slag

The fly ash samples used in this study were collected from the cyclone of a mass-burning incinerator located in the northern part of Taiwan. The incinerator has a daily processing capacity of 1350 metric tons and is equipped with air pollution control devices (APCDs) consisting of a cyclone, an adsorption reactor, and a fabric baghouse filter. The fly ash taken from the cyclone was homogenized and oven-dried at 105°C for 24 h. After the samples were dried and cooled, they were again ground and homogenized. Finally, the dried pulverized ash was sieved. The fraction passing through a no. 50 mesh was then analyzed to determine its principal properties (shown in Table 1).

In this study, synthetic MSWI fly ash slag samples with a high heavy metal content were prepared by adding heavy metal oxides and chlorides, for each target metal, to the MSWI fly ash before melting. The additions were conducted both to ascertain the leaching safety and for the possibility of treating industrial incinerator slag having high heavy metal contents. The amounts of heavy metal added were based on the averaged heavy metal content of waste incinerator fly ash from an industrial park, with the assumption that the heavy metals were present in equal amounts of chlorides and oxides. The spiked heavy metal compounds and their concentrations are summarized in Table 2. Finally, the spiked MSWI fly ashes were melted at 1300–1500°C in an electrically heated furnace to obtain slag samples with varying heavy metal contents. The resultant samples were water-quenched and further pulverized to obtain a specific surface of 557.1 m^2/kg.

2.2. Approach

The pulverized slag samples prepared as above were used as a cement replacement, and were blended with ordinary Portland cement (type I), at replacement ratios ranging from 0% to 60%, resulting in four types of slag-blended cement with different heavy metal contents. Pastes using the aforementioned blends were prepared with a water to binder ratio of 0.35. Test cubes of 25.4 × 25.4 × 25.4 mm (1 × 1 × 1 in.) were prepared according to ASTM-305, followed by moulding (ASTM C31-69). The specimens were demoulded and cured in a container at 100% humidity at 25°C for 3–28 days. The compressive strength development of the blends was then measured for specimens of different ages according to ASTM C39-72. The leachability of the specimens was then analyzed by the Toxicity Characteristic Leaching Procedure (TCLP) test. The composition changes and the hydraulic activity were analyzed, using both the XRD and NMR techniques, for pulverized and sieved (no. 300) samples whose hydration was terminated at the tested age by rapid cooling with acetone under a vacuum.

2.3. Analyses

Chemical and physical analyses of FASBC pastes at different ages were conducted as follows:

- Unconfined compressive strength (UCS): ASTM C39-72;
- Heavy metal leachability (TCLP): SW864-1311;

Table 2
Heavy metal content in MSWI fly ash, synthetic slag, and the concentrations of compound spiked

	MSWI fly ash		Spikes			Synthetic slag after melting	
Heavy metals	Contents (mg/kg)	TCLP Concentration (mg/l)	Compounds	Concentration (mg/kg)	Total contents in spiked fly ash (mg/kg)	Contents (mg/kg)	TCLP concentration (mg/l)
Pb	1393.4 ± 101.6	0.71 ± 0.18	PbO	4.6	10,000	971.5 ± 965.4	1.33 ± 0.57
			$PbCl_2$	5.8			
Cd	47.5 ± 7.8	1.85 ± 0.17	CdO	1.7	3000	28.2 ± 22.8	0.70 ± 0.03
			$CdCl_2$	2.4			
Cr	326.0 ± 33.5	0.58 ± 0.41	Cr_2O_3	3.4	5000	2622.7 ± 2226.6	0.94 ± 0.23
			$CrCl_3$	7.1			
Cu	1048.3 ± 51.7	0.35 ± 0.12	CuO	3.7	7000	1810.4 ± 1415.7	1.08 ± 0.33
			$CuCl_2$	6.3			
Zn	6240.3 ± 1237.8	24.00 ± 6.82	ZnO	24.0	45,000	28634.4 ± 13989.5	30.26 ± 10.84
			$ZnCl_2$	40.0			

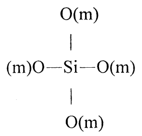
Table 3
Range of ^{29}Si chemical shifts of Q^n units in solid silicates

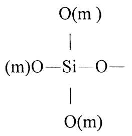
Types of Si–O–X group	Symbol	Range (ppm)
Monosilicates	Q^0	− 68 to − 76
Disilicates and chain end groups	Q^1	− 76 to − 82
Chain middle groups	Q^2	− 82 to − 88
Chain branching sites	Q^3	− 88 to − 92
Three-dimensional networks	Q^4	− 92 to − 129

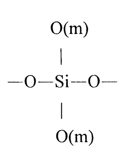
- Heavy metal concentration: Cd (SW864-7131A), Pb (SW864-7421), Zn (SW864-7951), Cu (SW864-7211), and Cr (SW864-7191);
- Chemical compositions: ICP; and
- ^{29}Si chemical shift of silicates: ^{29}Si NMR techniques (^{29}Si nuclear magnetic resonance).

