



The effects of the mechanical–chemical stabilization process for municipal solid waste incinerator fly ash on the chemical reactions in cement paste

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ABSTRACT

A water extraction process can remove the soluble salts present in municipal solid waste incinerator (MSWI) fly ash, which will help to increase the stability of the synthetic materials produced from the MSWI fly ash. A milling process can be used to stabilize the heavy metals found in the extracted MSWI fly ash (EA) leading to the formation of a non-hazardous material. This milled extracted MSWI fly ash (MEA) was added to an ordinary Portland cement (OPC) paste to induce pozzolanic reactions. The experimental parameters included the milling time (96 h), water to binder ratios (0.38, 0.45, and 0.55), and curing time (1, 3, 7 and 28 days). The analysis procedures included inductively coupled plasma atomic emission spectroscopy (ICP/AES), BET, mercury intrusion porosimetry (MIP), X-ray diffraction (XRD), and nuclear magnetic resonance (NMR) imaging. The results of the analyses indicate that the milling process helped to stabilize the heavy metals in the MEA, with an increase in the specific surface area of about 50 times over that of OPC. The addition of the MEA to the OPC paste decreased the amount of Ca(OH)₂ and led to the generation of calcium–silicate–hydrates (C–S–H) which in turned increased the amount of gel pores and middle sized pores in the cement. Furthermore, a comparison shows an increase in the early and later strength over that of OPC paste without the addition of the milled extracted ash. In other words, the milling process could stabilize the heavy metals in the MEA and had an activating effect on the MEA, allowing it to partly substitute OPC in OPC paste.

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1. Introduction

Cement production is a high-energy-consumption industry that can lead to the discharge of a great quantity of carbon dioxide into the atmosphere. Reducing the cement dosage is regarded as very important to counter the problems of carbon emissions. The mechanical reaction technique for the treatment of municipal solid waste incinerator (MSWI) fly ash is described. The technology takes advantage of mechanical energy to induce chemical reactions which will, in turn, lead to the decomposition of any contaminant in the ash or a decrease of their toxicity. For example, Hall et al. (1996) proved that the milling process could destroy DDT (2,2-bis (4-chlorophenyl)-1,1,1-trichloroethane) and chlorinated organic compounds along with the addition of CaO. Tanaka et al. (2004) used a similar method to destroy TCB (1,2,3-trichlorobenzene) and the difficult to decompose chlorinated organic compounds. Nomura et al. (2005) adopted the same method to destroy dioxins present in this type of ash. The product of that process appeared to be

black in color and was inferred to be chlorinated organic compounds that had been carbonized.

In 2008, Nomura et al. (2008) utilized a process whereby MSWI fly ash was milled with CaO. They found that the leaching concentration of the heavy metals could be reduced by as much as 93%. In another study, Li et al. (2010) found that the leachability of Pb could be reduced by about 96% after wet milling for 96 h. Sun et al. (2011a) indicated that different milling solutions (water, ethanol, 0.02 M H₃PO₄, 0.2 M H₃PO₄) can decrease the leaching concentration of the heavy metals. In particular, the residual fraction of Pb extracted from the MSWI fly ash by the sequential extraction procedure with 0.2 M H₃PO₄ of milling solution after 96 h of milling time can be increased. After the milling process water treatment plant sludge was added to the extracted MSWI fly ash (EA) followed by sintering at 900–1000 °C. The evaporation of heavy metals will obviously be restrained in the milled EA (MEA) during the sintering process (Sun et al., 2011b). Guo et al. (2010) noted that, compared with melting technology treated MSWI fly ash, this type of mechanochemical technology has the advantages of not only simplicity but also being environmentally-friendly and energy saving.

