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The hydration properties of pastes containing municipal solid waste incinerator fly ash slag

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Abstract

This study investigated the hydration properties of Type I, Type III and Type V cements, mixed with municipal solid waste incinerator fly ash, to produce slag-blended cement pastes. The setting time of slag-blended cement pastes that contained 40% slag showed significantly retardation the setting time compared to those with a 10% or even a 20% slag replacement. The compressive strength of slag-blended cement paste samples containing 10 and 20% of slag, varied from 95 to 110% that developed by the plain cement pastes at later stages. An increased blend ratio, due to the filling of pores by C–S–H formed during pozzolanic reaction tended to become more pronounced with time. This resulting densification and enhanced later strength was caused by the shifting of the gel pores. It was found that the degree of hydration was slow in early stages, but it increased with increasing curing time. The results indicated that it is feasible to use MSWI fly ash slag to replace up to 20% of the material with three types of ordinary Portland cement.

Keywords: Municipal solid waste incinerator; Setting time; Slag-blended cement; Hydration; Porosity distribution

1. Introduction

The disposal of municipal solid waste in landfills has become a less attractive management option because of diminishing landfill availability. Municipal solid waste incineration (MSWI) is a viable management option, achieving up to an 80 and 90% reduction in the waste mass and volume, respectively. However, municipal solid waste incineration produces effluents which include stack emissions, solid residues, and wastewater that must be considered and managed in an environmentally acceptable manner. Solid residues from municipal solid waste incinerators are of particular concern, because heavy metals, such as lead, cadmium, chromim and other inorganic species originally present in the municipal waste are concentrated in the fly ash [1,2]. The Taiwan Environmental Protection Agency's (Taiwan EPA) regulations classify MSWI bottom ash as non-hazardous, whereas the fly ash is classified as hazardous. This hazardous fly ash has to be detoxified or disposed of in a secure landfill.

There is no benefit from the cement industry's point of view, in replacing clinkers by another material that also requires a high temperature treatment. The increasingly limited landfill capacity for the disposal of incinerator ash, the need for the detoxification of MSWI fly ash before it can be properly disposal of, and the enhancement of energy consumption for the production of cement, all these considerations have made the recycling of incinerator fly ash as a partial substitute for cement an economically beneficial alternative. Therefore, from the viewpoint of life cycle analysis, the recycling of MSWI fly ash as a cement substitute by melting process would seem economically feasible. To meet the goals of zero-emissions and reuse waste material, MSWI fly ash can be recycled by melting at a temperature higher than 1300 °C, this could allow for ash detoxification and the recovery of heavy metals and slag. During the melting process, the heavy metals in the thermally treated slag are evaporated, or immobilized in a Si–O matrix [3,4]. This process allows for the recovery of the metals and the detoxification of the fly ash. The slag can then be recycled as construction materials, which can be used to produce such products

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Table 1
Chemical composition of fly ash, slag, and types of cement

Chemical composition	Fly ash	Pulverized slag	Type I cement	Type III cement	Type V cement
CaO (%)	14.7	27.2	63.71	61.92	63.52
Si_2O (%)	35.8	38.9	21.21	19.96	21.15
Al_2O_3 (%)	9.8	23.3	5.29	4.89	3.82
Fe_2O_3 (%)	4.91	5.3	3.07	3.04	4.17
Na_2O (%)	5.9	1.2	–	0.32	0.16
K_2O (%)	5.3	–	–	1.09	0.51
MgO (%)	0.83	3.6	2.25	3.21	3.04
Free CaO	–	0.3	0.6	0.8	0.5
Constituents	–	–	–	–	–
C_3S (%)	–	–	48	51	59
C_2S (%)	–	–	24	21	16
C_3A (%)	–	–	8.8	9.2	3.2
C_4AF (%)	–	–	9.3	9.3	12.4
Specific surface, Blaine (m^2/kg)	–	550	335	833	370
Pozzolanic activity index			103	102	104

Table 2
Toxicity characteristic leaching procedure (TCLP) test results

Heavy metal	Fly ash	Melting slag	TCLP regulatory limits
Cd (mg/L)	1.8 ± 0.03	ND	1.0
Cr (mg/L)	4.3 ± 0.13	0.27 ± 0.01	5.0
Pb (mg/L)	0.7 ± 0.02	0.36 ± 0.02	5.0
Cu (mg/L)	0.6 ± 0.01	3.21 ± 0.05	–
Zn (mg/L)	16.2 ± 0.30	9.10 ± 0.33	–

as vases, flower pot, ash tray [5], fine aggregates, fill for roadbeds, or permeable bricks and inter-locking blocks [6].

