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Effects of Al_2O_3 on the hydration activity of municipal solid waste incinerator fly ash slag

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Abstract

This study investigates the effects of slag composition on the hydration activity of slag-blended cement (SBC) pastes. Synthetic slag samples were prepared by melting Al_2O_3-modified, municipal solid-waste incinerator (MSWI) fly ash. In addition to the original slag (containing 25.0% CaO and 17% Al_2O_3), two other synthetic slag types, A1 and A2 slag, were prepared, having a 15% or 5% Al_2O_3 content, respectively. These synthetic slags were blended with ordinary Portland cement (OPC) at weight ratios ranging from 10% to 40%. The results indicate that the incorporation of 10% A1 slag tended to enhance the degree of hydration in SBC pastes during the early ages (3–28 days), but at later ages, significant difference in the degree of hydration between the OPC and SBC pastes with 10% A1 slag was not observed. The tendency of the 10% A2 slag case was similar, but with a limited enhancement during the early ages (3–28 days). However, samples that incorporated the Al_2O_3-modified slag (AMS) showed decreased degrees of hydration. The degree of hydration of the 40% blend ratio sample decreased significantly.

Keywords: Slag blended cement; Hydration activity; Melting process; Degree of hydration; Blend ratio

1. Introduction

Municipal solid waste results in an approximately 90% reduction of mass, in the amount of residue remaining to be disposed after incineration. In addition, for reasons of energy cost savings as well as environmental protection concerns (e.g., reduction of CO_2 emissions), the clinkers in cement should be, wherever possible, replaced by other latent hydraulic materials [1]. The major components in municipal solid-waste incinerator (MSWI) fly ash include SiO_2, Al_2O_3, CaO, and Fe_2O [2,3]. These compounds are also common in ordinary Portland cement (OPC) and can function as binders, as they exhibit self-hardening characteristics.

As sustainable development has become an important trend in waste treatment and management, MSWI fly ash is now being recycled after thermal treatment for construction purposes, such as in permeable bricks, interlocking blocks, and aggregates [4], or slag-blended cement (SBC) [5]. The results indicate that these latent hydraulic pozzolans can be used to partially replace the mineral pozzolans in cement paste or concrete. Furthermore, by recycling MSWI fly ash slag into valuable, high-grade materials, environmental protection aims can be met.

The paper is concerned with the effect of modifying of MSWI fly ash slag for use as latent hydraulic material. The performance of synthetic slag produced by the melting of MSWI fly ash at 1400 °C for 30 min in the presence of alumina is tested to determine the chemical composition that would be most suitable as a pozzolanic material.

2. Materials and methods

2.1. Materials

2.1.1. MSWI fly ash

The fly ash used in this study was collected from a cyclone boiler of a mass-burning incinerator located in the

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Table 1
Chemical composition and pozzolanic activity index of OPC and modified slags

Samples	Pozzolanic activity index[a](%)	Chemical composition[b](%)								
		CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	SO_3	Na_2O	MgO	Cl
OPC	–	62.5	20.5	6.5	3.2	<0.01	2.2	<0.01	1.9	<0.01
MSWI fly ash	–	14.7	35.8	9.8	4.9	5.3	2.2	5.9	0.8	0.25
MSWI fly ash slag	79.2	25.0	35.1	16.5	3.8	1.3	1.4	3.2	2.8	0.07
A1 slag	94.2	22.5	29.7	38.3	3.4	1.6	0.6	1.9	2.5	0.03
A2 slag	91.4	23.6	31.8	22.8	3.8	2.1	1.1	2.0	2.4	0.04

[a] Analyzed by ASTM C311.
[b] Analyzed by ICP-AES after $HF/HClO_4/HNO_3$ digestion.

northern part of Taiwan. The incinerator, capable of processing 1350 tons of local municipal solid waste per day, is equipped with some air-pollution-control devices, consisting of a cyclone, a semidry scrubber, and a fabric baghouse filter. The fly ash was homogenized, oven dried at 105 °C for 24 h, and desiccated before testing. The chemical composition of the fly ash is shown in Table 1. SiO_2, CaO, and Al_2O_3 comprise 35.8%, 14.7%, and 9.8%, respectively. The next most abundant components are Na_2O, K_2O, and Fe_2O_3, contributing about 5.9%, 5.3%, and 4.9% each. The ash has a basicity (defined as CaO/SiO_2) of 0.41, and a pouring point of approximately 1200 °C.

