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Recycling MSWI bottom and fly ash as raw materials for Portland cement

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Abstract

Municipal solid waste incineration (MSWI) ash is rich in heavy metals and salts. The disposal of MSWI ash without proper treatment may cause serious environmental problems. Recently, the local cement industry in Taiwan has played an important role in the management of solid wastes because it can utilize various kinds of wastes as either fuels or raw materials. The objective of this study is to assess the possibility of MSWI ash reuse as a raw material for cement production. The ash was first washed with water and acid to remove the chlorides, which could cause serious corrosion in the cement kiln. Various amounts of pre-washed ash were added to replace the clay component of the raw materials for cement production. The allowable limits of chloride in the fly ash and bottom ash were found to be 1.75% and 3.50% respectively. The results indicate that cement production can be a feasible alternative for MSWI ash management. It is also evident that the addition of either fly ash or bottom ash did not have any effect on the compressive strength of the clinker. Cement products conformed to the Chinese National Standard (CNS) of Type II Portland cement with one exception, the setting time of the clinker was much longer.

1. Introduction

In Taiwan, landfill disposal is the major strategy for disposing of municipal solid waste incineration (MSWI) ash. Due to limited land availability in Taiwan, landfill disposal is no longer a feasible choice. Since MSWI ash contains high levels of various heavy metals and salts, serious environmental problems will occur if the waste is not treated properly before final disposal. Some approaches for MSWI ash disposal have been proposed, mainly for recycling into construction materials (Schreurs et al., 2000; Mangialardi, 2003; Nishigaki, 2000). MSWI ash typically contains heavy metals, salts and toxic organic substances, especially the fly ash. As construction material, the salts and dioxins in the MSWI ash have a potential to leach into the environments through the long-term flushing of rainwater. The leaching of salts from the ash may devastate the soil environment, both chemically and biologically. Poly et al. (2002) discovered that the leaching of salts into the soil after 30 day washing greatly reduced the activities of the nitrogen-fixing and denitrifying bacteria. In most cases, solidification can immobilize heavy metals; however, it does not stabilize salts such as chloride salts (Baur et al., 2001). As for melting, although it produces stable slags for construction, the process consumes a high level of energy. In addition, the heavy metals with a low-melting point may escape during the melting process, and HCl may be released.

Recently, the local cement industry in Taiwan has provided a new route for the reuse of solid and liquid wastes. The wastes can be used as fuels or raw materials in the cement manufacturing process. Onaka (2000), Chen et al. (2002) and Pan et al. (2004) have tried to include waste glasses and sludge in the raw materials of cement production. Ferreira et al. (2003) has also indicated that fly ash could potentially be used to produce cement powder. There are advantages of using a cement kiln for waste treatment. The high temperature (above 1450 °C) in the kiln can

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capture most of heavy metals in the clinker; the ash can be efficiently used since its major constituents are similar to those of the cement raw materials; no secondary waste is generated; and the production capacity of a cement kiln is very large (Forgey, 2000).

In this study, the feasibility of reusing the MSWI fly ash and bottom ash as secondary materials for cement production was evaluated. Pre-treatment was utilized to remove readily soluble salts including chlorides, and a sintering treatment was used to simulate the cement making process. The ash was added to replace the clay component of the raw materials to the cement process. The cement quality was investigated to evaluate the feasibility of MSWI ash reuse in cement production.

2. Material and methods

2.1. Experimental materials

The MSWI ash was obtained from the municipal solid waste incinerator of the Hsinchu City in Taiwan. The raw materials for cement, including limestone, iron slag, clay, sand and gypsum, were provided by the Taiwan Cement Corporation. The MSWI ash and the cement raw materials were first dried until a constant weight was reached. The samples were ground and sieved through a 200-mesh sieve (equivalent to 0.074 mm). A series of experiments involving water and/or acid washing has been performed to explore the possibility of removing chlorides from the fly ash and bottom ash. The chemical compositions of both the cement raw materials and the pre-washed MSWI ashes were determined according to the Chinese National Standard (CNS) method by using X-ray fluorescence spectrometry (XRF), as well as the wet tests.

