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Enhancement in early strengths of slag-cement mortars by adjusting basicity of the slag prepared from fly-ash of MSWI

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ABSTRACT

The insufficient early strengths of cement mortars in which partial cement had been replaced by pulverized slag melted from municipal solid waste incinerator (MSWI) fly-ash were tackled in this study by adjusting the basicity of the slag through the addition of various amounts of $CaCO_3$ into MSWI fly-ash, melted into a 'modified slag', pulverized to partially replace cement. Increased basicity in the modified slag manifestly improves the early compressive strengths of cement mortar with 20% Portland cement replaced by the modified slag powder (20 wt.% $CaCO_3$ added). The 14-day and 28-day compressive strengths of the mortars evidently increased to nearly that of the reference specimen made of only Portland cement mortar. The 90-day compressive strength is even higher than that of the reference specimen. Porosity and Fourier transform infrared spectra (FTIR) analyses evidenced the improvement in early strengths by hydration while the enhancement in long-term strength by pozzolanic reaction in the $CaCO_3$ added slag-cement mortar.

1. Introduction

Municipal solid wastes (MSW) in Taiwan are mostly treated in incinerators. The fly-ashes and scrubber-ash (called reaction products) from the municipal solid waste incinerators (MSWI) contain many species of hazardous heavy metals. They are solidified with cement to lessen the leaching out of heavy metals. According to the report of Taiwan Environmental Protection Agency (EPA, Taiwan), there were 22 large MSWIs in operation in Taiwan, 2006, which treated approximately 23,250 tons of solid wastes daily. The weight of combustion residues was about 15% that of the original solid wastes, while the weights of fly-ashes and scrubber-ash were about 3%. Hence, it was estimated that about 250,000 tons of fly-ashes and scrubber-ash was produced yearly, which needed to be carefully treated so that not to be harmful to the environment.

In general, MSWI fly-ashes are solidified using cement, and disposed by landfill. Besides the possibility of leaching out heavy metals [1], the lack of ample space for landfill is a common problem for municipal areas which have dense population in developing and developed countries. Thus the recycling as resources of MSWI fly-ashes is a suitable way of problem-solving.

MSWI bottom-ashes have been used in road construction, as raw materials of red bricks, water-permeable bricks, and ceramics. J. Pera et al. used MSWI bottom ash of sizes 4–20 mm to replace part of coarse aggregates of concrete [2]. Its 28-day compressive strength reached 25 MPa. Even with a massive replacement up to 50% gravel in concrete the durability was reported not affected. However, recycling of MSWI fly-ashes as resources is still under vigorous research and development. Bertolini et al. washed the MSWI fly-ash with water to reduce the chloride content, while bottom-ash was subjected to dry- or wet-grinding under water and each replaces 30% of Portland cement in cement mortar specimens [3]. It was found that the compressive strengths of the specimens containing wet ground bottom-ash were higher than that of the reference specimen and it revealed good pozzolanic reaction. Al-Rawas et al. studied the effects of replacing sand or cement in cement mortars by MSWI fly-ash in various ratios [4]. The results indicated that MSWI fly-ash caused a reduction in slump values when it was used as a replacement for sand; while an opposite trend was observed upon being used as a replacement for cement. The 28-day compressive strength of the latter was similar to or slightly higher than that of the control mix (0% MSWI fly-ash). Lin et al. melted the MSWI fly-ash to slag and ground it to powder [5]. Cubic specimens 25.4×25.4×25.4 mm were prepared for tests of compressive strength from a paste made of the slag and cement with 0%, 10%, and 20% cement replacements by the slag powder. The results showed that 28-day compressive strength of the slag-cement specimens were 84% to 90% that of plain cement specimen, while those of the 90-day ones were 95% to 110% that of plain cement specimen. Lin et al. further added Al_2O_3 to MSWI fly-ash, the mixtures were melted into slag and pulverized to replace part of cement for study [6,7]. The results indicated that Al_2O_3-modified slag tended to enhance the degree of hydration in the pastes during the

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Table 1
Notation of mortar specimens and their constituents for the compressive strength tests.

Designation	Portland cement I	Slag powder	Description of the slag powder
Mortar-Ref	26.7 wt.% solid content	Nil	Slag powder from unmodified MSWI fly-ash
Mortar-I	24.0 wt.% (10% less)	2.7 wt.%	Slag powder from unmodified MSWI fly-ash
Mortar-II	21.4 wt.% (20% less)	5.3 wt.%	Slag powder from unmodified MSWI fly-ash
Mortar-III	18.7 wt.% (30% less)	8.0 wt.%	Slag powder from unmodified MSWI fly-ash
Mortar-IV	16.0 wt.% (40% less)	10.7 wt.%	Slag powder from unmodified MSWI fly-ash
Mortar-II(10)	21.4 wt.% solid content	5.3 wt.%	The slag powder modified with 10 wt.% $CaCO_3$
Mortar-II(20)	21.4 wt.% solid content	5.3 wt.%	The slag powder modified with 20 wt.% $CaCO_3$
Mortar-II(30)	21.4 wt.% solid content	5.3 wt.%	The slag powder modified with 30 wt.% $CaCO_3$
Mortar-II(40)	21.4 wt.% solid content	5.3 wt.%	The slag powder modified with 40 wt.% $CaCO_3$

early ages (3–28 days). Lin replaced 10% to 40% of Type I, Type II Portland cements and Belite cement by MSWI fly-ash slag in cubic 25.4×25.4×25.4 mm specimens for tests of compressive strength [8]. The results also showed lower compressive strengths at early age of the slag-cement specimens than that of plain cement specimen, but those at the later ages were higher. All their specimens passed toxicity characteristics leaching procedure (TCLP) tests, the superior late compressive strengths exhibited characteristics of the pozzolanic material. The above studies mainly investigated the effects of MSWI fly-ash slag powder of particle sizes less than sieve # 200 as an additive on the compressive strength, degree of hydration, microstructure and the change in crystalline phases of the slag-cement mortars. All the reports have the common results of weaker early strengths for the slag-cement mixes.

