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# Replacement of raw mix in cement production by municipal solid waste incineration ash

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## Abstract

The feasibility of municipal solid waste incineration (MSWI) ash utilized as the replacement of raw mix in cement production is investigated. Result shows that sieving, self-grinding, and magnet separation processes are necessary to remove the debris, salt, and metallic contents that existed in the MSWI ash. By using the pretreated MSWI ashes, the produced cement specimens were in compliance with the unconfined compression strength (UCS) standard in Taiwan at small replacement percentage ( < 5%). When ash replacement percentage is large (more than 10%), the strength development of specimens would be hindered due to the deficient formation of the calcium silicate. Calculation on lime saturation factor (LSF) also shows a descending trend in consequence of the increase in replacement percentage. Thus, compositional effect should be taken into consideration for promoting the calcium silicate formation at the case of large ash replacement. In this research, adjustment of chemical composition was achieved by adding 183 g calcium oxide per kilogram of cement raw mixture with 15% ash replacement. After adjustment, the produced cement could develop seven- and fivefold increase on UCS compared with those without calcium oxide supplement at 3 and 7 days of curing, respectively. Results concluded that the MSWI ash was suitable in reuse for cement production under a well-conditioned situation.

*Keywords:* Waste management; Cement manufacture; X-ray diffraction; Compressive strength

## 1. Introduction

The management of municipal solid waste (MSW) in many countries has become a complicated task owing to the stress of limited landfill site. To reduce the quantity to be landfilled and recover energy from MSW through high-pressure steam, a large amount of MSW is incinerated. Though incineration process provides about 85% of volume reduction of MSW, incineration is not the final waste treatment stage; final disposal of the residues from incineration is required. Meanwhile, a new kind of waste is created through this process that also requires further treatment. The inorganic ash waste produced from the incineration of MSW is often disposed in ordinary landfills. Nevertheless, recent studies pointed out that heavy metal contents in municipal solid waste incineration (MSWI) ashes might be leachable under acidic condition [1–3], which is often the case in ordinary landfill site, that made MSWI ashes be classified as hazardous materials. Consequently, these MSWI ashes have to be stabilized/solidified before the final disposal. That makes the disposals of MSWI ashes more troublesome and more expensive. Hence, reusing/recycling should be a better strategy for the solution of MSWI ash problems in the viewpoints of environmental protection and resource conservation. And how to accomplish the reuse of the MSWI ashes has now become the state-of-the-art issue at the integrated solid waste management.

Owing to the exhaustion of suitable natural materials in some areas, the replacement of raw materials by utilization of industrial and other waste materials are of interest in cement production. Therefore, the use of industrial inorganic wastes such as waste gypsum, nonferrous iron slag, red mud from alumina production plants, low-calcium fly ash, and even MSW as alternatives to clay, shale, fuel, etc., for cement clinker production has been widely investigated [4–8].

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Inorganic MSWI ashes contain lots of silicates, calcium, and alumina, which are the basic constituents of cement. Therefore, the MSWI ash should have the chance to be utilized as a raw material in cement production and that would solve the problems for both ash treatment and exhaustion of natural material. To achieve the goal of utilizing MSWI ash for cement production, the most direct and easiest way is to replace the raw mix in cement production with MSWI ash. Nonetheless, few works have been conducted to deal with the proper amount and operating criteria for the replacement of raw mix by ashes in cement production.

In this study, we propose a complete reuse of MSWI ash as replacement of raw mix for cement production. Feasibility of utilizing MSWI ashes as cement raw mix replacement is investigated by means of compressive strength tests of specimens made from sintered clinkers. In addition, the influences of the replacement of MSWI ashes on the variation of chemical composition and crystalline phases for cement clinker have also been evaluated by the present study.