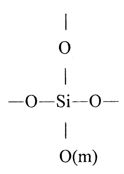
The degree of hydration of the cement clinkers, C_2S and C_3S, and the average length of linear polysilicate anions in calcium silicate hydrates (C-S-H) gels, primarily responsible for the strength, were analyzed by using high-resolution solid state ^{29}Si MAS/NMR techniques as follows:

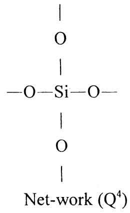
The increase of the diamagnetic shielding to the ^{29}Si nuclei, which resulted from the degree of increasing condensation, from the single tetrahedral structure of monosilicates (Q^0) to chain end groups (Q^1), to chain middle groups (Q^2), to layers and branching sites (Q^3), and finally to three-dimensional networks (Q^4), led to well-separated and analytically useful chemical shift ranges for each type of the SiO_4 units [5,6]. That is, the C-S-H, the hydration products in cement, can be semi-quantified using chemical shifts in the ^{29}Si nuclei in Si–O–X groups, whose structures are shown below [7]:


Tetrahedra (Q^0)


Chain end (Q^1)


Chain middle (Q^2)


Chain branch (Q^3)


Net-work (Q^4)

High-resolution ^{29}Si MAS/NMR spectra were recorded at 39.72 MHz on an MSL Bruker MAS/NMR-200 solid-state high-resolution spectrometer, using rapid (about 3 kHz) sample spinning at the magic angle to the external magnetic field. The ^{29}Si chemical shifts are given relative to the primary standard liquid tetramethylsilane (TMS) in the delta scale (the negative signs correspond to up-field shifts.) The sharp ^{29}Si signal chemical shifts for the above S–O–X groups in solid silicates are summarized in Table 3.

The hydration degree (designated as alpha) of the cement clinkers, C_2S and C_3S, can be evaluated as follows by the integral intensity of the signals at − 70 ppm (Q^0) for hydrated cement paste and cement powders [8,9], i.e., $I^0(Q^0)$ and $I(Q^0)$, respectively [Eq. (1)]:

$$\alpha\ (\%) = 100 - [I(Q^0)/I^0(Q^0)] \times 100 \qquad (1)$$

Moreover, the averaged length of linear polysilicate anions in C-S-H gel, expressed as Ψ, can be estimated as follows [Eq. (2)]:

$$\Psi = 2 \times [I(Q^1) + I(Q^2)]/I(Q^1) \qquad (2)$$

where $I(Q^1)$ and $I(Q^2)$ represent the integral intensity of the signals at − 80 ppm (Q^1) and − 87 ppm (Q^2), respectively.

To evaluate the hydraulic activity of MSWI FASBC paste, three replacement ratios, 20%, 40%, and 60%, were used in this study.

3. Results and discussion

3.1. Characterization of MSWI fly ash and slag

The properties of the MSWI cyclone ash used in this study were analyzed and are summarized in Table 1. It is noted that SiO_2, CaO, Al_2O_3, comprising 58.7% of the ash, were the primary components found in the ash. In addition, there was a high content of heavy metals, such as Pb, Zn, and Cu, in the fly ash, as shown in Table 2. However, the Cd TCLP leaching concentration exceeds the EPA's regulatory thresholds. The MSWI fly ash has a basicity (CaO/SiO_2) of 0.48, and a loss on ignition of 2.4%.