We designed to tackle the weaker early strengths of the slag-cement by tuning the basicity of the MSWI fly-ash slag. So far as we know, very few in literature investigated the effects of basicity adjustment, modified by $CaCO_3$ as an additive to the MSWI fly-ash, on the compressive strength of the resultant slag-cement mortar.

In this study, the first step was to melt the MSWI fly-ash into slag and to examine with SEM/EDS to check the chemical composition. The second step was to pulverize the MSWI fly-ash slag to fine powder with particle sizes smaller than sieve #400 which were served to replace part of cement in cement mortar (denoted as slag-cement mortar). Test cubes of 50×50×50 mm were prepared and cured for various tests and analyses to investigate the performance of the slag-cement mortar. The third step was to investigate the effect of tuning slag basicity by using $CaCO_3$ as an additive to the fly-ash on the compressive strengths of modified slag-cement mortar, specifically the early strengths.

2. Materials and methods

2.1. Materials

The fly-ash used in this study was collected from the Hsinchu municipal solid waste incinerator located at northwest of Taiwan. The slag was prepared by melting the above MSWI fly-ash in an electric-furnace at 1450 °C for 1 h. The melt was air cooled to obtain lumps of fly-ash slag. Two kinds of powder were prepared:

a. Unmodified fly-ash slag powder which was obtained by pulverizing the fly-ash slag with ball mill to powder of particle sizes smaller than sieve #400.
b. Modified slag powder: Fly-ash was first mixed with 10 wt.%, 20 wt.%, 30 wt.% and 40 wt.% $CaCO_3$ powder, respectively. The admixtures were then melted under the same condition mentioned above and then pulverized with ball mill to powder of particle sizes smaller than sieve #400.

2.1.1. Cement

Type 1 Portland cement, manufactured by the Taiwan cement company. This cement has a specific gravity of 3.15, while its physical and chemical properties meet ASTM C150 specifications.

2.1.2. Sand

The reference sand was Ottawa-type sand that adhered to ASTM C778 specifications. This sand has a specific gravity of 2.63.

2.1.3. Calcium carbonate

White calcium carbonate ($CaCO_3$) powder, purity=99.3 wt.%, chemical grade, specific gravity=2.71, manufactured by the Taiwan Diamond chemical company.

2.2. XRD analyses

The MSWI fly-ash, unmodified fly-ash slag powder, and modified slag powder were prepared for X-ray diffraction (XRD) analyses, which were carried out by an X-ray diffractometer (Rigaku, D/Max-2200, Japan) with Cu $K_{\alpha 1}$ radiation and 2θ scanning ranging between 5° and 70° scanning in 0.05° steps, with a one second counting time.

2.3. Preparation of mortar specimens for testing of compressive strength

The mortar test cubes (50×50×50 mm) were prepared according to Taiwan's testing reference CNS 1010 for tests of compressive strength, water to cement ratio (W/C) of 0.485 was used. A notation Mortar-Ref is defined as the reference specimen made of Portland cement I, reference sand and water. The cement to sand ratio in the mortar was 1:2.75 (weight ratio), such that the cement is 26.7% by weight of the solid content. Certain amounts of the cement in the mortar were then replaced by slag powders (with or without modification) made from MSWI fly-ash. The specimens

Table 2
Chemical composition of cement, MSWI fly-ash, slag powder and modified slag powders.

Chemical composition	Type I Portland cement	MSWI fly-ash	Unmodified slag powder	10% $CaCO_3$-modified slag powder	20% $CaCO_3$-modified slag powder	30% $CaCO_3$-modified slag powder	40% $CaCO_3$-modified slag powder
Na_2O (wt.%)	–	5.93	1.12	2.39	2.18	2.16	1.99
K_2O (wt.%)	–	5.68	–	0.22	0.20	0.16	0.11
CaO (wt.%)	62.12	29.66	32.07	36.96	41.84	45.56	49.79
ZnO (wt.%)	–	2.12	1.87	0.78	0.63	0.57	0.44
CdO (wt.%)	–	0.86	–	–	–	0.20	0.15
MgO (wt.%)	2.79	3.96	2.51	3.94	3.40	3.42	2.35
SiO_2 (wt.%)	22.31	18.81	35.22	33.71	30.49	28.66	25.93
Al_2O_3 (wt.%)	5.74	6.49	16.73	13.63	10.92	6.68	4.29
Fe_2O_3 (wt.%)	3.36	1.97	3.68	3.55	3.39	2.89	2.90
TiO_2 (wt.%)	–	2.35	3.07	2.75	2.75	2.59	2.01
Basicity	2.43		0.76	0.99	1.23	1.53	1.89

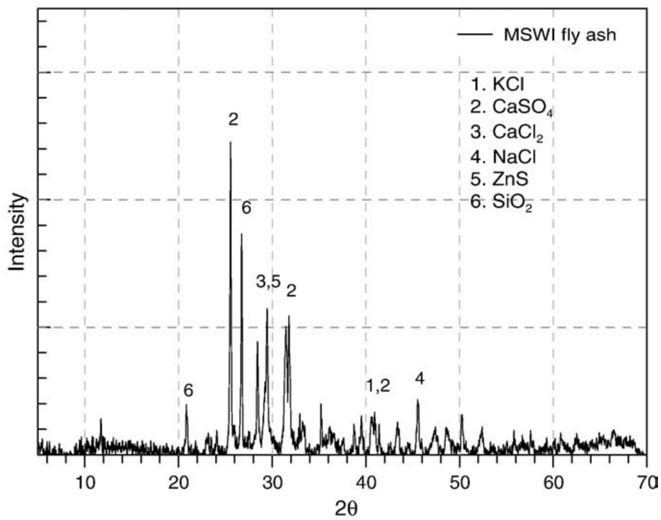

Fig. 1. X-ray diffraction pattern of the MSWI fly-ash.