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Mechanical milling is commonly used to modify the characteristics of waste materials destined to be utilized as additives in cement. Sekulić et al. (1999) used this process to alter the microstructure of coal fly ash which was then added to cement. They found a significant increase in the compressive strength of the cement paste after 7 days of curing. The reference to the work of Sobolev (2005) can be confirmed by the relevant remark that the ground blast furnace slag cement is a regularly used cement type since decades. Ryou (2004) compared the different characteristics of both mixed and separated waste materials after milling. Bertolini et al. (2004) added wet milled MSWI bottom ash and unmilled fly ash to cement pastes. They found that the addition of milled MSWI bottom ash can improve the compressive strength. The nature of the additives that can partly be substituted for cement has become an important issue. The addition of smaller particle powder to the cement could strengthen the filler effect and the pozzolanic reactions, thereby improving the various characteristics of the cement. Payá et al. (1995) for example, pointed out that particle size has a significant effect on the compressive strength of the cement products. Justnes et al. added milled quartz sand to cement mortar to be incorporated into the cement. In addition to increasing the amount of $\text{Ca}(\text{OH})_2$, the additive promoted the pozzolanic reactions, which improved the compressive strength of the resultant cement mortar (Justnes et al., 2005, 2007). Johansson et al. (1999) used ^{29}Si solid state NMR to find that the kinetics of the hydration reaction of the mechanochemically modified cement (MSH) was rapider than the rapid-hardening ordinary Portland cement by about 15–20%. This study suggested that SiO_2 layers would form in addition to C_3S , which would accelerate the pozzolanic reaction and promote the growth of more extensive nets of the hydrate product. Pipilikaki and Bwazi-Katsioti (2009) noted that the main factor affecting the characteristics of cement is its pore structure. The filler effect and the corresponding hydration reaction would lead to the generation of smaller pores. Lange et al. (1997) used the mathematical model to analyze the filling effect. Their results indicated that the filler effect can affect the density of the microstructure and strengthen the mechanical characteristics.

It follows that particle refinement would contribute to strengthening the mechanical characteristics of the resultant cement paste, by improving the hydration and pozzolanic reactions. In contrast, Erdoğan and Türker (1998) and Cheriaf et al. (1999) claimed that decreasing the particle size would cause a higher activation energy, hydration would be accelerated and the setting time would be shortened. According to Kiattekomol et al. (2001) the pozzolanic reactions are correlated to the amount of particles less than $10\ \mu\text{m}$ in size in the coal fly ash. Benezet and Benhassaine (1999) found that the reaction with the quartz could be strengthened, especially when the particle size was smaller than $5\ \mu\text{m}$. In another study, Cordeiro et al. (2008) added sugar cane bagasse ash with different particle sizes into cement mortar. They found a significant relationship between the particle size and particle fineness, and the pozzolanic reactions.

In this study, the milling process was used to change the characteristics of the EA so as to observe the leaching concentration of the heavy metals. In addition, the MEA was used as a partial substitute for the OPC so as to understand its effects on the hydration and pozzolanic reactions.

2. Materials and methods

2.1. Materials

The MSWI fly ash included both Air Pollution Control (APC) residues and boiler fly ash collected from a large-scale municipal solid

waste incineration plant located in northern Taiwan. The incinerator's air pollution control devices (APCDs) include cyclone dust collectors, semi-dry scrubbers and bag-filters. The mixing rate of the sample ash was based on the daily production of the plant as follows: APC residues: boiler fly ash = 1.71: 1 (w/w). Type I ordinary Portland cement (OPC) was used in all experiments. All the samples were stored in vacuum sealed bags for future use.

2.2. Experimental procedure

The MSWI fly ash was treated using a two-stage extraction process with deionized water: the ratio of water to MSWI fly ash was 5 (w/w) and the extraction time was 5 min. During the extraction process, the highly soluble chloride would be transferred into the deionized water, which decreased the chloride content in the MSWI fly ash (Chimenos et al., 2005; Jiang et al., 2009; Zhu et al., 2009). Every extraction stage was carried out for the separation of solid and liquid. After the extraction process, the EA was placed in vacuum bags that had been dried in an oven heated to $105\ ^\circ\text{C}$ (Chuang, 2006) for future use. The dried EA was then milled by wet milling with the following parameters: the milling slurry ratio was 9 (w/w), the ratio of milling balls to EA was 30% (v/v), the milling time was 96 h, the critical rotation speed of the chamber was fixed at around 93 rpm, the milling solution was deionized water and the milling atmosphere was air (Li et al., 2010). The same parameters have been used for the milling process in the control experiment but without the addition of the milling balls. The MEA was dried at $105\ ^\circ\text{C}$ in an oven and ground in a pestle for future use.