In the alkaline environment of ordinary Portland cement, the fly ash derived slag is chemically active and exhibits self-cementing properties when pulverized and activated by the cement [7,8]. Pulverized slag is a latent hydraulic material and can thus be utilized as a cement replacement [9]. The purpose of this investigation was, to substitute various amounts of pulverized slag for three types Portland cement, then to study the hydration properties of the municipal solid waste incinerator fly ash slag-blended cement (SBC). In the present work, the effects of varying the relative proportions of these constituents on the characteristics of the slag and, to a limited extent, of three types of Portland cement, were studied at various ages.

2. Materials and methods

2.1. Materials

The fly ash samples used in this study were collected from the cyclone of a municipal solid waste 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 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

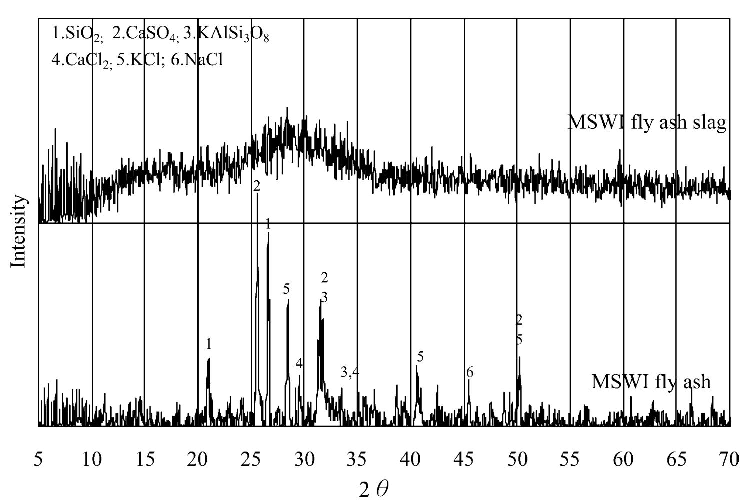

Fig. 1. XRD patterns of MSWI fly ash and slag.

pulverized ash was sieved. The fraction passing through a no. 50 mesh was then analyzed to determine its chemical composition (shown in Table 1). The X-ray diffraction patterns of the MSWI fly ash are shown in Fig. 1. Fig. 1 shows the speciation in the fly ash, as identified by the XRD techniques: indicated that the major components were quartz (SiO_2), anhydrite ($CaSO_4$), microcline ($KAlSi_3O_8$), $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$, Sylvite (KCl), and Halite (NaCl). The leachability of the MSWI fly ash was then analyzed by the toxicity characteristic leaching procedure (TCLP) test [10]. Table 2 shows the high leachability of the target metals Zn, Cr, and Cd. In particular, the leaching concentration of Cd reached 1.82 mg/L, more than ROC EPA's current regulatory thresholds, a level classified as hazardous.

The three types of Portland cements used in this research were Type I (ASTM Type I ordinary Portland cement), Type III (high early strength Portland cement) and Type V (sulfate resistant Portland cement), respectively. Finally some other types of cements were used in order to compare the influence of the MSWI fly ash slag additions. Table 1 shows the composition of the cements.

2.2. Preparation of slag-blended cement paste specimens

MSWI fly ash slag was prepared by first melting the MSWI fly ash at 1400 °C for 30 min in an electrically heated furnace. Slag samples were then obtained. The resultant slag samples were water-quenched, then further pulverized with a ballmill. The fraction passing through a no. 200 sieve was stored in a desiccator for subsequent use for the characterization and engineering property tests.

The pulverized slag samples prepared as above were then used as a cement replacement, being blended with Portland cement (Type I, Type III and Type V cement), at replacement ratios ranging from 0 to 40%, resulting in three types of slag-blended cement. Pastes using the aforementioned blends were prepared with a water to binder ratio of 0.38. Test cubes of 25.4 mm × 25.4 mm × 25.4 mm (1 in. × 1 in. × 1 in.) were prepared according to ASTM STP 897 [11]. The specimens were demoulded and cured in a container at 97% humidity at 25 °C, for periods ranging from 1 to 90 days. Three specimens were used for compressive strength tests and the other one was used for microstructural examination. 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 TCLP testing. The composition of the pulverized slag and mixed cement pastes was analyzed using a Siemens D5000 sequential X-ray diffraction spectrometer (XRD). Subsequently, the hydration reactions of crushed samples were terminated with methanol under a vacuum at the tested age, then dried at 60 °C for 24 h before measurement. After oven drying, the samples were analyzed with XRD, Mercury Intrusion Porosimetry, and the degree of hydration test.