## 2. Experimental

### *2.1. Materials*

MSWI bottom ash obtained from MSW incineration plant (Taipei, Taiwan) was originally in a damp appearance. Water content of 10% in the bottom ash was removed by drying at 105 °C for 24 h. Then the ash was sieved and size category from 0.074 to 2 mm was sampled (MSWI ash in this study). Magnet-repelled (MR) ash was prepared by passing the MSWI ash through a magnetic separator to remove its metallic content. Both the MSWI and MR ashes were ground to 74 μm size with a centrifugal ball mill (Fritsch, pulverisette 6) for further experiments.

### *2.2. Procedure*

Different proportion of the MSWI ash or MR ash was homogenized with cement raw mix supplied from a cement production plant (Kaohsiung, Taiwan); the mixture was pelletized into 20-mm diameter cylindrical pellets with uniaxial compression. To simulate the calcining process in cement production, the pellets were ramped to 900 °C for 1 h with a heating rate of 30 °C/min in an electric furnace (Nabertherm HT08, Germany), then slowly heated to 1400 °C for 3 h afterward and cooled in furnace to room temperature. Clinkers were ground to ASTM 170 mesh and blended with Ottawa standard sand (Illinois, USA) and water to form specimens of 50 × 50 × 50 mm cube. The specimens were cured at 20 °C with 95% humidity for 24 h and consequently cured in saturated calcium carbonate solution. Unconfined compression strength (UCS) tests for specimens were done according to the CNS 1010 (Chinese national standard, R.O.C.).

### *2.3. Analysis*

Materials were microwave digested with nitric, phosphoric, and fluoroboric acids. Digests were diluted and underwent inductively coupled plasma spectrometry (ICP, Jobin Yvon JY38 Plus) analysis for inorganic content determination. Chloride and sulfate content analyses were done according to the CNS 1078. The identification of the crystalline phases was made through X-ray diffraction (XRD) using a Rigaku D diffractometer (max 3.VX-Ray) with Cu Kα radiation.

## 3. Results and discussions

### *3.1. MSWI ash*

MSWI ash is gathered from incinerator with combustion at 950 °C and should contain large amount of oxides. The MSWI ash sampled with size larger than 2 mm is mostly composed of gray gel-like substances, glasses, and iron shavings, which might increase the energy consumption in following milling and mixing processes of ash. At the same time, according to chloride and sulfate content analyses data listed in Table 1, ash with the size smaller than 0.074 mm contains substantial amount of chloride and sulfate, which might cause the corrosion of reinforcement, strength loss, expansion, cracking, and therefore the disintegration of the concrete [9]. In order to diminish these possible interferences, the MSWI ash was sieved and only the ash with the size between 2 and 0.074 mm was collected for further process.

Chemical compositions of cement raw mix and sieved MSWI ash are given in Table 2. MSWI ash and cement raw mix contain mostly oxides of calcium, silicon, aluminum, and iron. However, MSWI ash is produced from the combustion of diverse sources of MSW and its composition would be variable and differ from the cement raw mix, which is blended from well-known materials such as limestone, clay, or shale. In this study, iron oxide and silicon oxide contents in the MSWI ash are larger while calcium oxide content is smaller than the cement raw mix (although the high iron oxide content in MSWI ash would enhance the grindability of clinker [10]), but the increasing quantity of metallic content in raw mix could also cause the destabilization and disintegration of tricalcium silicate resulting in

Table 1
Chloride and sulfate content of the MSWI ash within different size ranges

| Mesh | Size range (μm) | Total Cl (%) | S as $SO_3^{2-}$ (%) |
|---|---|---|---|
| >#10 | >2000 | 0.21 | 0.44 |
| #10–#20 | 841–2000 | 0.43 | 0.69 |
| #20–#40 | 420–841 | 0.42 | 0.51 |
| #40–#100 | 149–420 | 0.59 | 1.60 |
| #100–#200 | 74–149 | 1.29 | 0.87 |
| < #200 | < 74 | 1.81 | 2.25 |