In order to obtain synthetic ash slag with a high heavy metal content, the cyclone ash was spiked with heavy metal compounds before melting (Table 2). Comparisons between the content of the spiked ash and the resultant slag indicated

Table 4
Development of unconfined compressive strength development for the slag-blended cement pastes (unit:MPa)

Curing time (days)	Cement replacement by weight (%)				
	0	10	20	40	60
3	29.7 ± 3.4	19.3 ± 1.4	17.2 ± 2.2	9.0 ± 0.5	8.2 ± 0.6
7	48.1 ± 0.2	41.6 ± 2.2	33.8 ± 3.4	16.0 ± 1.7	12.3 ± 2.1
14	50.1 ± 1.2	56.3 ± 4.0	44.6 ± 7.3	26.1 ± 2.9	16.9 ± 0.9
28	67.9 ± 0.3	80.2 ± 4.4	69.8 ± 3.9	38.9 ± 7.8	28.7 ± 1.3

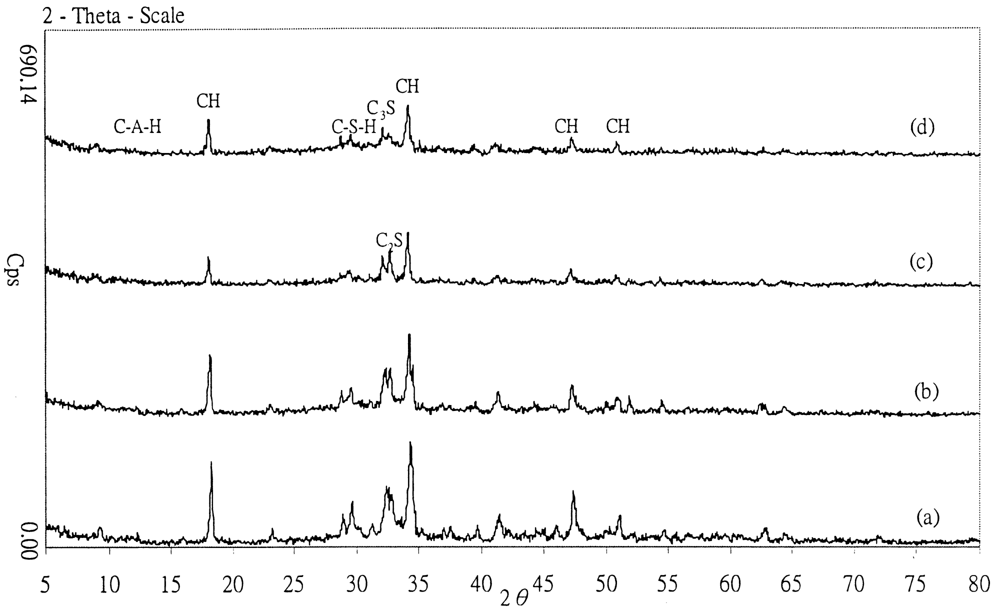


Fig. 1. XRD patterns of FASBC at 3 days with various cement replacement ratios (cement/slag): (a) 100:0; (b) 90:10; (c) 80:20; and (d) 60:40.

that the volatile metals, such as Cd and Pb, evaporated during the melting process, whereas the non-volatile metals, such as Cu and Cr, were, for the most part, retained and incorporated into the glassy Si–O matrix. Therefore, it was found that the heavy metal contents of the slag were high, but their leaching concentrations were relatively low, all meeting the regulatory thresholds.

3.2. Compressive strength of FASBC pastes

Table 4 shows the development of compressive strength in the slag-blended paste with the cement replacement by fly ash slag, ranging from 0% to 60% (by weight), for curing times from 3 to 28 days. It was found that the early compressive strength of the slag-blended cement pastes was lower than for the plain pastes, which may be explainable by the fact that the early strength as contributed by the cement hydration, was decreased by the dilution effects due to the addition of slag. Therefore, the greater the weight percentage of the cement replacement, the lower the early compressive strength of the FASBC pastes. However, at later stages (28th day), the compressive strength of blended cement pastes, with replacements of 10% and 20%, outperformed the plain paste, as the latent pozzolanicity was