2.3. Analyses

Chemical and physical analyses of slag-blended cement pastes at different ages were conducted as follows:

- Unconfined compressive strength (UCS): ASTM C109.
- Setting time: the setting times of the cement mixes were determined according to ASTM C191 using a Vicat apparatus at room temperature. The initial setting time was defined as when a Vicat needle 1 mm in diameter would penetrate the sample to a point 5 ± 1 mm from the bottom of the mould. The final setting time was defined as when a 5 mm cap ring would leave no visible mark when placed on the surface of the sample.
- Pozzolanic activity index: the test was performed, according to ASTM Designation C 311.
- Heavy metal leachability (TCLP): SW846-1311.
- Heavy metal concentration: Cd (SW846-7131A), Pb (SW846-7421), Zn (SW846-7951), Cu (SW864-7211), and Cr (SW846-7191).
- Mercury Intrusion Porosimetry (MIP): a Quantachrome Autoscan Mercury Intrusion Porosimeter was used with intrusion pressures up to 60,000 psi. By using the Washburn equation, with $p = -2\gamma \cos\theta / r$, the pore volume ($V$) and the corresponding radius (r) were synchronously plotted by an *X–T* plotter, under the assumption that the wetting angle of mercury is $\theta = 140°$. In this equation, p, γ, r and θ, stand for the applied pressure, surface tension, pore radius and wetting angle, respectively.
- Mineralogy: the XRD analysis was carried out using a Siemens D-5000 X-ray diffractometer with Cu Kα radiation and 2θ scanning, ranging between 5° and 70° (2θ). The XRD scans were run in 0.05° steps, with a 1 s counting time.
- The degree of hydration: the degree of hydration of the SBC pastes was determined by thermal analysis [12]. Differential thermal and thermogravimetric analysis were performed on pastes prepared with a water to cement weight ratio of 0.38, at various curing ages. The hydration degree could then be calculated as follows:

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

where α is the degree of hydration (%); n the fixed water in completely hydrated cement pastes, 0.24 for the OPC paste; W_{105}, W_{580}, W_{1007} the sample weights at 150, 580

Table 3
Setting times of SBC pastes

Cement	Setting time (h)							
	OPC		10%		20%		40%	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Type I	3.68	7.25	3.97	7.75	4.15	8.37	4.86	9.76
Type III	1.63	4.00	2.15	4.75	2.63	5.33	4.02	6.67
Type V	5.67	8.08	6.16	8.50	6.32	8.83	6.62	8.95

Table 4
Effect of the amount of fly ash slag on the compressive strength and the degree of hydration

Replacement ratio (wt.%)		Compressive strength (MPa)						Degree of hydration (%)					
Cement	Fly ash slag	1 day	3 days	7 days	28 days	60 days	90 days	1 day	3 days	7 days	28 days	60 days	90 days
Type I													
100	0	50	67	81	95	97	98	43.6	51.8	59.8	70.0	75.4	83.2
90	10	45	59	70	91	96	100	42.5	42.8	59.1	67.7	70.8	81.1
80	20	30	44	60	80	92	95	38.0	39.1	53.4	62.0	66.0	78.6
60	40	21	34	47	59	67	79	29.0	30.4	43.8	51.9	53.6	61.0
Type III													
100	0	59	67	68	73	73	75	56.9	57.5	62.7	69.4	72.1	74.8
90	10	53	59	63	73	76	81	45.3	54.2	59.8	66.9	69.8	72.5
80	20	44	54	59	69	75	83	44.9	52.7	57.4	66.5	69.2	71.4
60	40	34	37	42	55	58	67	30.7	38.7	47.7	55.3	57.6	59.2
Type V													
100	0	56	75	87	96	99	102	55.7	61.8	65.2	70.6	72.2	73.7
90	10	49	70	81	93	97	104	44.0	52.7	59.5	66.1	70.5	72.1
80	20	40	55	63	86	93	98	39.5	48.0	54.6	63.3	67.4	68.4
60	40	25	37	44	78	81	85	25.7	32.8	41.9	50.8	53.2	54.3

and 1007 °C, respectively (g); 0.41 the Conversion factor for molar ratio of $CaCO_3$-derived CO_2 to H_2O.

3. Results and discussion

3.1. Characterization of MSWI fly ash slag

Table 1 lists the major components of the MSWI fly ash slag used in this study. The slag was composed of SiO_2 (38.9 wt.%), CaO (27.2 wt.%), and Al_2O_3 (23.3 wt.%), and had a pozzolanic activity index of 103, 102 and 104, for Type I, Type III and Type V, respectively. The results show that the pozzolanic activity of the slag, make MSWI fly ash slag suitable as a component in blended cement. The amount of lime contained in the slag was 0.3%. The TCLP leaching concentrations for the target metals were all met the ROC EPA's regulatory thresholds (Table 2).