Table 2
Chemical compositions of the experimental materials

| Chemical composition (%) | Cement raw mix | MSWI ash | Magnet repelled ash |
|---|---|---|---|
| CaO | 63.8 | 27.2 | 27.4 |
| $SiO_2$ | 19.8 | 29.4 | 46.4 |
| $Al_2O_3$ | 5.0 | 18.0 | 9.5 |
| $Fe_2O_3$ | 3.5 | 13.3 | 7.1 |
| MgO | 2.1 | 1.6 | 1.7 |
| $Na_2O$ | 2.0 | 3.6 | 3.2 |
| $K_2O$ | 1.2 | 0.9 | 0.8 |

loss of mechanical strength in specimens made from produced clinker [11]. Consequently, it is preferred to remove the metallic content in MSWI ash before heating. Pitifully, metallic content is mostly sealed inside silicate debris and is difficult to remove directly by magnet separation. To accomplish this separation tactic, a self-grinding technique was used since the brittleness of MR substance (silicate debris) is different from that of magnet-attracted substance (metallic content). Usually, silicate debris is brittler than metallic content. With self-grinding technique, silicate debris is very easy to flake off metallic content. Therefore, all sieved ash was milled without grinding balls at 500 rpm in this study. This process promotes magnet separation efficiency and also reduces iron oxide content in the magnet-repelled MSWI ash (MR ash). Nonetheless, the reduction of iron oxide content causes the silicon oxide content in MR ash to rise, resulting in the deviation of the chemical composition of MR ash from cement raw mix further.

### 3.2. UCS of uncompressed raw material

The cement raw material replaced with the MSWI ash or MR ash was homogenized in a ball mill for 30 min. Then, the powder was placed into crucibles, heated to 900 °C for 1 h, consequently, to 1400 °C for 3 h, and was cooled at room temperature to produce cement clinker. All specimens made by the clinkers with MSWI ash and MR ash replacement develop considerable UCS at 3 days of curing until the amount of ash replacement increased to 10%. Nevertheless, UCS of all specimens, even obtained by pure raw mix (without ash replacement) from a local cement production plant, could not meet the CNS standard (12.4 MPa). The reason might be that the electric furnace is unfeasible to create a fully stirred circumstance as the rotary kiln. Therefore, the contact of raw mix particles was not enough to complete the solid-state reaction for the formation of cement product in this calcination process. Thus, the formation of strength development material such as calcium silicate is retarded.

To modify the calcination process, raw mix without ash replacement was pelletized by compression before calcination to enhance the contacts between material powders. Raw mix was compressed into 2-cm diameter pellets at different pressure. All compressed samples were calcined according to the process described in Section 2.2. XRD patterns of the clinkers made with compression pelletization are shown in Fig. 1. Alite ($Ca_3SiO_5$), belite ($Ca_2SiO_4$), tricalcium aluminate ($Ca_3Al_2O_6$), and calcium oxide, the major crystalline phases in ordinary portland cement (JCPDS-ICDD file numbers 86-0402, 86-0399, 33-0251, and 04-0777), are present in the XRD spectra of clinkers produced with compression pelletization. The compression pelletization did successfully increase the strength of crystalline phases than the uncompressed sample. This result shows that compression pelletization of raw mix before heating improves the contact of particles and enhances the formation of the major crystalline phases. On the other hand, intensities of the major crystalline phases in the XRD pattern under different pelletization pressures do not show significant difference. These results indicate that pelletization proce-