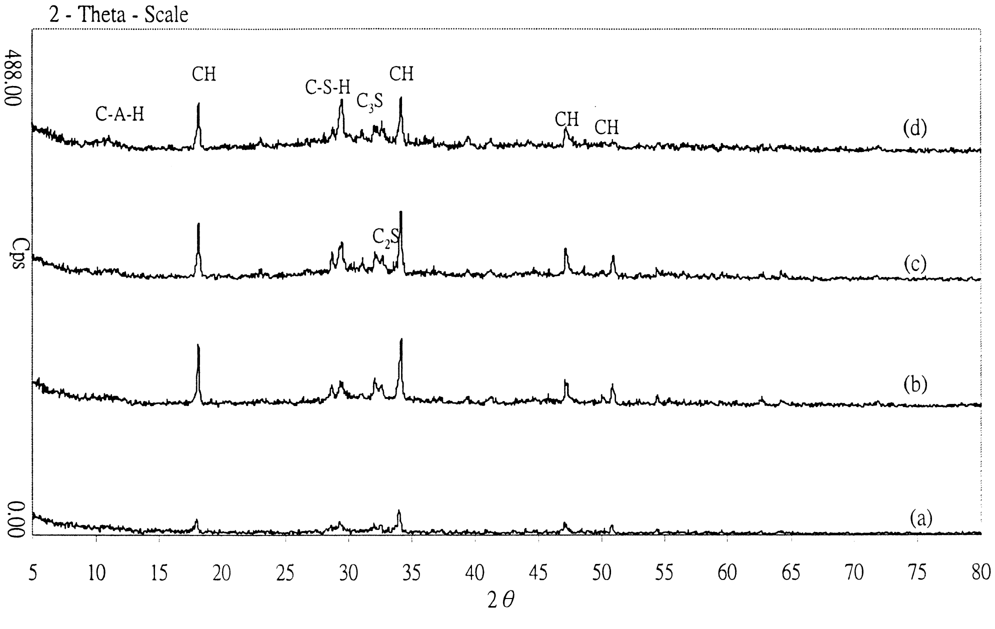


Fig. 2. XRD patterns of FASBC at 28 days with various cement replacement ratios (cement/slag): (a) 100:0; (b) 90:10; (c) 80:20; and (d) 60:40.

activated by alkalis, such as OH$^-$, which was released during cement hydration. The FASBC strength development trends reflect this lower early strength, longer setting time, but higher later strength of pozzolanic materials. It is supposed that the slag provides Si, which enhances the formation of C-S-H, a gel in cement responsible for strength development. However, the excessive replacement of cement, up to 40%, resulted in a relative deficiency of the