There were four different cement paste substitution conditions tested in the experiments: the addition of 5% MEA (OPC-MEA 5%), the addition of 10% MEA (OPC-MEA 10%), the addition of 5% EA (OPC-EA 5%) and OPC with no addition. In this experiment, the production of cement paste was based on the research of Lin et al. (2003, 2004) and Wang et al. (2004), who found that a W/B ratio of 0.38 was feasible for cement paste. Thus, the test samples subject to X-ray diffraction (XRD), ^{29}Si MAS-nuclear magnetic resonance (NMR) and mercury intrusion porosimetry (MIP) used a W/B of 0.38 in their discussion of the hydration reaction and pozzolanic reaction. In addition, W/B ratios of 0.38, 0.45 and 0.55 were used in the condensation test and compression test to discuss the effect of milling on the workability. The sample was prepared according to ASTM C192/C192M-07 and cured in a thermostatic water bath according to ASTM C511-09. The samples were conserved in saturated limewater for 1, 3, 7 or 28 days. The sample surfaces needed to be cleaned before testing.

The tests for characterization of the cement pastes included setting time (ASTM C191-08), compressive strength (ASTM C109/C109M) and the distribution of micro-pores. In order to understand the hydration and the pozzolanic reaction effects, XRD and NMR testing were used to identify the $\text{Ca}(\text{OH})_2$ and silicate polymer content in the different cement pastes.

2.3. Analysis

The samples were digested by alkali fusion by placing $0.025 \pm 0.005\ \text{g}$ of ash with 1 g of H_3BO_3 and 0.3 g of Li_2CO_3 into a platinum crucible and then completely melting them at $1000\ ^\circ\text{C}$. After the samples have been cooled down to room temperature, the slag was put into a plastic bottle with 100 mL of pure water and 10 mL of nitric acid to completely dissolve. The heavy metal content and chemical composition were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jobin Yvon Horiba, Ultima-2000). The toxicity characteristic leaching procedure (TCLP; US EPA Method 1311) was used to extract the heavy metals from the samples. Some of the MEA particles were re-

moved after the milling process but before solid–liquid separation and ethanol was added to the MEA particles to avoid particle agglomeration. A particle size analyzer was then used to find the particle size (Malvern, Mastersizer, 2000a). The specific surface area was detected by BET nitrogen adsorption (Micrometrics, ASAP2010). The samples were crushed into particles after the MEA was dried in an oven. The pore structure was detected by MIP (Micrometrics, Autopore II 9220), all of which were measured in order to understand changes in size of the micro-pores. A sample near the center of the past sample was taken for compressive strength testing. Each sample was cut into 0.5 g pieces. The XRD (Cu tube, 40 kV, 30 mA, 10–80°, 0.02°/step, 1.25°/min) (Bruker, D8A) was carried out on the samples. The particles and paste were ground in an agate mortar until they could pass through a #300 mesh. The NMR (Varian, Solid State NMR Spectrometer) spectra were used to identify C–S–H structures. The same preparation method as for the XRD testing was used. Chemical shifts were converted to ppm values relative to the tetramethylsilane (TMS) as a reference standard.

3. Results and discussion

3.1. Effects of milling on the powder

Tables 1 and 2 show the content of the main elements and heavy metals for different samples. It can be seen in Table 1 that both types of ash contained high concentrations of calcium, sodium and potassium. A large amount of the sodium and potassium were removed by the water extraction process, which is important for stabilization during the recycling of MSWI fly ash. The extraction process could remove some Ca (37.32%) from the solution, but the ratio of loss was no more than Na (79.69%), K (89.34%) and Cl (82.00%) (Chuang, 2006). Therefore, there is no significant change in the content ratios (w/w) of Ca of the EA in Table 1. The composition of the control experiment ash is shown in Tables 1 and 2. As can be seen in Table 1, the control experiment ash is comparable to the water extract. The easily dissolvable elements like K, Na and Ca were still dissolved in the water. Table 2 shows no significant change in the heavy metal content in this step.

There were obvious changes in the physical and chemical characteristics after milling the EA during 96 h. The physical change included the particle size, specific surface area and microstructure. The chemical change contained the crystalline structure of the powder. For example, the d_{50} of the EA changed from 72.5 μm to 3.95 μm (see Fig. 1). Clearly, the milling process reduced the particle size. Furthermore, the specific surface area increased as shown in Table 3. Before milling, the specific surface areas of the EA and the OPC were 22.46 m^2/g and 0.98 m^2/g , respectively. After milling for 8 h, the specific surface area was almost double that before milling. After milling for 96 h, it reached up to 79.66 m^2/g . The decrease in particle size would be helpful to enhance the filling effect in the cement paste while the increase in the specific surface area

would improve the reaction between the MEA and water during hydration. Both these phenomena would act to promote the compressive strength.