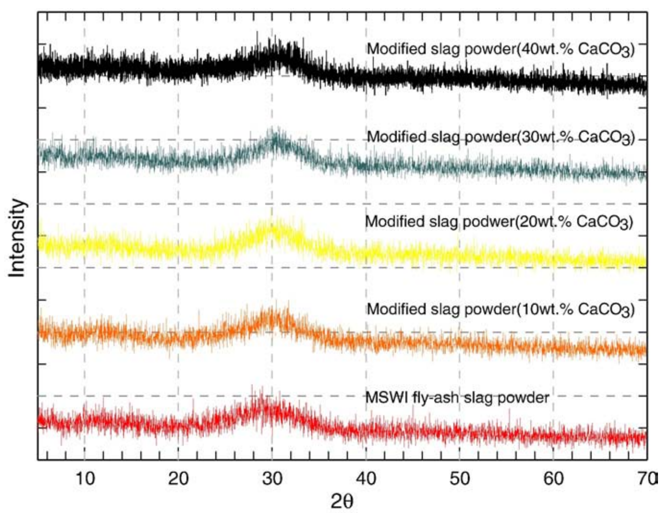

Fig. 2. X-ray diffraction patterns of the MSWI fly-ash slag and modified slag powders.

were cured in saturated calcium hydroxide solution at 23.0 ± 1.7 °C in a chamber with programmable temperature and humidity for 1 to 90 days. These cubes were subjected to testing of compressive strength.

Subsequently, hydration reactions in the crashed samples were terminated using pure methyl alcohol. They were then subjected to porosity tests using mercury intrusion porosimetry (MIP) and FTIR analysis.

Two groups of the specimens were prepared for testing of compressive strength:

(1) Cement in the test cubes (50 × 50 × 50 mm) were partially replaced by slag powder from MSWI fly-ash. The weight ratios of replacement were 10%, 20%, 30% and 40%, respectively. Testing on compressive strength was conducted on cubes cured for 1 day, 3 days, 7 days, 14 days, 28 days and 90 days, respectively. We denote these specimens mortar group I–IV and designate as Mortar-I where I denotes 10 wt.% cement replaced by the unmodified slag powder, II means 20 wt.% cement replaced and so on.

(2) Cement in test cubes was 20% replaced by the above mentioned $CaCO_3$-modified slag powder. The ratios of $CaCO_3$ in the original admixture of $CaCO_3$ to fly-ash were 10%, 20%, 30%, and 40 wt.%, respectively. These mortars were from Mortar-II, and being designated as Mortar-II(x) where x means the weight percent of fly-ash being replaced by $CaCO_3$. Testing on compressive strength was done on cubes cured for 1 day, 3 days, 7 days, 14 days, 28 days and 90 days, respectively.

The notation of test specimens is summarized in Table 1. Composition of materials used for the preparation of test cubes is shown in Table 2.

2.4. SEM study

For scanning electron microscope (SEM) study of slag powders melted from fly-ash there were no pre-treatments required except drying. For cured slag-cement mortars, cut samples were first oven-dried at 105 °C for 24 h, and then cooled in a desiccator. The samples were then fixed on a sample holder, gold-coated, and examined under a Scanning Electron Microscope (JEOL, JSM-5600, JAPAN). Composition of fly-ashes, fly-ash slag and modified slag powders was analyzed by energy-dispersive spectroscopy (EDS) attached to the SEM.

2.5. FTIR analysis

Bonding characteristics of the slag-cement mortar specimens was analyzed with a Fourier transformed infrared spectroscopy (FTIR, Jasco, FT/IR-300E, Japan). Test sample was ground and uniformly mixed with KBr at a weight ratio KBr:specimen = 100:1. The mixture, 0.2 g, was pressed to a disk of 13 mm in diameter for analysis. The wavenumber was ranging from 500 to 4000 cm^{-1}.

2.6. Mercury intrusion porosimetry analysis for porosity of cured slag-cement mortar specimens

The slag-cement mortar cured for certain days was taken out, oven-dried at 105 °C for 24 h, cooled in a desiccator, and evacuated. The 105 °C drying is the safe upper limit that C-S-H bonds will not be broken [9]. Then it was moved to a mercury intrusion porosimetry (MIP) facility (PMI Automated Porosimeter Model: 60K-A-2, USA), evacuated for 1 h, and then pressurized with mercury from 0 psi gradually to 30,000 psi.

3. Results and discussion

X-ray diffraction patterns of MSWI fly-ash, and MSWI fly-ash slag, modified slag was shown in Figs. 1 and 2, respectively. The MSWI fly-ash sample shows the different mineral phases as shown in Fig. 1, and all slag samples appear amorphous (glassy) in nature, as shown in Fig. 2, characteristic of no diffraction peaks, typical of random packing of atoms and molecules. This meets our purpose to attain glassy slag in order that heavy metal ions can be immobilized in the network of the glass matrix [5,7,8].