The X-ray diffraction patterns of the MSWI fly ash slag are shown in Fig. 1. It can be seen that the slag contained large amounts of glass, as indicated by the broad diffuse bands between 24° and 37° (2θ).

3.2. Setting time

As the cementitious hydraulic reactions progress the cement hardens and develops strength. Basically, this is setting behavior is a result of the cement grains dispersing (dissolving) and hydrating in water, gradually forming a solid/liquid suspension of the various hydrates. As the process continues, the inner structure of the cement paste is further reinforced, forming a network structure which causes the cement to set and gain strength.

Setting times as determined for various replacement levels of MSWI fly ash slag, are presented in Table 3. For ordinary Type I, Type III and Type V Portland cement, the setting time decreased in the following sequence Type III > Type V > Type I. The sequence corresponding to that of the Type III cement had greater Blaine fineness.

Table 3 indicated that of the three types of cement contained of 40% slag had a significantly retarded setting time compared to the 10 or even the 20% slag replacement. The initial set retardation for the Type I cement pastes incorporating MSWI fly ash slag were 0.29, 0.47 and 1.18 h for the 10, 20 and 40% slag content mixture, respectively. The final set retardations were 0.5, 1.12 and 2.51 h for the 10, 20 and 40% slag content mixture, respectively. For the Type III cement pastes the incorporation of MSWI fly ash slag, led to initial set retardations of 0.52, 1.0 and 2.39 h for the 10, 20 and 40% slag content mixture, respectively. The final set retardations were 0.75, 1.33 and 2.67 h for the 10, 20 and 40% slag content mixture, respectively. Initial setting occurred at 2.39 h and final set retardation at 2.67 h, for the 40% slag content mixture. The Type V cement pastes incorporating MSWI fly ash slag exhibited 0.95 h initial set and 0.87 h final set retardation, for 40% slag content mixture. This indicated that the setting time of SBC pastes is retarded when a portion of the cement is replaced by MSWI fly ash slag.

3.3. Compressive strength of MSWI fly ash slag-blended cement pastes

Table 4 showed the compressive strength of the Type I, Type III and Type V cement pastes incorporating MSWI fly ash slag. For plain Type I, Type III and Type V Portland cement, the 1 day compressive strength development increased in the following sequence Type III > Type V > Type I. The sequence corresponds to that of the Type III Portland cement with greater Blaine fineness, leading to appearance of higher early strength. However, the compressive strength development of plain Type I, Type III and Type V cement pastes increased in the following sequence: Type V > Type III > Type I after 3–90 days.

It can be observed from Table 4, that the compressive strength of the slag-blended cement pastes in the early stages (1–28 days) was reduced when the cement replacement levels increased. However, at a later stage, the compressive strength of the slag-blended cement paste samples incorporating 10 and 20% of slag, varied from 95 to 110% of that developed by the plain cement pastes. On the other hand, the SBC samples that incorporated 40% of slag exhibited a decline in the compressive strength. The results indicated that the SBC pastes had a slower compressive strength development in the early stages, but the strength obviously increased at later ages.

3.4. Porosity distribution in MSWI slag-blended cement pastes

Figs. 2–4 showed the porosity distribution in the MSWI slag-blended cement pastes. The pore size distribution varies with the replacement levels of the slag and curing time, as shown from Figs. 2–4. In general, for both the three types of ordinary Portland cement and the SBC pastes, the pore volume in general decreased as the curing time increased. For plain Type I, Type III and Type V cement pastes, dramatic variations occurred from 1 to 28 days, but little variation was observed from 60 to 90 days, implying that active hydration reactions took place during the early ages.