Fig. 2 shows SEM images of the microstructure of the EA before and after 96 h of milling time. Fig. 2b shows that the surface morphology of the MEA was like the melting state, in which the particles have melted together. Fig. 2a shows the particles of EA stacked together and one can be more accurate than the outline of the particles. Comparing the MEA with EA, the effects of long-term application of the mechanical force appear visible. The microstructure has collapsed, as if it had been melted. It can be seen from the XRD spectrum in Fig. 3 that the crystalline structure has become largely amorphous, like that of the melted fly ash slag.

The results of the control experiment are shown in Table 4. After 96 h, the heavy metal concentration in the milled solution (with milling balls) is lower than in the control experiment solution (without milling balls). The particle size would be fragmented in early milling, and the heavy metals would be released into the milling solution. Extending the milling time, the particle will bring about the concurrent actions of fragmentation and/or agglomeration, which will stabilize the heavy metals of milling solution into the milled sample. Therefore, the heavy metals content of the milling solution would be decreased with the milling time increase. However, the control experiment did not cause the stability of the heavy metals because the milling ball were not added. The crystal structure was also destroyed and the amorphous phase generated. At this time, the heavy metals will be adsorbed and sealed in the MEA and stabilized (Nomura et al. 2006; Montinaro et al. 2007; Li et al. 2010). Furthermore, the easily dissolvable elements would still dissolve during the milling process, so that the concentrations of K and Na were higher in the milled solution than in the control experiment solution (as shown in Table 4). Table 5 shows the TCLP leaching concentration of the heavy metals in the EA after 96 h of milling. The Pb concentration is lower than the detectable inductively coupled plasma (ICP) limit (Pb: 5 $\mu\text{g}/\text{L}$), and there is a tendency for the amount of other heavy metals to decrease as well. It is assumed that the heavy metals have been sealed in the like-melted amorphous material, thereby reducing their mobility and stabilizing the MEA. When the EA was treated by a milling process, all of heavy metals could meet the regulatory limits of TCLP. This means that the risk of heavy metal leaching would be less for the MEA than the EA, APC residue and boiler ash, so it may be suitable as a partial substitute for OPC. The final product should remain safe even after weathering of the cement structures, thereby reducing any negative environmental impact.

3.2. Effects of the MEA on the microstructure of the cement paste

Calcium hydroxide is consumed during the pozzolanic reactions and calcium–silicate–hydrates (C–S–H) form in the cement paste. The C–S–H can fill in the big pores and the amount of middle-sized pores and/or gel pores will increase, which improves the densifica-

Table 1
Elements concentrations in the ash and the OPC.

Elements (%)	Boiler ash	APC residues	EA	Control experiment ash	MEA	OPC
Ca	25.5 ± 0.30	30.9 ± 0.80	30.7 ± 0.26	26.3 ± 1.4	18.14 ± 0.23	32.1 ± 0.19
K	3.39 ± 0.05	4.60 ± 0.11	0.75 ± 0.01	0.59 ± 0.01	0.91 ± 0.20	1.31 ± 0.09
Na	3.46 ± 0.05	4.24 ± 0.13	1.36 ± 0.04	0.38 ± 0.05	0.96 ± 0.06	0.71 ± 0.06
Al	3.55 ± 0.04	0.36 ± 0.00	2.81 ± 0.08	0.51 ± 0.02	7.83 ± 0.37	2.36 ± 0.08
Fe	1.42 ± 0.04	0.24 ± 0.00	1.18 ± 0.01	0.44 ± 0.02	0.75 ± 0.01	2.17 ± 0.05
Mg	2.33 ± 0.02	0.50 ± 0.00	1.77 ± 0.03	0.53 ± 0.01	0.83 ± 0.01	1.68 ± 0.03
Si	7.04 ± 0.15	1.08 ± 0.04	6.5 ± 0.18	4.02 ± 0.32	4.05 ± 0.26	9.21 ± 0.15
Ti	1.14 ± 0.03	0.08 ± 0.00	0.82 ± 0.03	0.13 ± 0.02	0.35 ± 0.02	0.31 ± 0.06

Mean ± standard deviation (n = 3).

Table 2
Heavy metals in the ash and the OPC.