2.2. Cement design

The maximum amounts of fly and bottom ashes in place of cement clay were determined by their chloride contents. Cement raw materials were blended in proportions following the Cement Modulus commonly used by cement industry: hydration modulus (HM) = 2.08, iron modulus (IM) = 2.65 and silica modulus (SM) = 1.40. For each cement design, 2 kg of sample was molded into cylindrical samples of 15 mm diameter and 20 mm height for sintering. Each cylinder weighed 8 g.

2.3. Cement production

The samples were clinkered in an electrical resistance furnace. The heating process was conducted in three stages to simulate the sintering condition of the cement kiln. In the first stage, the temperature was raised to 1000 °C at the rate of 10 °C/min, followed by a 5 °C/min increase to the maximum temperature of 1450 °C. In the last stage, the furnace was maintained at the maximum sintering temperature for 30 min. After the sintering, the sample was removed from the furnace and cooled to room temperature in 30 min by cold air.

2.4. Analysis of the clinker

The chemical composition of the clinker was determined using a Rigaki 3370 X-ray fluorescence (XRF) spectrometry. The analytical results were reported as metal oxides. The mineral phase of the clinker sample was observed by an Olympus BH2-MJLT Optical Microscope. The clinker samples were cross-sectioned and polished, and the surface of the cross-section was etched by hydrofluoric acid. The detailed procedure can be found in the publication by the Portland cement association (Campbell, 1986).

2.5. Tests of cement quality

The cement property was assessed based on the standard methods given by the ASTM (American Society for Testing and Materials) and CNS which includes CNS786 (Vicat Needle Test), CNS1010 (Compressive Strength) and CNS2924 (Air Permeability Apparatus). The fineness of cement, determined by CNS2924, is measured indirectly by measuring the surface area with the Blaine air permeability apparatus.

3. Results and discussion

3.1. Chemical composition of MSWI ash

The chemical analysis of fly and bottom ashes was performed by using X-ray fluorescence spectrometry (XRF). The results are given in Table 1. The major components of both ashes, i.e., CaO, SiO_2, Fe_2O_3, and Al_2O_3, are similar to that of ordinary Portland cement, suggesting that both incineration ashes are suitable for reuse as cement materials. On the other hand, volatile components such as chlorine, alkali metals (Na^+, K^+) and sulfates are also abundant in both fly ash and bottom ash, which may corrode the cement kiln, particularly chlorides. Therefore, a pre-wash procedure by acid and water was investigated to reduce the amount of chlorides. After a series of washing with water and a variety of organic acids, the greatest level of chloride removal was achieved by a 15 min washing with water at a liquid to solid (L/S) weight ratio of 10 followed by a 30 min wash with 0.1 M acetic acid at $L/S = 20$. The chloride content of the fly ash can be reduced by over 90%, in comparison to 82% removal by water-wash alone. Since the purpose of this study was to evaluate the reuse of fly and bottom ash in cement production, the acid-washed MSWI ashes were used as test sample in order to incorporate as much ash as possible.

3.2. Cement design

Chemical analysis was also performed to determine the chemical composition of ash and individual raw material

Table 1
Chemical composition of fly ash and bottom ash determined by X-ray fluorescence spectrometry (XRF) (% by weight)

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	Fe_2O_3	TiO_2	Cr_2O_3	CuO	ZnO	PbO	NiO	Br
Fly ash	4.16	3.16	0.92	13.60	1.72	6.27	9.73	3.85	45.42	3.83	3.12	0.19	0.25	2.32	0.57	nd	0.35
Bottom ash	12.66	2.26	1.26	13.44	3.19	1.79	3.24	1.78	50.39	8.84	2.36	0.18	1.51	2.60	2.11	0.16	0.06