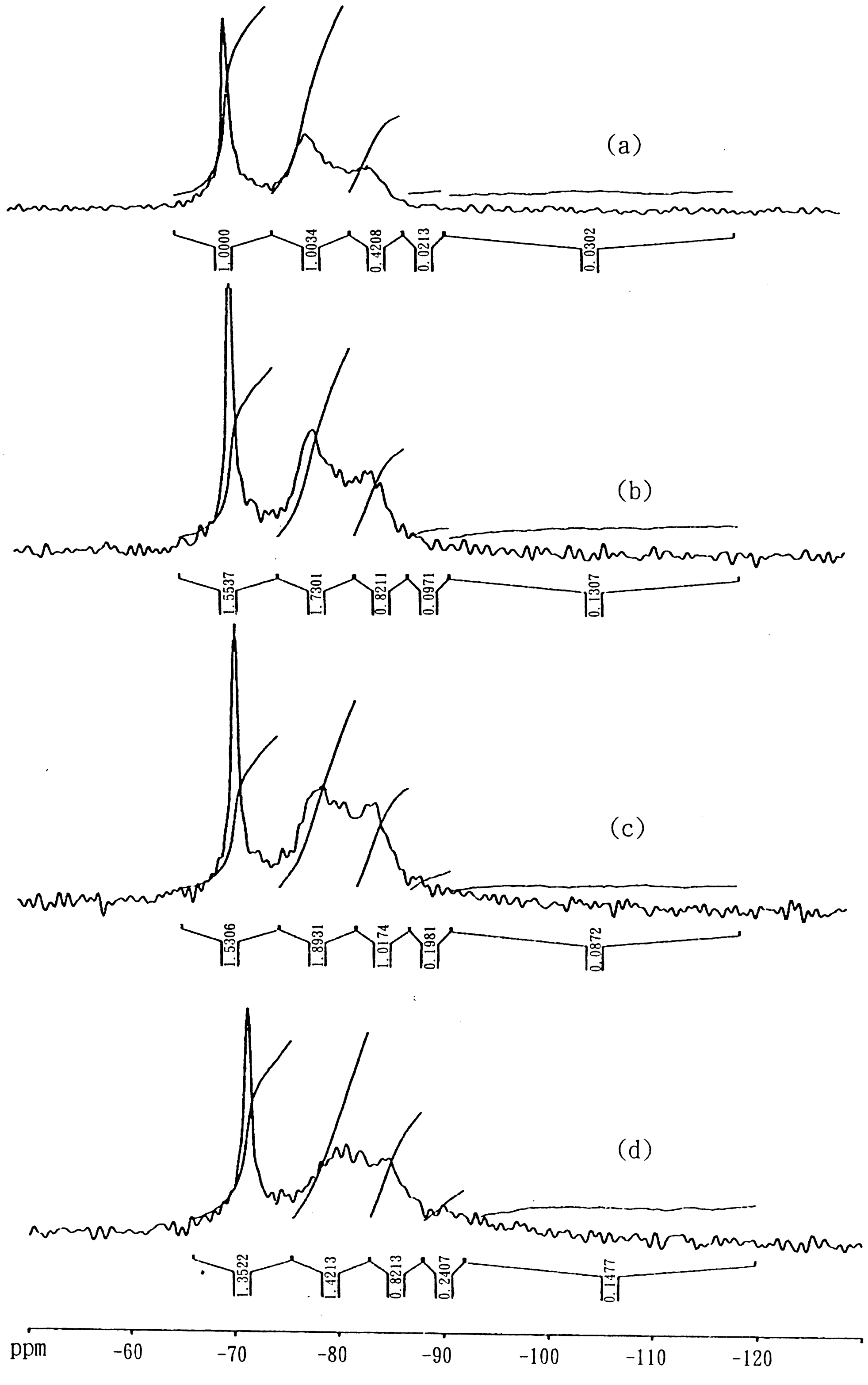


Fig. 3. ^{29}Si MAS/NMR spectra of FASBC at 28 days with various cement replacement ratios (cement/slag): (a)100:0; (b) 90:10; (c)80:20; and (d) 60:40.

Table 5
NMR analysis for slag blended monolith curing at 25°C for 28 days

FASBC cement/slag	Integral intensities of Q^n, ^{29}Si NMR							
	$I(Q^0)$	$I(Q^1)$	$I(Q^2)$	$I(Q^3)$	$I(Q^4)$	Total	α (%)	Ψ[a]
100:0	1 (40.39)[b]	1.0034 (40.53)	0.4208 (17.00)	0.0213 (0.86)	0.0302 (1.22)	2.4757 (100)	59.6	5.4
80:20	1.5537 (35.86)	1.7301 (39.93)	0.8211 (18.95)	0.0971 (2.24)	0.1307 (3.02)	4.3327 (100)	64.1	5.8
60:40	1.5306 (32.38)	1.8931 (40.05)	1.0174 (21.53)	0.1981 (4.19)	0.0872 (1.84)	4.7264 (100)	67.6	6.1
40:60	1.3522 (33.95)	1.4213 (35.68)	0.8213 (20.62)	0.2407 (6.04)	0.1477 (3.71)	3.9832 (100)	66.1	6.4

[a] Values modified according to sample weights.

[b] Values inside the brackets indicates percentage.

cement hydrate, $Ca(OH)_2$, thus decreasing the total volume of C-S-H, their deposition density, and thus the compressive strength of the FASBC paste.

3.3. FASBC pozzolanic reactions

When pozzolans are used in combination with cement, the faster hydration of cement releases hydroxyl ions (OH^-), which then break down and dissolve the glassy structure of the slag, forming C-S-H while consuming $Ca(OH)_2$ [10]. Since C-S-H contributes to the strength of the paste, it is possible to trace the advance of the pozzolanic reaction, by measuring the compressive strength and the $Ca(OH)_2$ content.

Fig. 1 and Fig. 2 show the X-ray diffraction (XRD) pattern results for FASBC, with 0%, 20%, 40%, and 60% cement replacement ratio at 3 days and 28 days, respectively. Higher peaks for CH, C_3S (tri-calcium silicate), and C_2S (di-calcium silicate) were identified for the plain paste as compared with the FASBC paste, suggesting a faster hydration process for plain cement at an early age, reflected by the stronger compressive strength of the plain paste.

In general, pozzolanic reactions start with the chemical adsorption of calcium hydroxide on the surface of silanol groups [11]. Since the pH of the solution is high, SiO_2 is dissolved, reacting with $Ca(OH)_2$ to form C-S-H on the surface of SiO_2 as follows [Eq. (3)]:

$$SiO_{2(S)} + Ca^{2+}_{aq} + 2OH^-_{aq} \rightarrow n_1CaO \cdot SiO_2 \cdot n_2H_2O \qquad (3)$$

Pozzolanic materials, when blended with cement, will affect the cementing properties of the cement, in particular, the later reaction of amorphous silicates with $Ca(OH)_2$ to form C-S-H and C-A-H [12].

Fig. 2 indicates that the CH, C_3S, and C_2S found in FASBC paste at a later age (the 28th day), had increased when the pozzolanic reaction consumed CH to form low density C-S-H and C-A-H gels, which contribute to the later strength of FASBC paste.