Elements (mg/kg)	Boiler ash	APC residues	EA	Control experiment ash	MEA	OPC
Cd	90.0 ± 4.0	218 ± 21	220 ± 26	265 ± 5	141 ± 30	ND
Cr	1120 ± 29	187 ± 6	276 ± 13	267 ± 11	428 ± 23	133 ± 4
Cu	ND	129 ± 224	199 ± 63	154 ± 15	174 ± 14	505 ± 36
Mo	60.7 ± 2.0	41.9 ± 6.9	102 ± 11	41.0 ± 0.4	73.2 ± 5.5	–
Pb	1540 ± 106	3900 ± 111	2200 ± 109	2337 ± 165	1950 ± 20	179 ± 3
Sb	1010 ± 15	609 ± 10	1157 ± 82	1230 ± 24	958 ± 3	–
Zn	11,900 ± 310	11,300 ± 74	13,800 ± 168	12,156 ± 320	12,500 ± 352	132 ± 9

Mean ± standard deviation ($n = 3$).

ND: not detectable.

Detection limit: Cd: 0.35 µg/L, Cu: 0.6 µg/L, Mo: 1.0 µg/L, Pb: 5 µg/L, Sb: 5 µg/L, Zn: 0.3 µg/L.

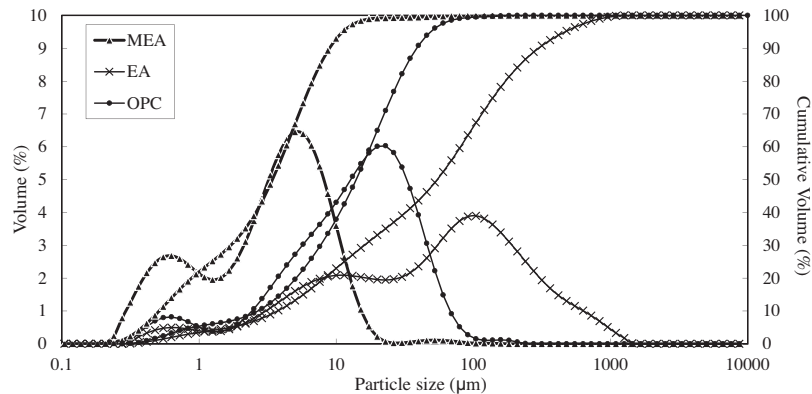


Fig. 1. Particle distribution in the OPC and EA before and after milling for 96 h.

Table 3
Specific surface area of the EA after different milling times.

Milling time (h)	Specific surface area by BET (m ² /g)
0	22.46
1	29.54
8	47.33
96	79.66

OPC: 0.98 m²/g.

tion of the cement paste. In this section, the XRD, NMR and MIP results used to analyze the calcium hydroxide crystal, C–S–H and pore size distribution are discussed.

Fig. 4 shows the XRD patterns of the OPC–MEA 10% and OPC pastes after 7 days and 28 days of curing. Table 6 shows the values of the integral peak area of 2θ (18.065° and 34.100°) from Fig. 4.

The value of the integral peak area is indicative of the relative crystalline content of the samples. It can be seen in Table 6 that the calcium hydroxide crystal content of the OPC–MEA 10% paste decreased with the curing time, which indicates that the MEA helped to strengthen the pozzolanic reactions in the cement paste at later ages. This phenomenon would increase the bulk density and the later strength of the cement. The calcium hydroxide crystal content in the OPC–MEA 10% paste was lower than that in the OPC paste. The calcium hydroxide would be consumed during early stages of curing thereby promoting the early strength of the cement.

The NMR spectra showed that in the initial stages, the silicate polymer SiO_4^{4-} (Q^0) appeared at –70 ppm but this changed to SiO_3^{3-} (Q^1) or SiO_2^{2-} (Q^2) through the hydration and pozzolanic reactions, appearing in the NMR spectra at –80 ppm or –87 ppm, respectively. The integral values of the Q^1 peak and Q^2 peak were calculated using the formula, $\text{Psi} = 2 * ((I(Q^1) + I(Q^2))/I(Q^1))$ (Justnes et al., 1990), to obtain the length of linear poly-silicate anions