3.1. Composition and TCLP analyses

Compositions of Portland cement, fly-ash, fly-ash slag and modified slag added with different amounts of $CaCO_3$ are shown in Table 2. Composition of MSWI fly-ash varies batch to batch, and there is subtle difference even in the same batch yet different powders. The much less Na_2O and K_2O contents in the slag were due to evaporation loss

Table 3
TCLP leaching concentrations from the MSWI fly-ash, fly-ash slag and modified slag.

	Ni	Zn	Cd	Pb	Cr	Cu
TCLP (mg/L)						
MSWI fly-ash	4.48	33	1.02	0.55	0.62	0.86
MSWI fly-ash slag	1.44	3.9	0.08	0.14	0.28	0.68
MSWI Slag ($CaCO_3$—10%)	1.51	2.36	0.07	0.2	0.16	0.67
MSWI slag ($CaCO_3$—40%)	1.48	1.33	0.06	ND	0.06	0.5
Mortar-Ref	ND	ND	ND	ND	ND	0.14
Mortar-II (10)	ND	ND	ND	ND	ND	0.14
Mortar-II (40)	ND	ND	ND	ND	ND	0.15
Regulatory limits	–	–	1	5	5	15

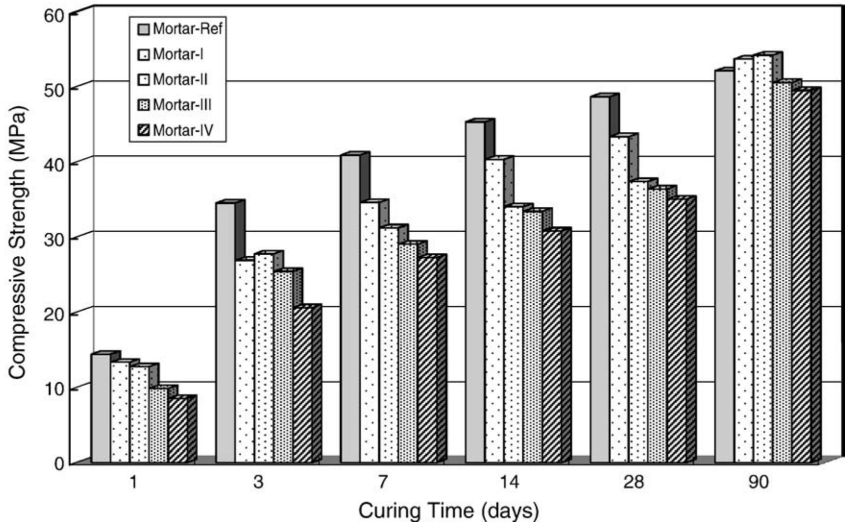

Fig. 3. Evolution of compressive strength in 0–40% slag powder replaced cement mortars during curing in day 1 to day 90.

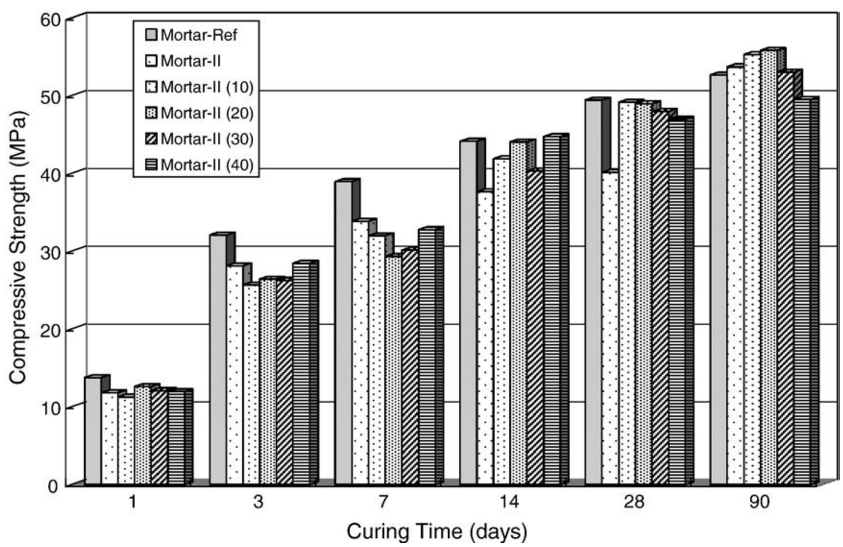

Fig. 4. Evolution of compressive strength in mortars of plain cement and those replaced with 20% modified slag powder using the 0%, 10%, 20%, 30%, or 40% $CaCO_3$ added slag powder.

during melting at 1450 °C, and the other heavy metals were immobilized in a Si–O matrix due to its strong bonding with oxygen in the glass network [5,7,8]. The contents of $SiO_2+Al_2O_3+Fe_2O_3$ of the unmodified slag and modified slag by 10% $CaCO_3$ was larger than 50.0%, which meets the requirement of grade C fly-ash of ASTM C618.

The composition analysis of glassy slag is more accurate due to homogenization of constituents during high temperature melting and liquid mixing.

By definition, the basicity of a slag or glassy material is the ratio between total contents of basic constituents and total contents of acidic constituents [10]. Considering the constituents in our fly-ash and slag, it is given by:

$$\text{Basicity} = (\text{CaO} + \text{MgO} + \text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3),$$

where Al_2O_3 being amphoteric behaves acidic in the presence of CaO, MgO, etc. Hence it is added in the acidic side of the above formula.

Comparing the high basicity of Portland cement I, 2.43, the basicity of unmodified slag is only 0.76. It was the reason why we proposed to add $CaCO_3$ to modify the basicity of the slag composition. The CaO content of the modified slag increases with more added $CaCO_3$ as seen in Table 2, the basicity of the modified slag increases with the added $CaCO_3$ content as also shown in Table 2, the last row.