3.4. ^{29}Si NMR analysis on FASBC

^{29}Si MAS/NMR spectra for plain and FASBC pastes with different cement replacement weight percentages are shown in Fig. 3. It is found that an increase in the replacement weight percentage will result in an intensity variation in the components, centered at about −72, −81, −86, −90, and −110 ppm, each corresponding to the single tetrahedra of monosilicates (Q^0), chain end groups (Q^1), chain middle groups (Q^2), layers and branching sites (Q^3), and three-dimensional networks (Q^4), respectively. The hydration degree of the cement clinkers, C_2S and C_3S, and the average length of the linear polysilicate anions in C-S-H for the plain and FASBC pastes at 28 days, were calculated and are summarized in Table 5, showing that both the hydration degree and the averaged length of linear polysilicate anions increased with the increasing weight percentage of cement replacement in FASBC.

Hydration in cement paste generates hydrates such as C-S-H, $Ca(OH)_2$, Ettringite (Aft, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) and monosulpho-aluminate Hydrate (Afm, $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$). Of these hydrates, $Ca(OH)_2$ is essential for the following pozzolanic reactions in the slag. The degree of hydration for FASBC cement paste increased, as evidenced by the analysis of the XRD and ^{29}Si MAS/NMR results, with increases in the weight percentage of cement replacement of up to 40% at the later age (28 days), indicating that the advance in hydration was still in progress.

On the other hand, at 28 days, the average length of linear polysilicate anions in the C-S-H also showed an increase, with the increasing cement replacement percentage. This suggests that more silica was provided by the blended slag to react with the cement hydrates, $Ca(OH)_2$, and contributed to pozzolanic reactions in the pastes.

3.5. Heavy metal leachability of the FASBC

Table 6 lists the heavy metal leachability of the synthetic slag and the FASBC paste. The synthetic slag was prepared

Table 6
Heavy metal concentration in TCLP leachate for FASBC paste (unit: mg/L)

Heavy metal	Cement replacement (w/w %)				EPA's regulatory thresholds
	0	10	20	40	
Pb	0.44	0.4	0.45	0.47	5.0
Cr	0.03	0.03	0.03	0.04	5.0
Cd	0.08	0.09	0.09	0.09	1.0
Cu	0.04	0.05	0.05	0.05	–
Zn	0.04	0.04	0.04	0.04	–

by spiking the MSWI fly ash before melting with a large amounts of heavy metals, based on the average heavy metal content for incinerator fly ash obtained from an industrial park. It is obvious that the heavy metal leaching concentrations for the synthetic slag and the FASBC paste were significantly low, since heavy metals with different volatility were evaporated or incorporated into the glassy Si–O matrix during the melting process. Although the Cd leaching concentration in the synthetic slag exceeded the EPA's regulatory standards, all the target heavy metal leaching concentrations in FASBC paste complied with the regulatory thresholds. It is assumed that both the incorporation of heavy metals into the slag's Si–O network during the melting process, and the immobilization effects of cement paste, both contributed to the extremely low heavy metal leachability and the increased environmental safety of the FASBC paste.

4. Conclusions

The properties demonstrated by pulverized slag as a latent pozzolanic material for the replacement of cement, based on synthetic slag obtained from MSWI fly ash prepared with a high heavy metal content, lead to the following conclusions.

The early compressive strength of the FASBC pastes was lower than that of the plain pastes; the greater the weight percentage of the cement replacement, the lower the compressive strength of the FASBC pastes. This may be explained by dilution effects from the addition of the latent hydraulic material (the pulverized slag) decreasing the early strength from the hydration of cement in the FASBC paste.

At later stages (28th day), however, the compressive strength of the blended cement paste, (10% and 20% cement replacement, respectively), outperformed the plain paste, because the addition of pulverized slag offered more silicon, enhancing the formation of C-S-H thus increasing the later strength. However, an excess replacement percentage of up to 40% would decrease the later strength, possibly due to a relative deficiency of $Ca(OH)_2$ provided by cement hydration.

The XRD and ^{29}Si MAS/NMR results for the older FASBC pastes (28th day) indicate that both the hydration degree and the average length of the linear polysilicate anions increased with increasing cement-replacement percentage, suggesting an on-going later strength development contributed by the addition of MSWI fly ash slag.

The target heavy metal leaching concentrations for the synthetic slag and the FASBC paste were significantly low, and all the leaching concentrations in the FASBC paste complied with the EPA's regulatory thresholds, indicating the feasibility and safety of the MSWI fly slag in slag-blended cement.

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