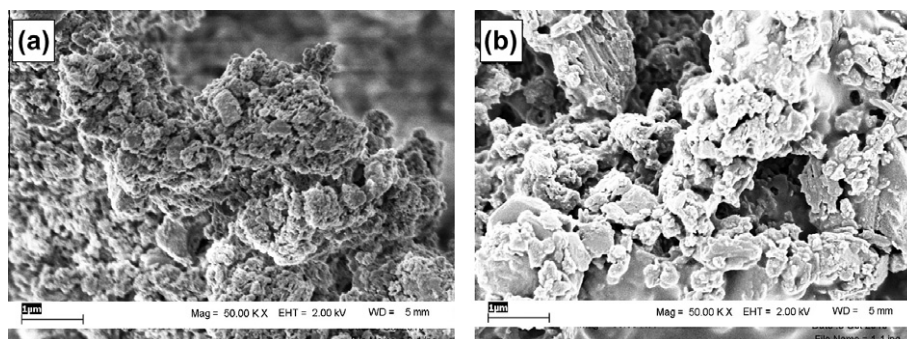


Fig. 2. SEM microstructure of the EA (a) before and (b) after milling for 96 h.

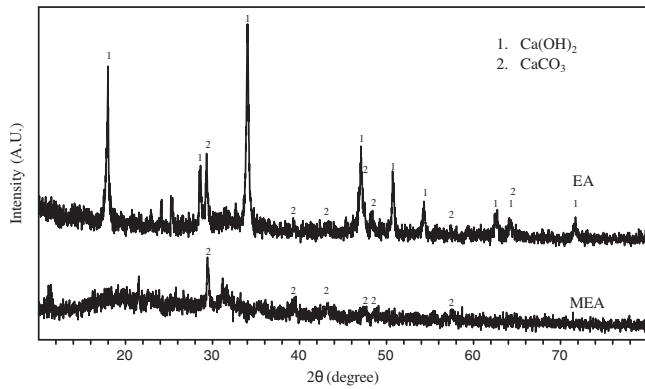


Fig. 3. XRD patterns of the EA before and after milling for 96 h (MEA).

Table 4

Elements and heavy metals in the control experiment solution and the milled solution after a 96 h of reaction time.

Elements	Control experiment solution	Milled solution	Elements	Control experiment solution	Milled solution
Ca	190 ± 36	201 ± 69	Cd	0.01 ± 0.01	0.01 ± 0.01
K	109 ± 34	491 ± 4	Cr	0.61 ± 0.13	0.06 ± 0.03
Na	78.1 ± 30.9	344 ± 97	Cu	0.10 ± 0.04	0.05 ± 0.04
Al	0.19 ± 0.06	0.21 ± 0.13	Pb	14.3 ± 2.55	2.56 ± 0.10
Fe	0.01 ± 0.00	0.01 ± 0.01	Zn	1.91 ± 0.09	0.61 ± 0.21
Mg	0.02 ± 0.01	0.01 ± 0.01			
Si	0.23 ± 0.09	0.16 ± 0.03			
Ti	0.05 ± 0.01	0.05 ± 0.01			

Unit: mg/L.

in the C–S–H gel called Psi. The pozzolanic reactions consume $\text{Ca}(\text{OH})_2$ (CH) to form more small C–S–H gels. When more C–S–H gel is produced, the length of the anionic poly silicon will be greater and Psi value higher. It can be seen in the NMR spectra (Fig. 5) that the Q^2 peak of the OPC-MEA 10% paste is obviously higher than the OPC paste one after 28 days of curing. This indicates that the pozzolanic reaction has already occurred. At the same time, there is an obvious decrease in the Q^0 peak. Johansson et al. (1999) also indicated that adding calcium silicates ($2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$) and silica fume (SF) for mechanical activation can increase the peak of Q^2 in the NMR spectra. A comparison is made with the paste formed with the addition of 10% EA. The degree of reduction of Q^0 peak was higher than the OPC one, but still lower than the OPC-MEA 10% paste one, while the Q^2 peak increased only slightly. The calculation results show that the Psi values of the OPC-MEA 10%, the OPC-EA 10% and OPC are 3.982, 3.670 and 3.407, respectively. Therefore, more C–S–H were generated in the OPC-MEA 10% than in the other substitution percentages, which would enhance the length of linear poly-silicate anions. Moreover, Wang et al. (2001) indicated that the hydration degree increased as the value of Psi increased, which was helpful to raise the compressive strength. Fig. 6 shows the mercury penetration curves obtained by MIP after 28 days of curing for the different substitution ratios: OPC-MEA 5%, OPC-MEA 10%, OPC-EA5% and without substitution. The pore distributions in the four samples were between 0.1 and 0.001 μm . The main pore sizes of the OPC, OPC-MEA 5% and OPC-MEA 10% were about 0.031 μm , 0.020 μm and 0.016 μm , respectively. Fig. 7 shows the gel pore and the middle-sized pore content calculated from Fig. 6 for the four pastes. Comparison of the OPC-MEA 10% and the OPC showed that the addition of the MEA would increase the amount of gel pores and middle-sized pores in the paste. Pipilikaki and Bwazi-Katsioti (2009) showed that produces smaller gel pores and that is related

Table 5

TCLP leaching concentration of different ash.