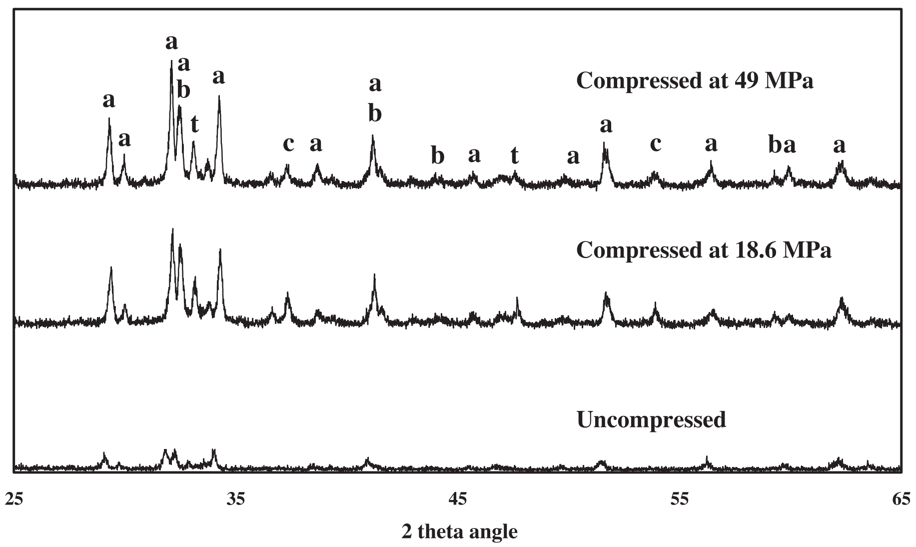

Fig. 1. XRD patterns of clinkers produced by compression pelletization at different pressure; a = alite, b = belite, t = tricalcium aluminate, and c = calcium oxide.

Table 3
UCS of cement specimens made from clinkers produced at different pelletization pressure

| Curing day | UCS at different pelletization pressure (MPa) | | | CNS standard |
|---|---|---|---|---|
| | None | 18.6 | 49 | |
| 3 | 9.0 | 17.1 | 19.2 | 12.4 |
| 7 | 16.2 | 25.1 | 25.8 | 19.3 |
| 28 | 27.1 | 29.9 | 36.2 | 27.6 |

dure before heating would increase the solid-state reaction but pelletization pressure might not have significant improvement on the crystallization of major species.

To further investigate the influence of pelletization procedure, UCS of the specimen produced at different curing ages is shown in Table 3. Uncompressed samples develop considerable, however, unqualified strength (9.0, 16.2, and 27.1 MPa compared to 12.4, 19.3, and 27.6 MPa for the CNS standard at 3, 7, and 28 days of curing, respectively). Pelletization procedure before calcination helps increase the UCS and also succeeds in meeting the standards. Even though different pelletization pressures do not influence the formation of crystalline phase significantly, higher pelletization pressure does promote the development of UCS of the cement specimens. At 3 days of curing, there is a 2.1-MPa (12%) difference in UCS between the samples produced by pelletization pressure of 190 kgf/cm$^2$ (18.6 MPa) and 500 kgf/cm$^2$ (49 MPa). The difference expands to 6.3 MPa (21% increase) at 28 days of curing. Since higher pelletization pressure obtained better UCS development, pelletization pressure of 49 MPa is chosen in the following experiments.

### 3.3. Calcination with MR ash replacement

Samples with MR ash replacement were compression pelletized and calcined with the same process. Fig. 2 shows the influence of MR ash replacement on the UCS development at various curing ages. Comparing with the UCS obtained without pelletization described in Section 3.2, the specimens with pelletization develop a better UCS at 3 days of curing. Nevertheless, there seems to be an acceptable range for the ash replacement in cement production. As replacement percentage was below 5%, all the UCS of the specimens produced with ash replacement could meet the CNS standard, and no significant influence caused by ash replacement was found. Beyond 5% replacement, UCS drops dramatically. With MR ash replacement above 10%, specimens fail to meet the standard regardless of curing age. The reasons might be due to the alternation of chemical composition in raw mix or interferences that existed in MR ash restrain the formation of crystalline phase caused by large amount of replacement. The effect of large ash replacement has been examined by XRD analysis. From the XRD spectra shown in Fig. 3, both the XRD intensity of alite ($2\theta = 32.19^\circ$, $34.36^\circ$, $51.71^\circ$) and calcium oxide ($\theta = 37.36^\circ$, $53.85^\circ$) in the clinker decreases as the replacement percentage of MR ash increases. Especially, the characteristic peaks of calcium oxide almost vanish at a large amount of ash replacement. The formation of alite in cement clinkers was deducted as cement raw mix has been replaced by large amount of ash. In addition, the insufficiencies of calcium oxide for the crystalline formation might be the major inducement of the deduction of alite phase.