Table 2
Chemical composition of ash and cement materials (% by weight)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Fly ash	30.66	22.25	3.60	24.85	4.29	1.69	1.50	5.18
Bottom ash	25.68	16.74	6.96	23.17	5.91	1.42	1.37	0.50
Limestone	2.44	0.60	0.20	51.57	1.75	0.04	0.09	0.00
Clay	58.88	12.80	4.20	8.97	1.48	1.40	2.10	0.48
Iron slag	2.24	0.05	94.61	0.25	0.11	0.00	0.10	0.16
Sand	86.24	7.10	1.30	0.37	0.40	0.09	1.98	0.00

Chlorides content: fly ash = 5749 ppm, bottom ash = 2876 ppm.

for cement design. The results were given in Table 2. Because the two major constituents, namely, SiO_2 and Al_2O_3, of the MSWI ash are the same as those of the clay, the pre-washed ash was added into the cement raw materials to replace the clay component in the cement design. Due to the hazardous nature of fly ash, the cement design of this study was targeted at Type II Portland cement, which could be applied in infrastructure projects such as roads or dams.

The cement modulus for cement design are HM = 2.08, SM = 2.65 and IM = 1.40, which results in a cement composition of 22.98% for SiO_2, 5.06% for Al_2O_3, 3.6% for Fe_2O_3 and 65.84% for CaO. Table 3 shows the three formulas by weight: F1 without fly ash or bottom ash; F2 with fly ash; and F3 with bottom ash. The cement plant requires that the maximum chloride content of the raw meal should not exceed 100 ppm. Accordingly, the maximal amounts of fly ash and bottom ash that can be added are 1.75% and 3.50%, respectively. Although the amounts of fly ash and bottom ash that can be added in cement production are small, their reuse in cement can be an ultimate solution for their disposal. The annual cement production in Taiwan is 20 million tons, using 30 million tons of raw material. This implies the consumption of 525,000 tons fly ash or 1,050,000 tons bottom ash at the addition rate of 1.75% or 3.5%, respectively.

Table 3
Formula for Type II Portland cement (% by weight)

	F1	F2	F3
Limestone	77.23	76.79	75.94
Iron slag	1.31	1.36	1.28
Clay	21.4	18.56	17.11
Sand	0.07	1.54	2.17
Fly ash	0.00	1.75	0.00
Bottom ash	0.00	0.00	3.50

(a) F1: raw material of cement, F2: with fly ash, F3: with bottom ash.
(b) Cement design: SiO_2 = 22.98%, Al_2O_3 = 5.06%. Fe_2O_3 = 3.61%, CaO = 65.84%.
(c) Total chlorides <100 ppm.

3.3. Chemical composition of clinker samples

After the sintering, the clinker samples were ground and analyzed with XRF. The result is given in Table 4. The major components of the clinker samples are similar because of the same cement modulus adopted. It is obvious that the addition of fly ash and bottom has no effect on the chemical composition of the clinker, implying that all clinker samples should have similar mineral phase compositions. The addition of fly ash and bottom ash increases the content of P_2O_5 significantly. When the P_2O_5 content of the clinker exceeds 0.5%, the production of C_3A will

Table 5
Potential phase composition of clinker samples (% by weight)

	C_3S	C_2S	C_3A	C_4AF
F1	48	30	6.9	12
F2	49	29	7.3	11.4
F3	46	31	7.7	11.8

F1: raw materials of cement only, F2: with fly ash, F3: with bottom ash.

Table 4
Chemical composition of clinker samples (% by weight)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	f-CaO
F1	23.10	5.11	3.93	65.47	2.52	0.08	0.29	0.45	0.25	0.08	0.18
F2	22.94	5.14	3.17	65.36	2.51	0.06	0.22	0.16	0.33	0.26	0.24
F3	23.03	5.37	3.87	65.40	2.45	0.02	0.26	0.32	0.30	0.53	0.28

(a) F1: raw material of cement only, F2: with fly ash, F3: with bottom ash.
(b) Chlorides content: F1 = 21.7 ppm, F2=37.6 ppm, F3 = 36.9 ppm.

be reduced and the strength of the cement reduced. Free-lime (f-CaO) content of the clinker is an index of clinkerization. Because the hydration rate of f-CaO is low and its reaction product, $Ca(OH)_2$, increases the volume and decreases the compressive strength of the concrete, the f-CaO is generally required to be kept under 1%. All three samples were considered over-burnt (free-lime content of <0.2%), which could lead to over-sized crystal and decrease the activity of mineral phase of cement as suggested by Ono's criteria (Ono, 1980).