2.1.2. Cement

ASTM Type I Portland cement (OPC) from Taiwan Cement was used in this study. Its specific gravity was 3.15 and its physical–chemical properties met the requirements of ASTM C150. The major composition of the OPC is listed in Table 1.

2.1.3. MSWI fly ash slag

MSWI fly ash slag was prepared by first melting the MSWI fly ash at 1400 °C for 30 min. The molten slag was then water-quenched to produce a fine slag. The water-quenched slag was then further pulverized in a ball mill until particles could pass through a 200-mesh sieve. The resultant pulverized fly ash slag (or MSWI fly ash slag) was desiccated before the testing and subsequent preparation of SBC. The pozzolanic activity of the pulverized slag was analyzed according to ASTM C311, and the results are presented in Table 1.

2.1.4. Composition-modified slags

The mixing of MSWI fly ash with various amounts of Al_2O_3 produced composition-modified slag. The different proportions used in the melt are shown in Table 2. These mixtures were then melted at 1400 °C for 30 min. This process produced two types of synthetic slag. The unmodified slag is referred to as MSWI fly ash slag.

Table 2
Proportions of raw material used for the preparation of synthetic slags

Types of slag	Raw material (wt.%)	
	MSWI fly ash	Al_2O_3
MSWI fly ash slag	100	
A1 slag	85	15
A2 slag	95	5

2.2. Paste tests

SBC was prepared by mixing cement and modified slag. A1 or A2 slags were used to partially replace the cement at ratios of 10%, 20%, and 40%. The results for cement blends incorporating A1 slag and A2 slag at ratios of 10–40% are shown in Table 3.

The pastes used in this study were further prepared by homogeneously mixing the SBC with water in a mixer according to ASTM C311. The mixed SBC paste was tested. A slag blend ratio ranging from 10% to 40% was used with a constant water/binder (w/b) ratio of 0.38. SBC paste cubes were prepared according to ASTM C109 and cured for a period ranging from 1 to 90 days. At each given curing age, the SBC paste cubes were subjected to unconfined compressive strength (UCS) tests. Subsequently, hydration reactions in the crushed samples were terminated with methyl alcohol. They were then subjected to mercury intrusion porosimetry (MIP) and X-ray diffraction analyses.

2.3. Analytical methods

Analyses of both SBC paste samples and cubes were performed. The major analytical methods included testing

Table 3
Proportions of material used in the different paste series

Samples	Cement	Composition-modified slag (wt.%)		w/b
		A1 slag	A2 slag	
OPC paste	100			0.38
AMS paste				
HA1	90	10		0.38
HA2	90		10	0.38
MA1	80	20		0.38
MA2	80		20	0.38
LA1	60	40		0.38
LA2	60		40	0.38