### 3.4. Compositional effect of ash replacement

As mentioned previously, there is difference in composition between the MR ash and cement raw mix. Especially, silicon oxide in the MR ash is much richer than cement raw mix. In a large amount of replacement, the composition of cement raw mix is somehow changed, restraining the formation of crystalline phase in production of clinkers.

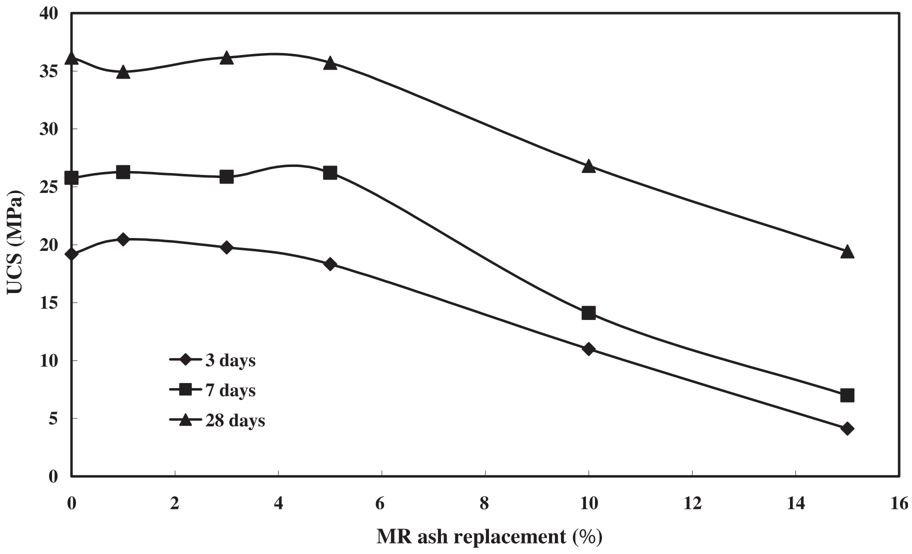

Fig. 2. UCS of specimens with MR ash replacement (compression pelletization at 49 MPa).

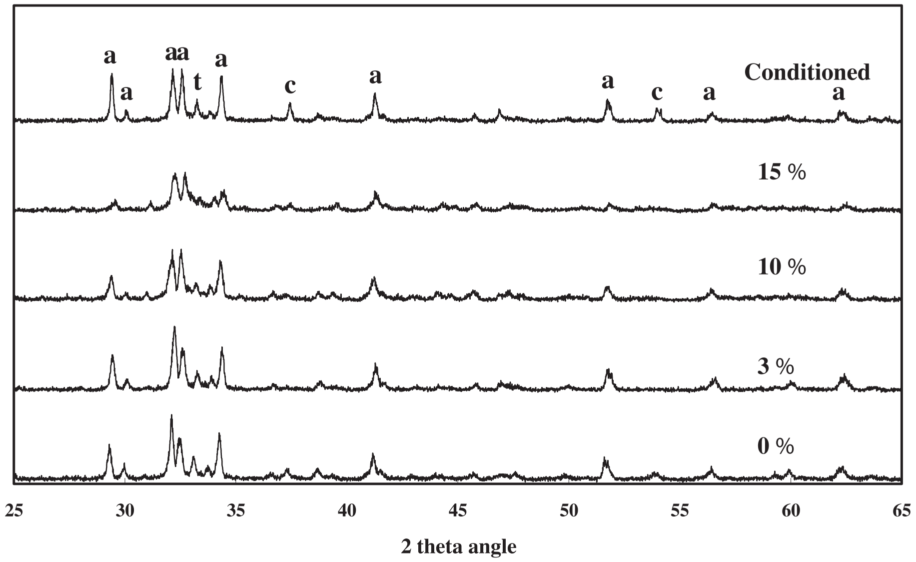

Fig. 3. XRD patterns of cement clinker with MR ash replacement (compression pelletization at 49 MPa); a = alite, c = calcium oxide, t = tricalcium aluminate.