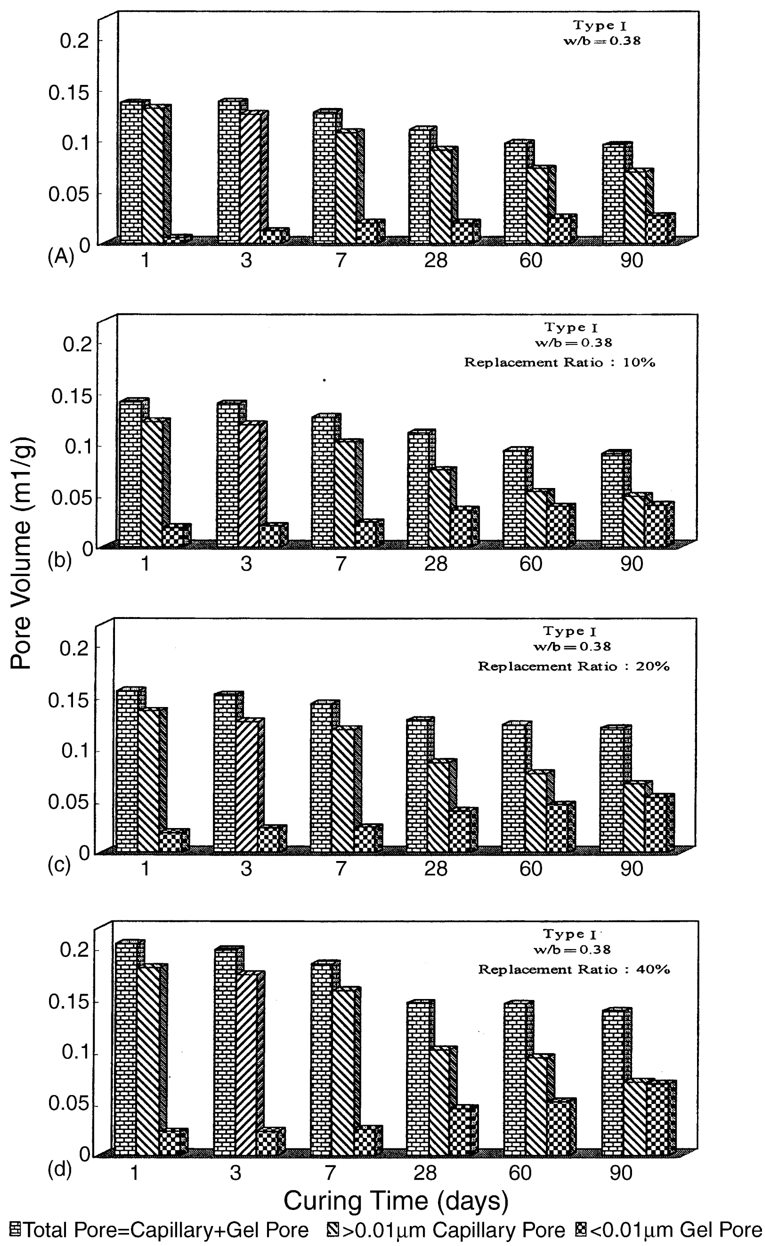

Fig. 2. Porosity distribution of the Type I cement pastes incorporating MSWI fly ash slag.

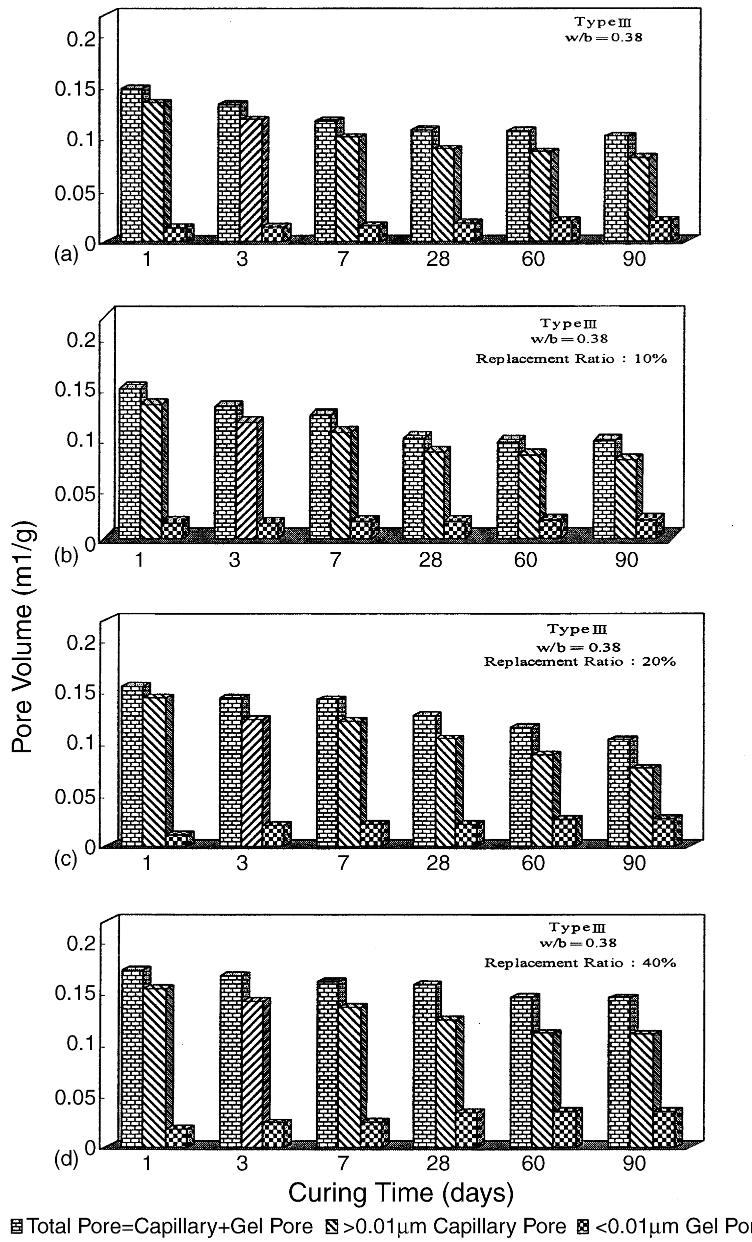

Fig. 3. Porosity distribution of the Type III cement pastes incorporating MSWI fly ash slag.