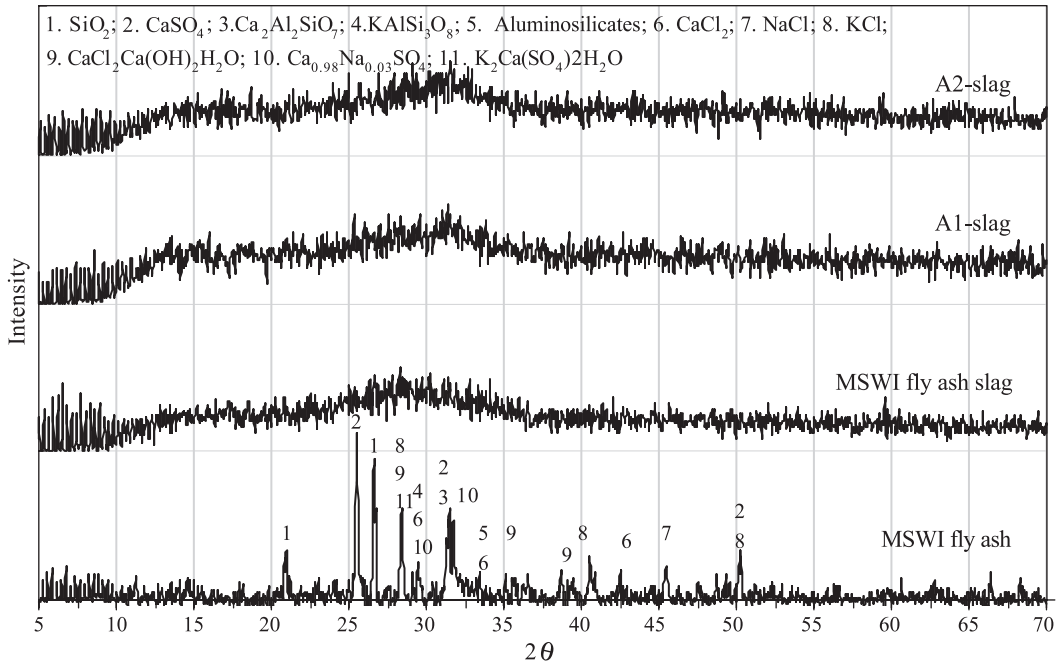

Fig. 1. The XRD patterns of MSWI fly ash, MSWI fly ash slag, and AMS.

for the compressive strength, the toxicity characteristic leaching procedure (TCLP), and chemical composition characterization:

(1) Compressive strength test: ASTM C39.
(2) Pozzolanic activity index: ASTM C311.
(3) TCLP test: SW846-1311[6].
(4) Leaching concentration: Cd (SW846-7131A), Pb (SW846-7421), Zn (SW846-7951), Cu (SW846-7211), Cr (SW846-7191).
(5) Chemical composition determination: inductively coupled plasma atomic emission spectroscopy (ICP-AES). Two-gram samples were digested with ultra-pure-grade reagents using a three-step procedure: hydrofluoric/nitric concentrated acid mixed at a ratio of 5:5 ml was added to the sample; after evaporation, a 3:9-ml mixture of nitric/hydrochloric concentrated acid was added; after another evaporation, the samples were dissolved in 5% nitric acid solution.
(6) Pore size distribution: MIP.
(7) Degree of hydration: The degree of hydration of SBC pastes was determined by thermal analysis [7]. A thermogravimetric analysis instrument was used to determine the degree of hydration of the SBC paste samples using the ignition method. The degree of hydration was then calculated as follows:

$$\alpha = \frac{(W_{105} - W_{580}) + 0.41(W_{580} - W_{1007})}{nW_{1007}} \times 100\%,$$

where α is the hydration degree (%); n is water fixed in completely hydrated cement pastes (0.24 for OPC paste); W105, W580, and W1007 are the sample weights at 150, 580, and 1007 °C, respectively (g); and 0.41 is the conversion factor for a molar ratio of CaCO3-derived CO2 to H2O.

3. Results and discussion

3.1. Characterization of the composition-modified fly ash slag

According to ICP-AES analysis, the major components observed in the composition-modified fly ash slag were SiO_2 (29–33%), CaO (22–42%), and Al_2O_3 (14–38%). The next most abundant components were Fe_2O_3 (3–4%), Na_2O (2–3%), and K_2O (1–2%). Fig. 1 shows the speciation in the fly ash, as identified by the XRD techniques, indicating that the major components were

Table 4
TCLP leaching concentration of the MSW fly ash and the modified slags

Element	MSWI fly ash	A1 slag	A2 slag	Regulatory limits
Cd (mg/l)	1.8	0.12	0.13	1.0
Cr (mg/l)	4.3	0.92	1.05	5.0
Pb (mg/l)	0.7	0.23	0.33	5.0
Cu (mg/l)	0.6	0.45	0.48	–
Zn (mg/l)	16.2	5.73	6.57	–

quartz (SiO_2), anhydrite ($CaSO_4$), gehlenite ($Ca_2Al_2SiO_7$), anorthite ($CaAl_2Si_2O_8$), microcline ($KAlSi_3O_8$), calcium chloride ($CaCl_2$), $CaCl_2{\cdot}Ca(OH)_2{\cdot}H_2O$, sylvite (KCl), and halite (NaCl). Fig. 1 shows that MSWI fly ash slag, A1 slag, and A2 slag contain large amounts of glass. The TCLP leaching concentrations for the target metals met the EPA's current regulatory thresholds and are presented in Table 4.

Note that all the modified slag samples in Table 1 have a pozzolanic activity index higher than the MSWI slag sample. Hence, it is suggested that the Al modifications contributed to the pozzolanic activity (at 28 days). Compared to 79.2% for the MSWI slag, the pozzolanic activity index of the Al_2O_3-modified slag (AMS) showed an enhanced pozzolanic activity index, reaching 94.2% and 91.4%, respectively, for the A1 and A2 slag samples. This is also higher than that of the MSWI slag sample.