To verify the compositional effect of ash replacement on the calcination, two parameters in cement chemistry were examined. The first one is hydraulic modulus, denoted by H.M., which gives the evaluation of hydraulic activity for strength development.

$$\text{H.M.} = \frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$$

The second one is lime saturation factor, denoted by LSF, which governs the ratio of alite to belite and also shows whether the clinker is likely to contain free lime.

$$\text{LSF} = \frac{\text{CaO}}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3}$$

Calculations for the H.M. and LSF of the clinkers are given in Table 4; H.M., LSF, and UCS all decrease with respect to the increase of MR ash replacement. Nevertheless, the change in composition is insignificant and the compositional effect is not important at small amount of ash replacement ( $<$ 3%). While at the large amount of ash replacement, especially cement with 15% ash replacement, H.M. is significantly lowered to about 28% indicating the hydraulic activity for strength development to be weak. In addition, the low LSF supports this point that calcium oxide content might not be enough to produce calcium silicates in the calcinations and hence causes the decrease of the hydraulic activity. Therefore, insufficient calcium oxide might be the predominant reason causing the poor strength development of specimens made from the MR ash replaced clinkers.

In order to increase LSF and to supply enough calcium oxide for calcium silicate formation, raw mix as 15% MR ash replacement was conditioned with the addition of a pure calcium oxide (Merck, Germany). The amount of calcium oxide added was decided according to both H.M. and LSF. The H.M. and LSF were adjusted in a manner that these values should be at least the same with the cement raw mix obtained from cement production plant. Cement clinker produced with the addition of calcium oxide is called the conditioned cement. Comparing the XRD results obtained by 15% MR ash replacement and without conditioning in Fig. 3, an apparent XRD intensity of free lime was found in the conditioned cement. The amount of calcium oxide is then enough to form crystalline phases needed for strength development. After conditioning, UCS was improved from 4.1 to 29.2 MPa at 3 days of curing, which is almost sevenfold increase, and also from 7.0 to 38.9 MPa at 7 days of curing, which is fivefold increase. Above results indicate that the compositional effect should be taken into consideration as ash replacement percentage is large. Therefore, utilizing MSWI ash as cement raw mix replacement in

Table 4
Effect of ash replacement on the UCS of cement specimens (with compression pelletization)

| | Without ash replacement | 3% ash replacement | 10% ash replacement | 15% ash replacement | Conditioned cement |
|---|---|---|---|---|---|
| H.M. | 2.25 | 2.14 | 1.91 | 1.76 | 2.31 |
| LSF | 1.00 | 0.95 | 0.84 | 0.77 | 1.01 |
| UCS (MPa) | | | | | |
| 3 days | 19.2 | 19.8 | 11.0 | 4.1 | 29.2 |
| 7 days | 25.8 | 25.9 | 14.1 | 7.0 | 38.9 |

cement production is applicable. While the replacement percentage is large, adjustment of composition is necessary.

## 4. Conclusions

The replacement of cement raw mix with MSWI ash was proved to be applicable in this study. Nevertheless, when ash replacement percentage is larger than 5%, there is a dramatic loss in UCS regardless of curing age. Both the XRD crystalline phases and the calculations on LSF show that the calcium oxide might be insufficient for the formation of alite phase at large amount of the ash replacement. With conditioning by the addition of calcium oxide to the raw mix with 15% ash replacement, the UCS could meet the standards. The MSWI ash, hence, is feasible to replace cement raw mix for cement production under a well-conditioned situation.

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