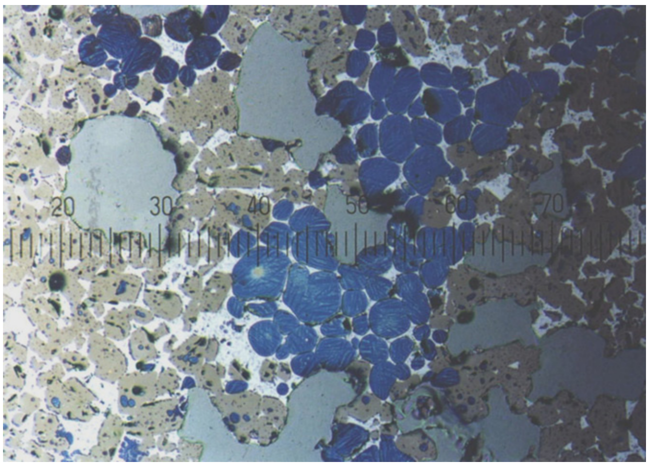

Fig. 1. Photomicrographs of clinker samples showing the angular alite crystals, the cluster of the blue belite crystals, and the liquid phase of a typical clinker (200×).

3.4. Potential phase composition of clinker sample

The potential content of the four major phases of the mineral, namely, tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF), in clinkers can be predicted by the Bogue equation from the chemical composition and f-CaO content of the clinker. Table 5 presents the potential phase composition of the three clinker samples. The predicted C_3A contents are less than 8%, conforming to the standard of Type II Portland cement.

3.5. The mineral phase composition of cement clinker

Microscopic observation reveals the microstructure and the degree of crystallization of the clinker samples, which reflects the quality of the clinkers. By etching the cross-sectioned clinker with HF vapor, the mineral phases can be differentiated by color and shape. A typical micrograph of the clinker is given in Fig. 1, in which the four mineral