3.2. Strength development of SBC pastes

Fig. 2 presents the strength development of SBC samples incorporating the A1 and A2 slags. The 7-day strength of SBC pastes incorporating A2 slag, at a blend ratio of 10%, surpassed that of OPC pastes. At curing times beyond 28 days, the strength of the HA2 paste was similar to that of the OPC paste, whereas the strength of the HA1 pastes leveled off to about 80% of the strength of the OPC samples. It can be seen from the results that increasing the amount of aluminum oxide increased the early strength of SBC, but an excess amount of aluminum decreased the later strength. In addition, blend ratios greater than 10% tended to decrease the strength of SBC pastes that incorporated A1 and A2 slags. The results indicate that increasing the amount of aluminum oxide will enhance early hydration, but an excessive amount of aluminum oxide adversely decreases the later strength.

3.3. Pore size distribution in SBC pastes

The variation of fine pores in the AMS pastes show different patterns in Figs. 3 and 4. The percentage of the volume of fine pores (pore diameter <10 nm) [8] increases with the curing time and the blend ratio for HA2, MA2, and LA2 pastes. In contrast, for HA2, MA2, and LA2, the volume percentage of fine pores tended to decrease at curing times longer than 28 days. One possible explanation for the pore size variation in the HA1, MA1, and LA1 pastes could be that the active reaction products, calcium sulfate hydrates (ettringite, monosulfate), produced swelling, thus decreasing the fine pore volume.

3.4. SBC hydrates with synthetic slags

The hydration products of SBC pastes incorporating synthetic slags and characterized by a modified Al_2O_3 content were identified by XRD techniques. The results are listed in Fig. 5. Ettringite ($Ca_6Al_2(SO_4)_3{\cdot}32H_2O$, AFt), monosulfate ($Ca_4Al(SO_4){\cdot}18H_2O$, AFm), and C_3A (i.e., $3CaO{\cdot}Al_2O_3$) were also identified in the SBC paste with AMS samples. More AFt than AFm was formed in the SBC paste with AMS samples. In the system of hydration, the addition of $CaSO_4$ is needed in proportion to the amount of Al_2O_3 added to accelerate the hydration of both ettringite

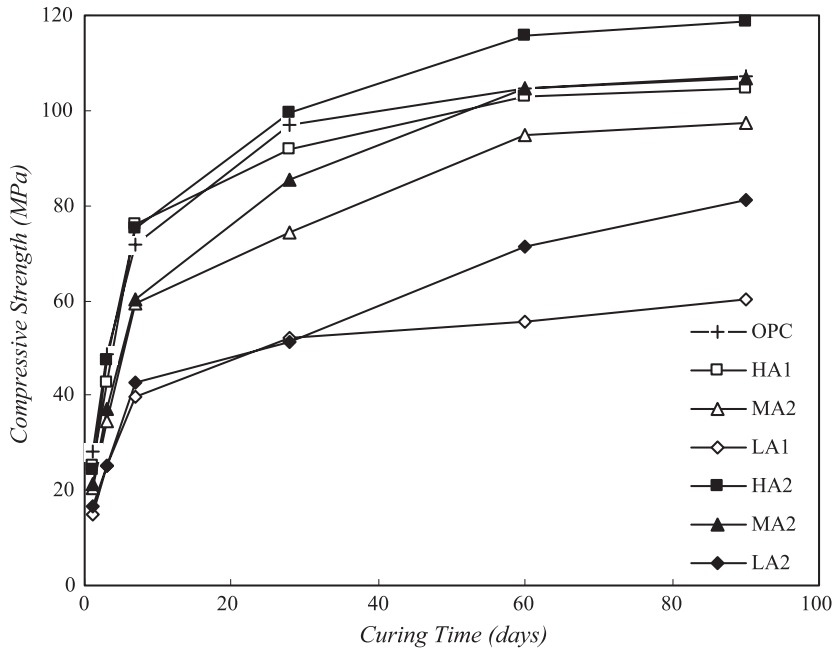

Fig. 2. Compressive strength development of AMS pastes.

and C-S-H gel. The formation of ettringite contributes to the strength at early ages, and then C-S-H gel contributes to the continuous strength development at late ages. The rapid transformation between AFm and AFt, as affected by the AlO_4^-, SO_4^{2-}, and Ca^{2+} concentrations, is generally considered to adversely affect the engineering properties of SBC pastes.