MSWI fly-ashes contain hazardous heavy metals [1,2,4,6,8], but test results of ‘toxicity characteristics leaching procedure (TCLP)’ of all our specimens met the EPA's current regulatory thresholds, after

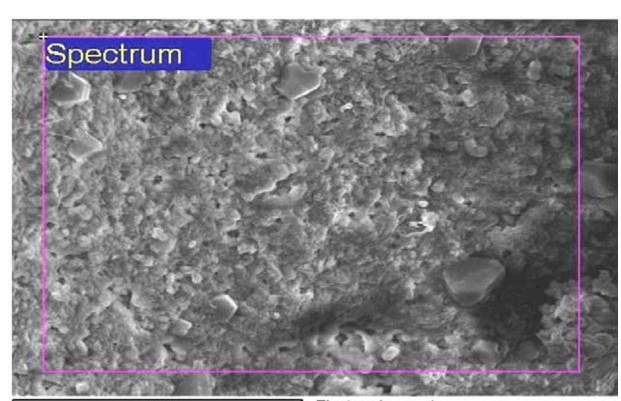

Fig. 5. SEM photo of a fly-ash particle.

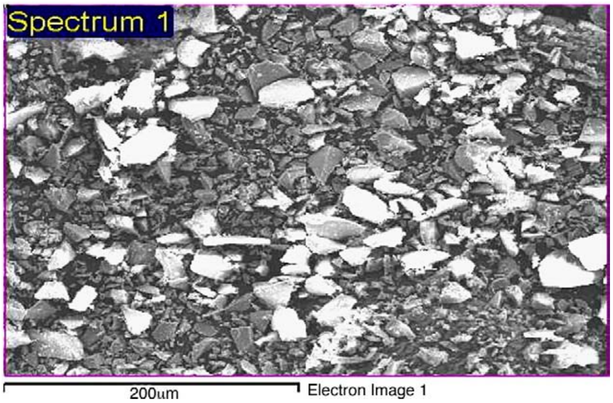

Fig. 6. SEM photo of MSWI fly-ash slag particles.

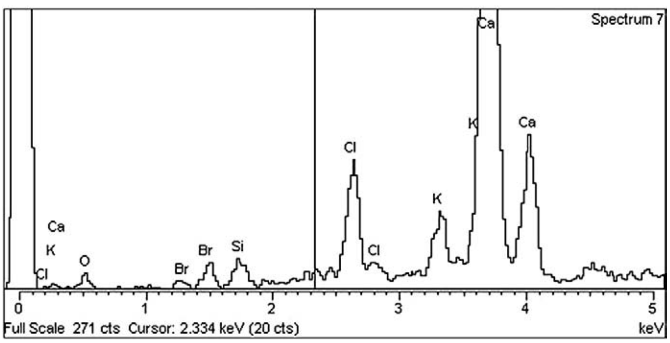

Fig. 7. EDS analysis of the fly-ash.

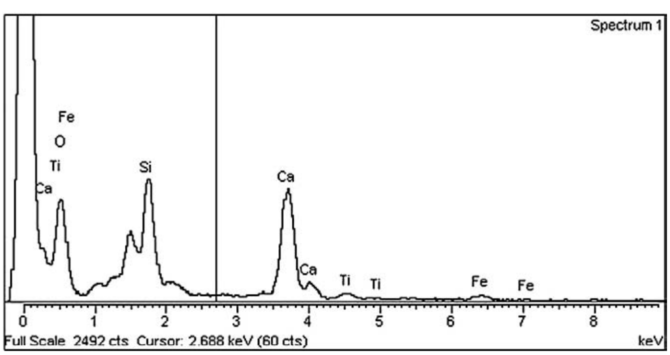

Fig. 8. EDS analysis of the fly-ash slag powder.

being melted to slag as seen in Table 3. Thus the slag-cement mortar is green in application.

3.2. Compressive strengths of the cured cement mortar specimens

Volcano ash, granulated blast furnace slag, and fly-ash from a coal-fired power plant are the most abundant sources of pozzolanic material. They are widely used as the additives in a concrete. A pozzolan is given by ASTM C618 as a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. A typical pozzolanic material features three characteristics: It should contain high silica content, be X-ray amorphous, and have a large specific surface area [11]. According to ASTM C618, material with particle size larger than 150 μm is not deemed as pozzolanic material. Thus volcano ash, granulated blast furnace slag, and fly-ash of coal-fired power plant with particle sizes larger than 150 μm (sieve # 100) are not pozzolanic material, those with particle size of 75 μm (sieve # 200) approach characteristics of the pozzolanic material, and those with particle sizes smaller than 38 μm (sieve # 400) meet the

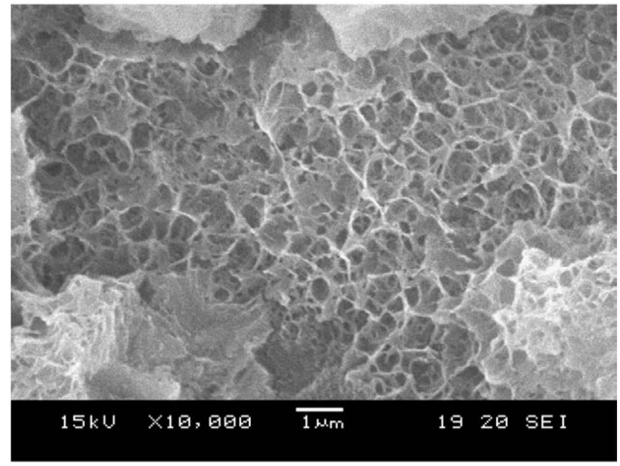

Fig. 9. Surface morphology of a modified slag-cement mortar specimen Mortar-II (10) cured for 28 days.