On the other hand, the results for SBC pastes incorporating slag at different replacement levels indicated that, for a larger blend ratio (>20%), the difference in the pore volume from 1 to 28 days was insignificant. The pore volume in the SBC paste samples shifted to the gel pores at later ages. The tendency was for this to be more pronounced for an increased blend ratio, due to the pores being filled with C–S–H gels that formed via pozzolanic reactions. This resulting densification and enhanced later strength was caused by the shifting of the gel pores.

3.5. X-ray diffraction analyses of hydration products

Figs. 5 and 6 shows the X-ray diffraction patterns of samples hydrated for 7 and 90 days, respectively. It can be seen that the main hydration products in the pure cement were C–S–H gels, $Ca(OH)_2$, and Ettrigite ($Ca_6Al_2(SO_4)_3{\cdot}32H_2O$, AFt), with unhydrated C_3S and C_2S still existing (Fig. 5). In addition, because a vast amount of $Ca(OH)_2$ was formed, the pozzolanic effects of the fly ash slag was greatly enhanced, and the rate of strength development of the SBC pastes was also obviously enhanced. When fly ash slag was substituted for 40% of the cement, the hydration products in the mixture were the same as those for plain cement pastes, primarily because the addition of fly ash slag to Portland cement may have a significant diluting effect, causing the degree of SBC paste hydration to decrease more than that of pure cement. Fig. 6 shows the XRD patterns for SBC pastes hydrated for 90 days. Comparing Fig. 5 with Fig. 6, we find that the strength of the AFt and $Ca(OH)_2$ diffraction peaks

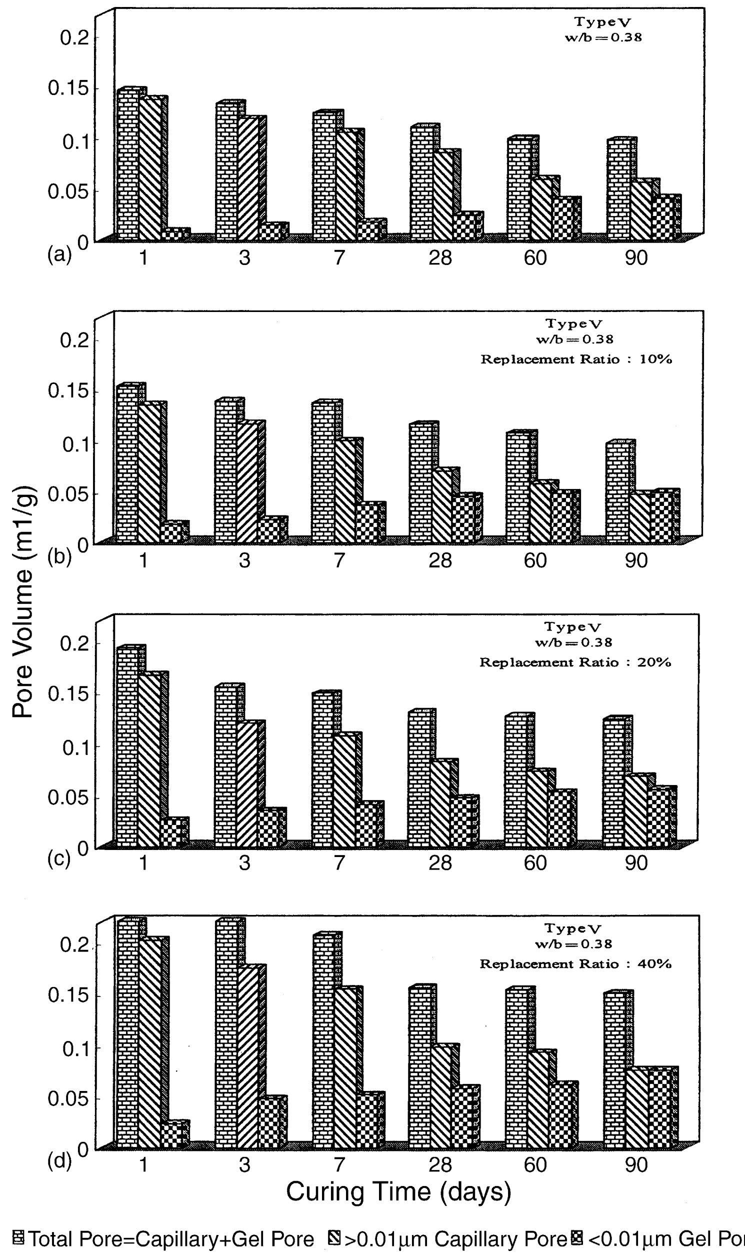

Fig. 4. Porosity distribution of the Type V cement pastes incorporating MSWI fly ash slag.