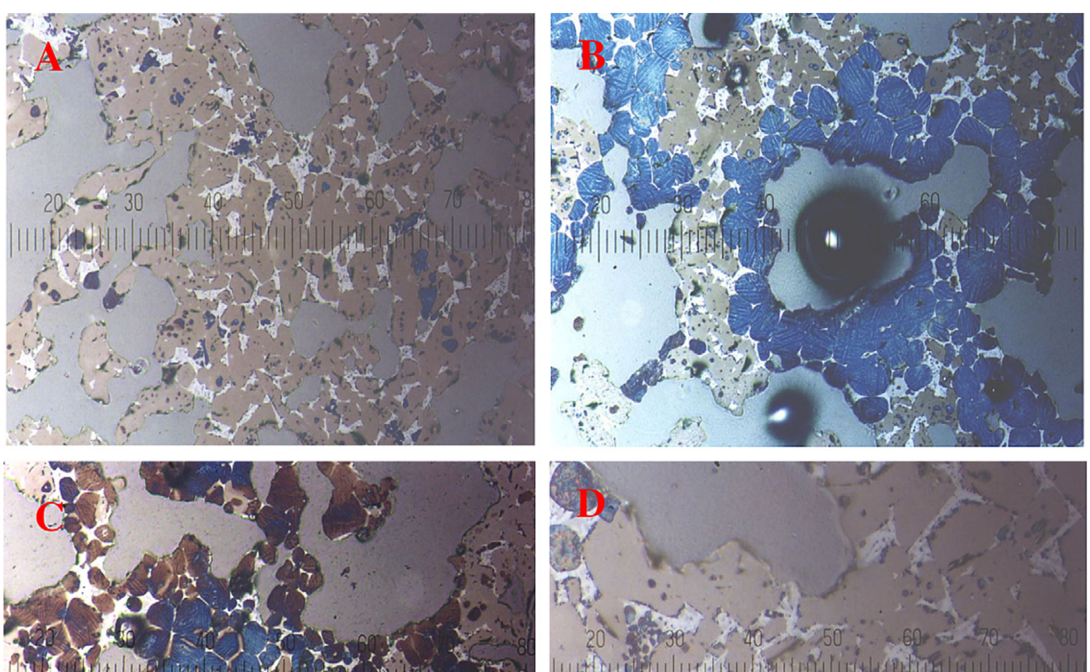

Fig. 2. Photomicrographs of clinker samples showing: (A) angular alite crystals in a F3 (with bottom ash) clinker (200×), (B) the cluster of belite crystals around a pore in a F3 (with bottom ash) clinker (200×), (C) the distribution of belite crystals in a F2 (with fly ash) clinker (200×), and (D) liquid phase distribution ($C_3A + C_4AF$) in a F2 (with fly ash) clinker (500×).

phases (C_3S, C_2S, C_3A and C_4AF), as well as the porosity distribution, are vividly shown. Alite, the mineral phase of C_3S, is yellowish brown and angular; and the belite, the mineral phase of C_2S, is blue and round. The calcium aluminate, the mineral phase of C_3A, and the calcium aluminoferrite, the mineral phase of C_4AF, are considered liquid phases. They are the white filling among alite and belite. The burning condition and the resulting hydraulic activity of the clinker can be estimated by the size, shape and distribution of the mineral crystal (Campbell, 1986). Four photomicrographs were presented here showing the representative alite distribution of F3 (Fig. 2A), belite distributions of F3 (Fig. 2B) and F2 (Fig. 2C), and porosity distribution of F2 (Fig. 2D). The crystal size of the alite is between 30 and 60 μm and that of belite is in the range of 20–45 μm, indicating that the sintering temperature is sufficient (Campbell, 1986). To produce a quality clinker, the sample must be cooled fast enough. The efficiency of cooling can be checked by the content of C_4AF and C_3A. The significant amount of C_4AF and C_3A, as shown in Fig. 2D, is an evidence for slow cooling as suggested by Campbell (1986) and Taylor (1997).

3.6. Cement quality

The fineness of the cement, calculated from the grinding time and time interval, is given in Table 6. They are all in the range of 3400–3600 cm^2/g, conforming to the fineness requirement for Type II Portland cement. The size distribution of the cement is also regulated. The most adopted criteria by cement industries is the quality control fraction (QCF), the fraction of cement particles in the size range of 3–30 μm. It is generally accepted that cement particles in this size range are the most crucial in determining cement strength. Moreover, the cement in this range promotes hydration efficiently. Beke (1973) has indicated that the QCF of the cement must be larger than 70% for desirable compressive strength. As shown in Fig. 3, the fraction distribution of the cement samples, the QCF are well over 70%.

The characteristics of the cement are compared with those of the blank sample (F1). The setting time and compressive strength of cement samples were measured. The result for setting times is shown in Fig. 4. The addition of the fly ash and bottom ash lengthened the setting time

Table 6
Grinding time, time interval, and fineness of cement samples prepared from F1, F2 and F3 by Blaine air permeability test

	Grinding time (min)	Time interval (s)	Fineness (cm^2/g)
F1	48	92.4	3480
F2	49	88.7	3410
F3	52	96.4	3550

F1: raw materials of cement only, F2: with fly ash, F3: with bottom ash.

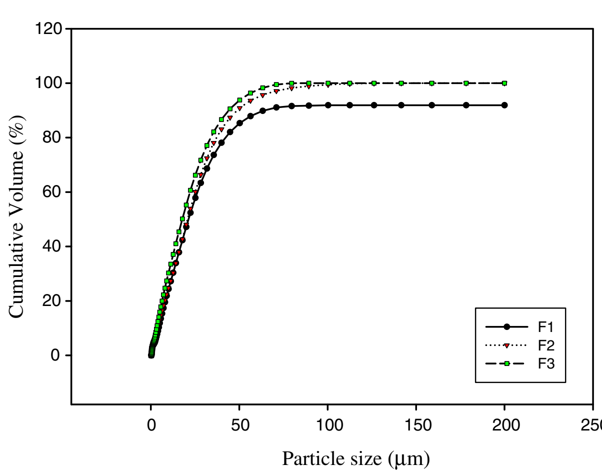

Fig. 3. Comparison of size distribution of cement samples prepared from F1 (raw materials of cement only), F2 (with fly ash) and F3 (with bottom ash).