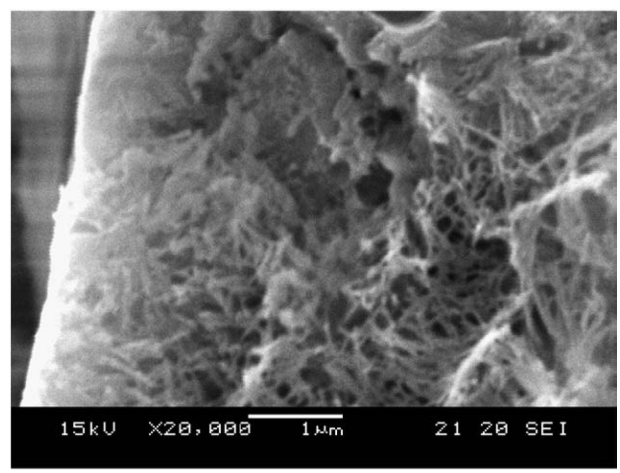

Fig. 10. Surface morphology of the specimen in Fig. 9 but cured for 90 days.

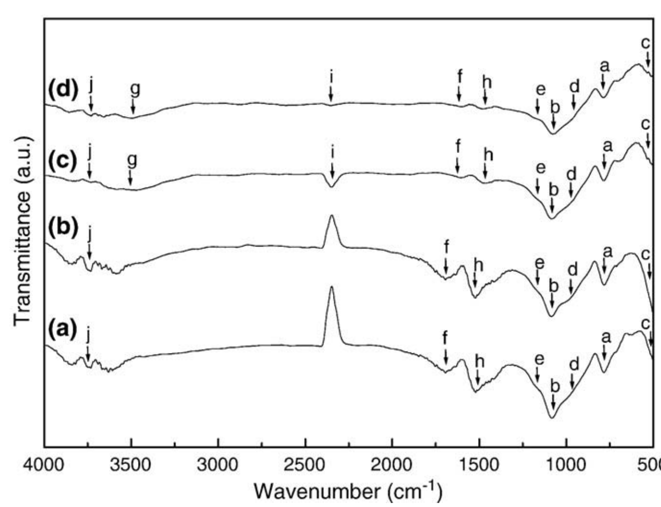

Fig. 11. FTIR spectra of Mortar-II cured for (a) 7 days, (b) 28 days, (c) 60 days, and (d) 90 days.

Table 4
Fourier transformed infrared spectra data.

Band assignments	Symmetric stretching vibration (cm^{-1})	(ν_2) In-plane-bending vibration (cm^{-1})	(ν_3) Asymmetric stretching vibration (cm^{-1})	(ν_4) Out-of-plane-bending vibration (cm^{-1})	Stretching vibration (cm^{-1})
Si–O–Si	800= a	–	1050 = b	525 = c	–
C-S-H	–	–	–	–	975 = d,1172–1207 = e
H–O–H	–	1640 = f	–	–	2800–3700 = g
CO_3^{2-}	–	–	1400–1500 = h	–	–
CO_2	–	–	–	–	2400–2500 = i
Ca,OH^-	–	–	–	–	3640 = j

a, adopted from [14]; b, j, [15]; c, [13]; d, f, [16]; e, [17]; g, [18]; h, [19]; i, [20].

requirement of the pozzolanic material. Results of the compressive strength tests on the slag-cement mortar specimens for investigating the effects of MSWI fly-ash slag powder, a pozzolanic material, on the slag-cement mortar specimens are delineated as follows.

3.2.1. Strengths of unmodified slag-cement mortar specimens

Results showed that the ratios of the 28-day compressive strengths are, in ascending order of replacement amount for cement (Mortar-Ref, Mortar-I to Mortar-IV), 1:0.89:0.77:0.75:0.72, and the 90-day ones are 1:1.03:1.03:0.97:0.95 (Fig. 3). The early strengths are much inferior to that of the reference specimen, same as those reported in literature [5–8]. It is also shown that the increase rate in compressive strength of the slag-cement mortars cured for 28 days to 90 days is higher than that of the reference specimen, revealing the characteristics of the pozzolanic reaction. As a result, the compressive strengths of the 90-day slag-cement mortars are slightly higher than that of the reference specimen, specifically for those of Mortar-I and Mortar-II both being 103% that of the reference specimen (Mortar-Ref). These observations are conformal with those reported earlier [5–8]. From the fact that the more the cement was replaced by the slag powder the lower was the early strengths, it was believed that the main reason is arisen from the low basicity of the slag powder. Thus $CaCO_3$ was designed to add into fly-ash then melting to modify it. In so doing, complete vitrification (fully amorphous state) of the modified slag was carefully maintained to make use of its immobilization capability in the glassy network to hazardous heavy metals.

3.2.2. Strengths of slag-cement mortars made of $CaCO_3$-modified slag powder

Fig. 4 shows the results of the compressive strength tests of the modified slag-cement mortar samples, Mortar-II(10)–Mortar-II(40). Their 14-day, 28-day and 90-day specific compressive strengths (versus the reference specimen, Mortar-Ref, being 1) are, in ascending additive amount of $CaCO_3$ in the fly-ash [Mortar-Ref:Mortar-II:Mortar-II(10):Mortar-II(20):Mortar-II(30):Mortar-II(40)], 1:0.85:0.95:1.00:0.91:1.01 (14-day); 1:0.81:0.99:0.99:0.97:0.95 (28-day); and 1:1.02:1.05:1.06:1.01:0.94 (90-day), respectively. Values of the 28-day compressive strengths of all the $CaCO_3$-modified slag-cement mortar specimens are approximately (99 to 95%) equal to that of the reference specimen, and those of 90-day ones are higher than that of the reference specimen except that of Mortar-II(40), revealing the advantageous effect of $CaCO_3$ as a MSWI fly-ash additive. Both the 28-day and 90-day compressive strengths of the modified slag-cement mortar specimens meet the requirements of construction purposes. Fig. 4 shows that Mortar-II(40) performs the best 14-day strength among all mortars yet with lower 90-day strength. This indicates that the early strength is contributed from the hydration of the CaO-rich constituent during the early agings. While at long-term aging (90-day) the pozzolanic reaction of Mortar-II(40) is inferior than those of Mortar-II(10) and Mortar-II(20).