3.5. The degree of hydration of OPC and SBC pastes

The degree of hydration in the cement pastes caused the particle size and the formation of hydrates in the cement to decrease. For example, C-S-H, $Ca(OH)_2$, AFt, and AFm filled pores between the particles, which increased the strength of the pastes. Bentur [9] determined the degree of hydration based on the loss on ignition, regarding the degree of hydration to be a result of the gels that grew in the pastes. Table 5 lists all the degrees of hydration for samples of OPC and SBC paste, blended with various synthetic slags at different ratios. Generally, the degree of hydration increases with the curing time but decreases with the blend ratio. The HA2 paste produced a similar degree of hydration at 90 days, but had a slower rate before 90 days. Generally, the HA1, MA1, and LA1 pastes had adverse effects on the degree of hydration. These effects were more profound at blend ratios greater than 10%.

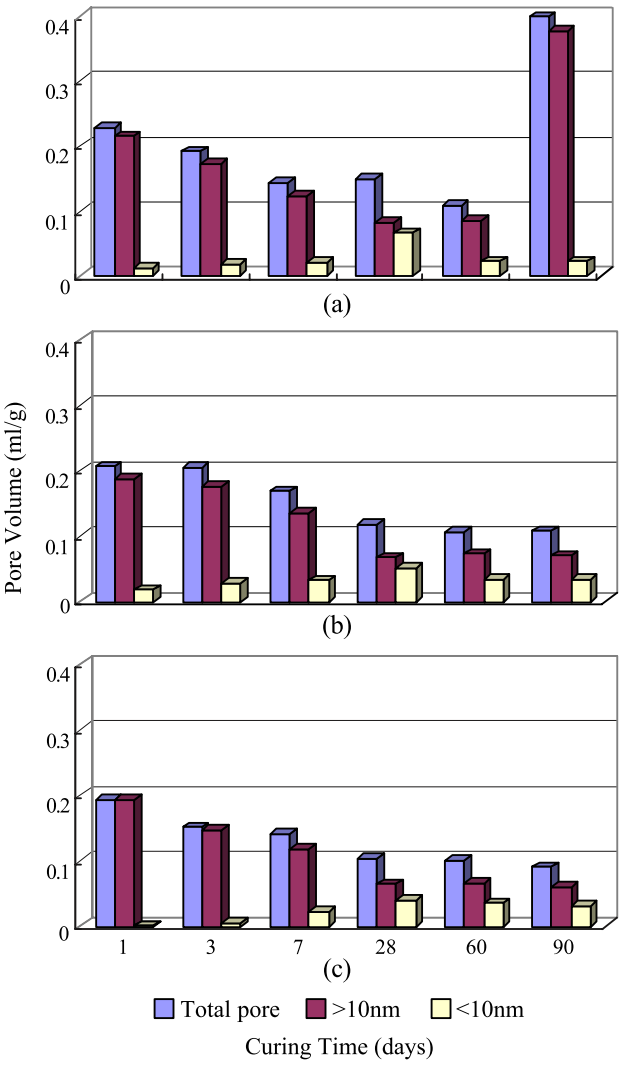

Fig. 3. Pore size distribution in blended cement pastes incorporating A1 slag: (a) HA1 (b) MA1, and (c) LA1.