were basically the same as that of those of plain cement, while the strengths of the C_3S and C_2S diffraction peaks clearly decreased at 90 days.

3.6. Degree of hydration of OPC and SBC pastes

Bentur has determined the degree of hydration based on the loss on ignition [13]. He regarded the degree of hydration to be a result of gels that formed in the pastes. Table 4 lists all the degrees of hydration for the OPC and SBC pastes. The slag was blended with various types of cement at different ratios. The decrease in the degree of hydration of SBC pastes when the replacement ratio of slag was increased became more marked. The Type I cement paste, incorporating 10% of MSWI fly ash slag, showed a degree of hydration similar to that of the plain cement after 90 days of curing time because the hydration reactions from the slag, and C_3S and C_2S in Type I Portland cement, were significant. On the other hand, in the SBC samples of the Type I cement paste incorporating 40% of MSWI fly ash slag, the dilution greatly reduced the C_3S, C_3A and C_2S content in the cement, which delayed the hydration process during the early stages of curing, as well as the degree of hydration.

For the SBC samples of the Type III cement paste incorporating 10% of MSWI fly ash slag, the degree of hydration of the sample, after 90 days of curing time, although close, was still 2.3% less than plain cement. The SBC samples

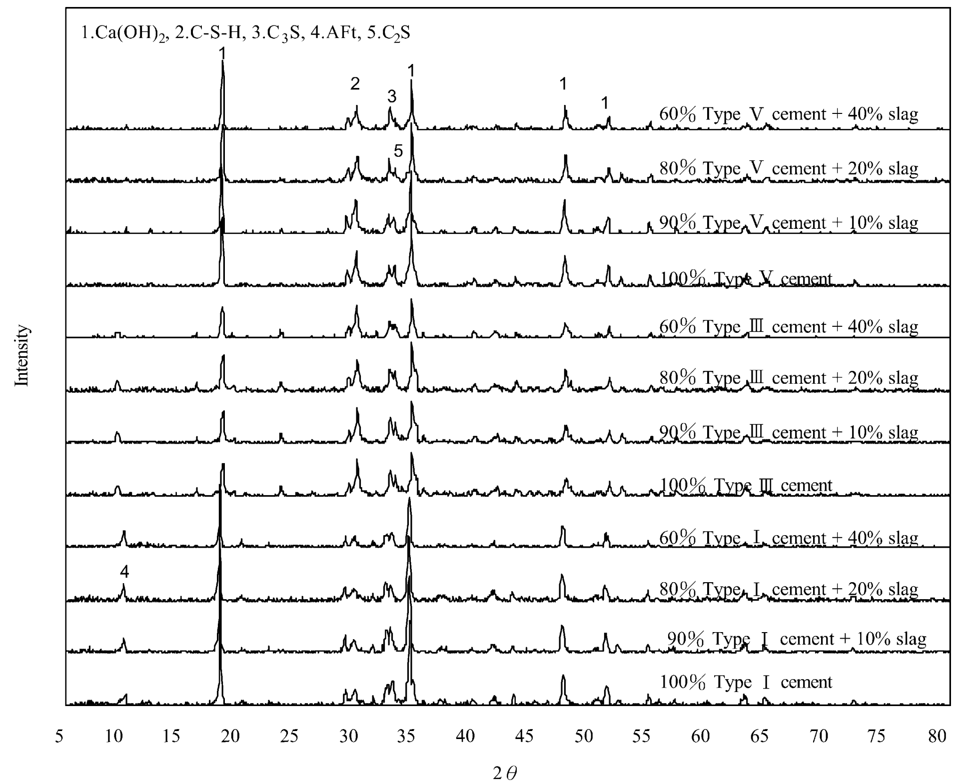

Fig. 5. XRD patterns for SBC pastes after 7 days.