Normally, the compressive strength of slag-cement mortar is contributed from hydration reaction, packing effect, and pozzolanic reaction. Tangpagasit et al. [12] studied the packing effect arisen from different particle sizes on the strength activity index of fly-ash mortar, keeping all other strengthening effects the same. It was found that the smaller the particle size is, the stronger is the strength. In this work, we used the same particle sizes and the same ratio of cement replacement by slag, so that the packing effect and hydration reaction were basically the same for all samples. It is thus conclusive that the differences in compressive strengths are due to pozzolanic reaction.

The above results preliminarily proved that the basicity modified MSWI fly-ash slags are truly beneficial in promoting early strength. These slag can be utilized to replace partial cement in cement mortar, its compressive strengths meet the requirements. These results revealed that we have overcome the problems of weaker early strengths. Research for the feasibility of practical applications is worthwhile.

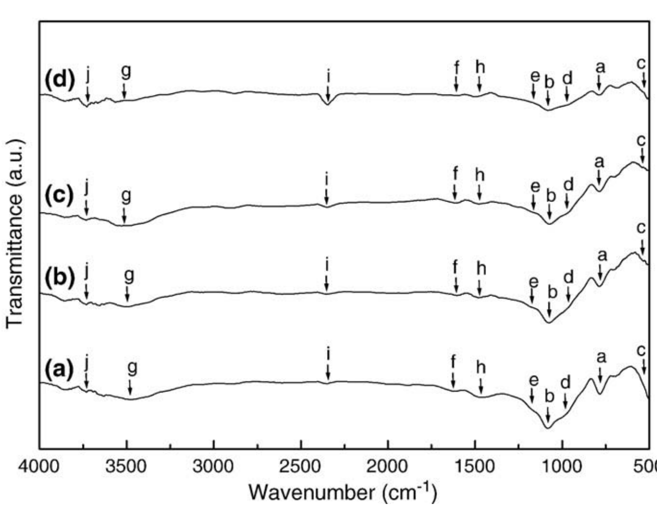

Fig. 12. FTIR spectra of various cement mortar specimens cured for 90 days. (a)Mortar-Ref, (b) Mortar-II, (c) Mortar-II(10), and (d) Mortar-II(40).

3.3. Microstructure analysis of MSWI fly-ash slag powder

The slag chunks melted from MSWI fly-ash showed dark brown in color. Microstructure and composition of powder sample pulverized from the slag chunks were examined under SEM equipped with EDS facility. The results are displayed in Figs. 5–8, and Table 2.

Figs. 9 and 10 show SEM photos of typical surface morphology of the 28-day and 90-day cured Mortar-II(10), respectively. The photos reveal large amount of C-S-H gel on the specimen surface, with 3D network structures intermingled among cement particles and silica sands. The voids become much smaller with increasing curing time.

3.4. FTIR studies

Fig. 11 shows FTIR spectra of Mortar-II cured for various time. The absorption peaks at 525 cm^{-1}, 800 cm^{-1} and 1050 cm^{-1} are attributed to Si–O–Si (ν_4) out-of-plane-bending vibration [13], Si–O–Si symmetric

Table 5
The pore sizes (in nm) after curing for 28 days and 90 days, respectively, by MIP analysis.

Specimen	Median pore diameter (28-day) (based on volume)	Average pore diameter (28-day) (4 V/A)	Median pore diameter (90-day) (based on volume)	Average pore diameter (90-day) (4 V/A)
(1) Mortar-Ref	15.5	13.8	13.0	12.6
(2) Mortar-II	22.3	21.1	11.3	12.1
(3) Mortar-II(10)	16.1	14.3	8.4	8.9
(4) Mortar-II(20)	17.6	13.9	7.5	8.2
(5) Mortar-II(30)	18.4	14.5	13.2	13.1
(6) Mortar-II(40)	19.2	15.6	15.3	14.3

stretching vibration [14], and Si–O–Si (ν_3) asymmetric stretching vibration [15], respectively. The band at 3640 cm^{-1} is the calcium hydroxide bond absorption band. The absorption bands at 975 and 1172–1207 cm^{-1} are C-S-H vibration [16,17]. Each absorption peak location and its corresponding bond states are summarized in Table 4. Spectra show that the intensities of the absorption peaks corresponding to Si–O–Si and $Ca(OH)_2$ decrease with increased aging time, revealing catalytic role of $Ca(OH)_2$ in pozzolanic reaction during aging. $Ca(OH)_2$ is finally converted into C-S-H colloids. Thus the intensity of $Ca(OH)_2$ bond absorption band gradually decreases after aging for 60 days, leading to increased strength of the specimen, which is in accordance with testing results of compressive strengths.