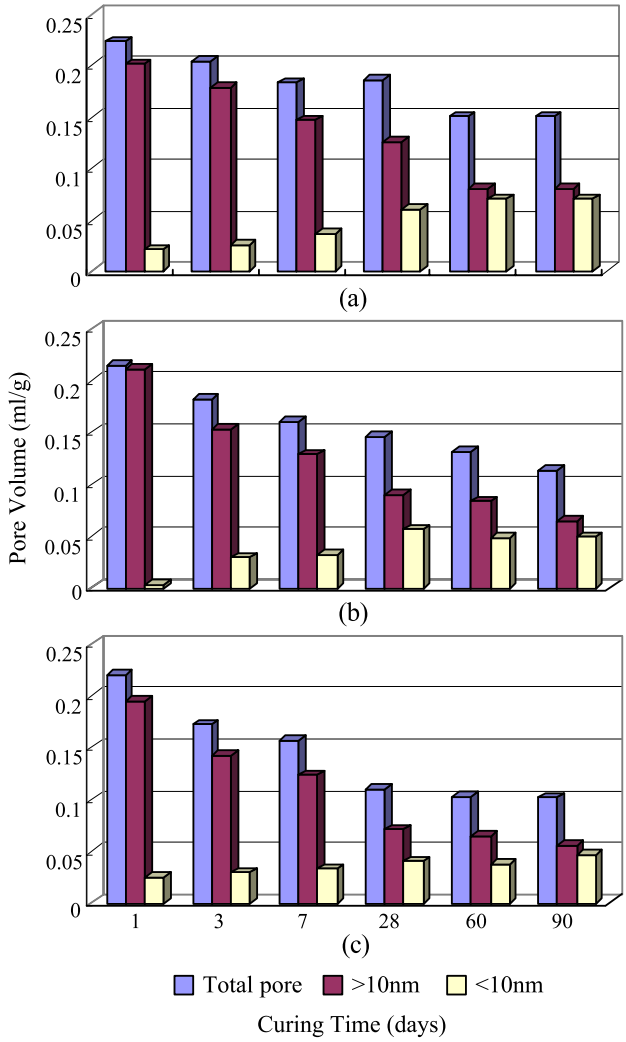

Fig. 4. Pore size distribution in blended cement pastes incorporating A2 slag: (a) HA2 (b) MA2, and (c) LA2.

4. Conclusions

The effects of the slag composition on the hydration activity of SBC pastes, prepared by melting Al_2O_3-modified MSWI fly ash, were examined. Based on the experimental results obtained, the following conclusions can be summarized:

1. The TCLP leaching concentrations for the target metals all met the EPA's current regulatory thresholds.

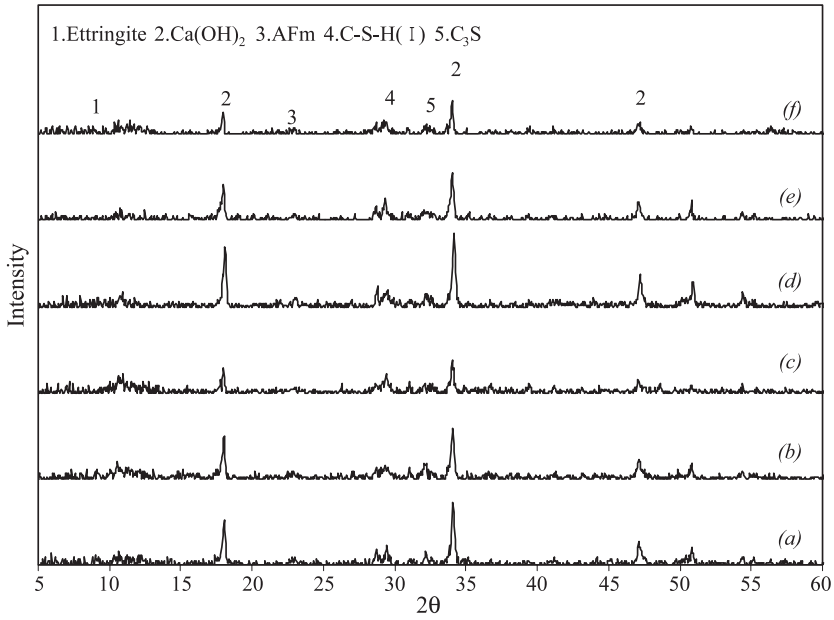

Fig. 5. X-ray diffraction patterns for hydrated SBC pastes incorporating AMS for 90 days: (a) HA1 (b) MA1 (c) LA1 (d) HA2 (e) MA2, and (f) LA2.

2. The pozzolanic activity index of AMS showed an enhanced pozzolanic activity index reaching 94.2% and 91.4%, respectively, for A1 and A2 slag samples. This was also higher than that of the MSWI slag sample.
3. The strength development results indicate that increasing the amount of aluminum oxide enhanced early hydration, but an excessive amount of aluminum oxide adversely decreased the later strength.
4. The incorporation of AMS tended to decrease the degree of hydration due to the adverse effects of Al2O3.
5. In all samples where the blend ratio was 40%, the hydration degree decreased significantly.

Table 5
Hydration degree of OPC and SBC pastes incorporating modified slags

Paste	Hydration degree (%)					
	1 day	3 days	7 days	28 days	60 days	90 days
OPC	43.6	51.8	59.8	70.0	75.4	82.9
HA1	33.4	44.9	52.9	64.2	66.9	68.2
MA1	26.5	38.7	47.7	58.8	65.6	66.1
LA1	21.3	30.7	37.7	48.4	57.0	64.0
HA2	30.6	41.3	49.0	58.4	69.3	80.1
MA2	25.3	37.2	43.3	54.2	66.0	76.0
LA2	21.7	28.6	35.3	43.8	55.7	60.4

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