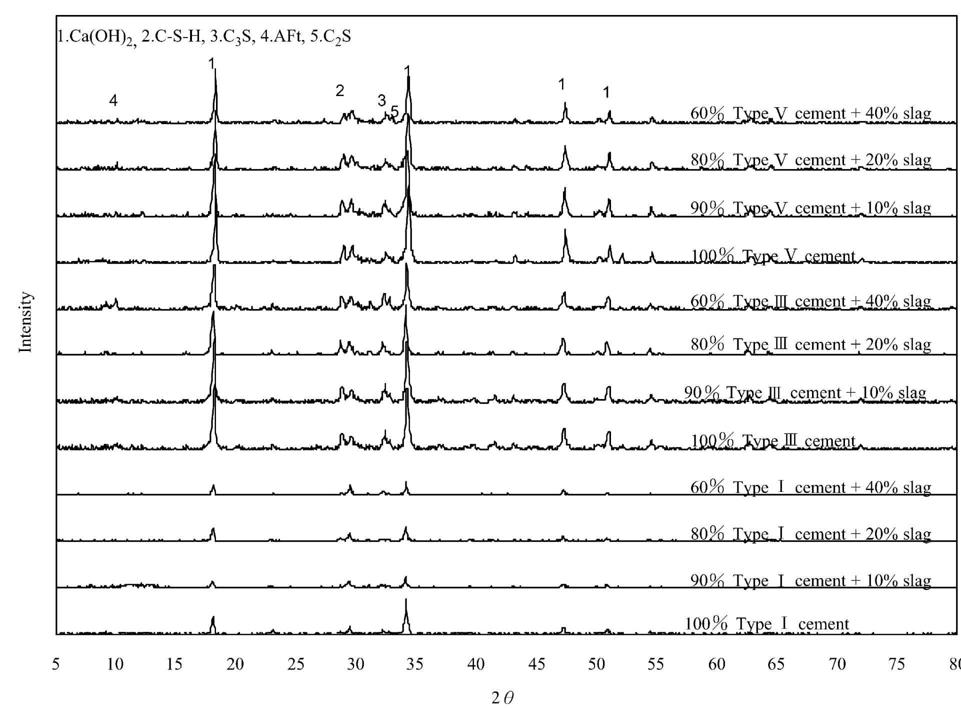

Fig. 6. XRD patterns for SBC pastes after 90 days.

of the Type III cement paste incorporating 20% of MSWI fly ash slag, presented a late acceleration of the hydration process, with a degree of hydration after 60 days that was 3.4% less than plain cement. The SBC samples of the Type III cement paste, incorporating 40% of MSWI fly ash slag, showed slowed hydration, since at 7 days the hydration of Type III cement was comparatively greater than other types of cement and a larger portion of pulverized slag had been added, which greatly reduced the amount of C_3S, C_3A, and C_2S.

In the SBC samples of the Type V cement paste incorporating 10% of MSWI fly ash slag, the degree of hydration in the pastes was 1.6% less than plain cement. In the SBC samples of the Type V cement paste, incorporating 20% of MSWI fly ash slag, the degree of hydration of the paste exceeded plain cement by 5.3%, for a curing time of 90 days. In the SBC samples of the Type V cement paste incorporating 40% of MSWI fly ash slag, since the hydration of the V cement is also slow, and the addition of a large amount of pulverized slag would greatly reduce the quantity of C_3S, C_3A, and C_2S, the degree of hydration was reduced. In addition, it was found that the degree of hydration generally increased with the curing age, but decreased with the blend ratio.

4. Conclusions

Experiments were conducted using pulverized slag produced from MSWI fly ash as a pozzolanic material for the replacement of cement. Based upon the experimental procedure reported on this paper, the following conclusions can be made:

1. The major components of the MSWI fly ash slag were SiO_2 (38.9 wt.%), CaO (27.2 wt.%), and Al_2O_3 (23.3 wt.%); the pozzolanic activity index was 103, 102 and 104, for Type I, Type III and Type V, respectively. The results show that the pozzolanic activity of the slag would make MSWI fly ash slag suitable as a component in blended cement.
2. The TCLP results show that the amount heavy metals all met the Taiwan EPA regulatory limits.
3. The setting time of the pastes was retarded when a portion of the types of Portland cement were substituted by MSWI fly ash slag.
4. The SBC pastes showed slower compressive strength development in the early stages, but the strength obviously increased at later ages.
5. For Type I, Type III and Type V ordinary cement pastes, dramatic variations occurred during 1–28 days, but little variation was observed from 60 to 90 days, implying that the active hydration reactions had taken place during the early ages. The pore volume in the SBC paste samples shifted to the gel pores at later ages. The tendency for an increased blend ratio, due to pores being filled with C–S–H gels formed by pozzolanic reactions was more pronounced.
6. In addition, it was found that the degree of hydration generally increased with the curing age, but decreased with the blend ratio.
7. The results indicate that it is feasible to use MSWI fly ash slag to replace up to 20% of the material, for the three types of ordinary Portland cement.

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