Fig. 12 shows FTIR spectra of 90-day cured Mortar-Ref, Mortar-II, Mortar-II(10), and Mortar-II(40) specimens. Curve (a) shows that the Si–O–Si bond absorption band of the reference specimen is much stronger than those of other specimens. This indicates that the pozzolanic reaction is the least in the 90-day cured reference specimen, leading to a lower resultant compressive strength. Curve (b) depicts decreased intensity of the Si–O–Si absorption band of Mortar-II, indicating that the pozzolanic reaction occurs in a greater extent by the addition of MSWI fly-ash slag, thus its 90-day compressive strength is higher than that of the reference specimen. Curve (c) is the spectrum of Mortar-II(10), the increased Ca^{2+} concentration at this condition seemingly catalyzes pozzolanic reaction. Thus the strength of the Si–O–Si absorption band decreases for the pozzolanic reaction. There are chemical pozzolanic reaction products to fill in the minute voids, leading to higher compressive strength than those of the other specimens. Curve (d), the spectrum of Mortar-II(40), shows higher intensity of $Ca(OH)_2$ absorption peak meaning that because of the increased Ca content, large amount of $Ca(OH)_2$ remains in the mortar after the catalytic reaction with pozzolanic material. However, the $Ca(OH)_2$ absorption remains manifest and does not turn into C-S-H bonding leading to lower 90-day strength. These variations in the FTIR spectra are in accordance with the results of compressive strength testing.

3.5. MIP analyses

Samples were tested under increasing intrusion pressure to 207 MPa (30 ksi). The distribution of their median pore diameters is: 15.5 nm to 22.3 nm (aged for 28 days) and 7.5 nm to 15.3 nm (aged for 90 days). The distribution of their average pore diameters is: 13.8 nm to 21.1 nm (aged for 28 days) and 8.2 nm to 14.3 nm (aged for 90 days). The decreasing tendency in pore size versus aging time is in accordance with the increase in compressive strengths of the specimens. The average pore size distribution is shown in Table 5, and Fig. 13.

4. Conclusions

In this study, MSWI fly-ash was melted to glassy slag and pulverized to powder of particle sizes smaller than sieve #400. Test cubes, 50×50×50 mm, of slag-cement mortar specimens with 10–40% Portland cement replaced by MSWI slag powder were prepared for compressive strength tests. With $CaCO_3$ as an additive, the basicity of MSWI fly-ash slag was modified by mixing with 10, 20, 30 and 40 wt.% $CaCO_3$ powder into the fly-ashes. This admixture was melted into modified slag and pulverized to powders of size smaller than sieve #400 to replace 20% cement in cement mortar specimens for compressive strength tests. The following conclusions can be drawn:

(1) The slag-cement mortar specimens with 10%, 20%, 30% and 40% cement replaced by MSWI fly-ash slag powder of particle sizes smaller than sieve #400 showed that their 28-day compressive strength is 72% to 89% that of the reference specimen (0% Portland cement replaced) and their 90-day compressive strength is 95% to 103% that of the reference specimen. This shows the feasibility of replacing partial cement by MSWI fly-ash slag if long-term strength is concerned. Increased 90-day compressive strength in the slag powder replaced cement mortar is due to pozzolanic reaction. However, the early strength is inferior.

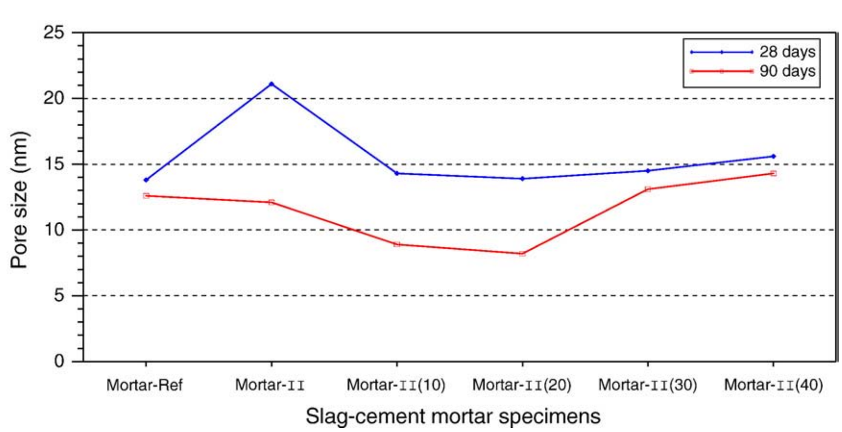

Fig. 13. Average pore size distributions by MIP analysis.

(2) The basicity modified MSWI fly-ash by mixing with 10, 20, 30 and 40 wt.% $CaCO_3$, respectively, was melted to modified slag then pulverized to powders to replace 20% of cement in the slag-cement mortar specimens. The 28-day compressive strength of these modified slag-cement mortar specimens is 95% to 99% that of the reference specimen, and the 90-day ones are 94% to 106% that of the reference specimen. These modified slag-cement mortar specimens showed good strength evolution. Among them the modified slag-cement mortar specimens with slag modified by 20% $CaCO_3$ show the 14-day, 28-day, and 90-day compressive strengths 100%, 99%, and 106% that of the reference specimen, respectively. Partial cement replacement by this $CaCO_3$-modified MSWI fly-ash slag for practical application is highly plausible.

(3) Results of porosity (MIP) analyses showed that the average pore size of the 28-day specimens is larger (median sizes: 15.5–22.3 nm) than that of the 90-day specimens (7.5–15.3 nm). This decreasing tendency is in accordance with the increased compressive strengths of the specimens.

(4) Results of FTIR analyses showed that the modified slag made from the admixture with suitable amount of $CaCO_3$ into MSWI fly-ash are characteristics of weakened intensities of the Si–O–Si while higher $Ca(OH)_2$ absorption peaks with increasing added amount of $CaCO_3$. This proves enhanced hydration and pozzolanic reaction of the specimen, and densification. This is in accordance with the increased tendency of the compressive strengths of the specimens.

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