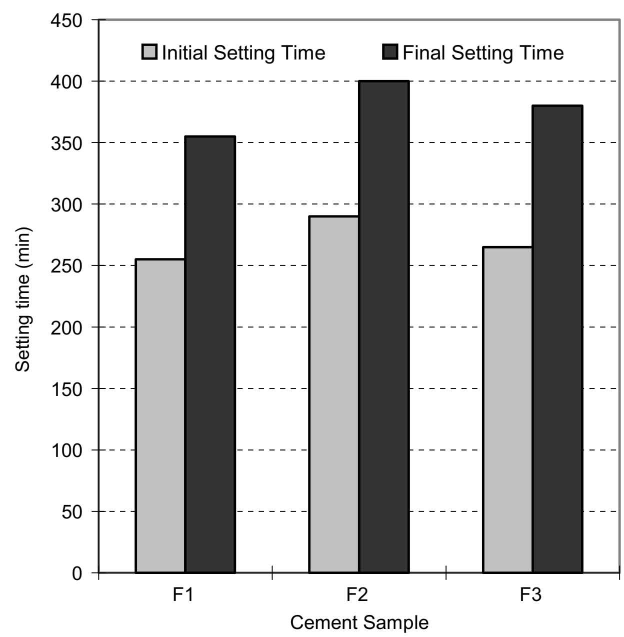

Fig. 4. Comparison of setting times of cement prepared from F1 (raw materials of cement only), F2 (with fly ash) and F3 (with bottom ash).

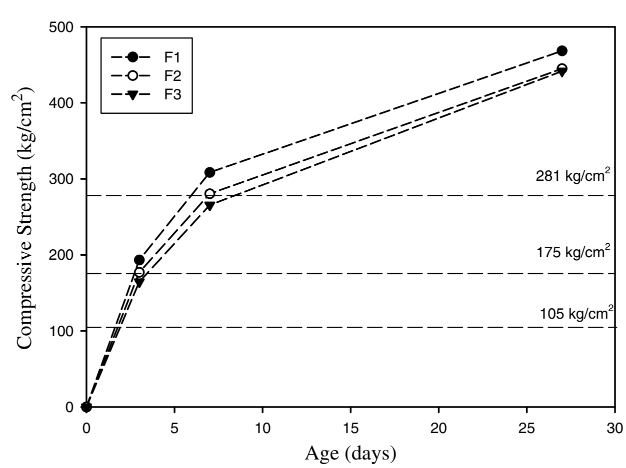

Fig. 5. Variation of compression strength of cement samples prepared from F1, F2 and F3 with curing time.

by approximately 15–5%, which can be explained by the heavy metals content such as ZnO and PbO in the fly and bottom ashes, as suggested by Olmo et al. (2001). The over-burnt condition, as indicated by the lengthened setting time, affects the activity of the mineral phases and results in a decreased hydration process.

The most concerned quality for cement is the compressive strength when used in a mortar or concrete. The compressive strength of mortar cubes of cement is shown in Fig. 5. The additions of fly ash and bottom ash in cement raw meal did not affect the compressive strength of the cement. The compressive strengths of all cement samples were greater than the standard values of the ASTM for Type II Portland cement.

4. Conclusion

The MSWI fly ash and bottom ash are suitable for reuse in cement production due to their high ash content. The amount of the waste ash that can be added in the cement raw materials is limited by the salts, especially chlorides, which can be effectively removed by water and/or acids. Inclusion of inorganic wastes in cement production is feasible provided that precise chemical analysis is provided. The laboratory-produced cement meets the requirements for Type II Portland cement, except that the setting times are slightly longer, possibly due to the over-burnt condition of the sintering. The addition of MSWI ash in cement raw materials does not affect cement quality.

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