Elements (mg/L)	Boiler ash	APC residues	EA	MEA
Cd	ND	ND	ND	ND
Cr	5.04 ± 0.01	0.18 ± 0.01	0.37 ± 0.06	0.51 ± 0.02
Cu	ND	0.28 ± 0.04	0.18 ± 0.02	0.14 ± 0.00
Pb	0.04 ± 0.01	63.8 ± 1.6	0.93 ± 0.31	ND
Zn	0.03 ± 0.03	4.96 ± 0.09	1.31 ± 0.15	ND
pH	10.48	12.10	10.47	10.47

Mean ± standard deviation ($n = 3$).

ND: not detectable.

Detection limit: Cd: 0.35 $\mu\text{g/L}$, Cu: 0.6 $\mu\text{g/L}$, Pb: 5 $\mu\text{g/L}$, Zn: 0.3 $\mu\text{g/L}$.

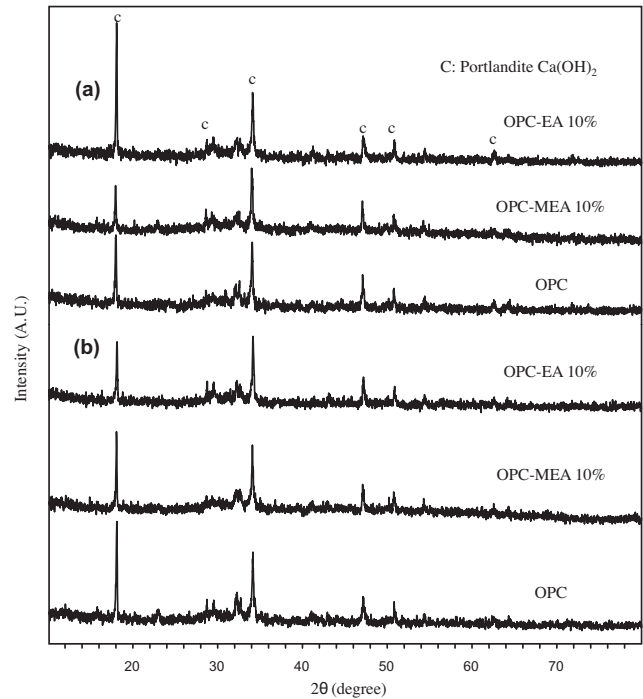


Fig. 4. XRD patterns of the OPC-EA 10%, OPC-MEA 10%, and OPC cement paste at W/B = 0.38 after curing for (a) 28 days and (b) 7 days.

to higher hydration rates when limestone is added to the cement. Increasing the gel and middle-sized pore content is helpful in increasing the mechanical strength of the pastes, because both types of pores formed by the C–S–H acted to fill the comparatively large pores. Specifically, under circumstances where the number of gel pores also increases, the addition of MEA fills the pores and could also increase the reaction activity. This result was similar to Zeng et al. (2012) who suggest that the pore change caused by particle stacking and gel/space produced by the hydration reaction also significantly affects the pore structure when low-calcium fly ash is used to conduct this experiment. This also strengthens the pozzolanic reactions leading to an improvement in the later strength of the cement.

3.3. Characteristics of the cement paste after the addition of MEA

It can be seen in Fig. 8 that the early strength of the OPC-MEA 5% and the OPC-MEA 10% pastes might be higher than the OPC one, when the W/B was 0.38. Furthermore, the same trend was observed with different W/B ratios. The results of the XRD, MIP and NMR tests show that the milling cannot only increase the amount of C–S–H gel which is caused by the higher hydration reaction, but

Table 6
Value of the integral peak area of 2θ (18.065° and 34.100°) from Fig. 4.

Sample	Curing time	2θ ($^\circ$)	
		18.065	34.100
OPC	7	9608	10949
OPC-EA 10%		6685	9045
OPC-MEA 10%		6584	8878
OPC	28	8869	10408
OPC-EA 10%		9825	9501
OPC-MEA 10%		4248	8446

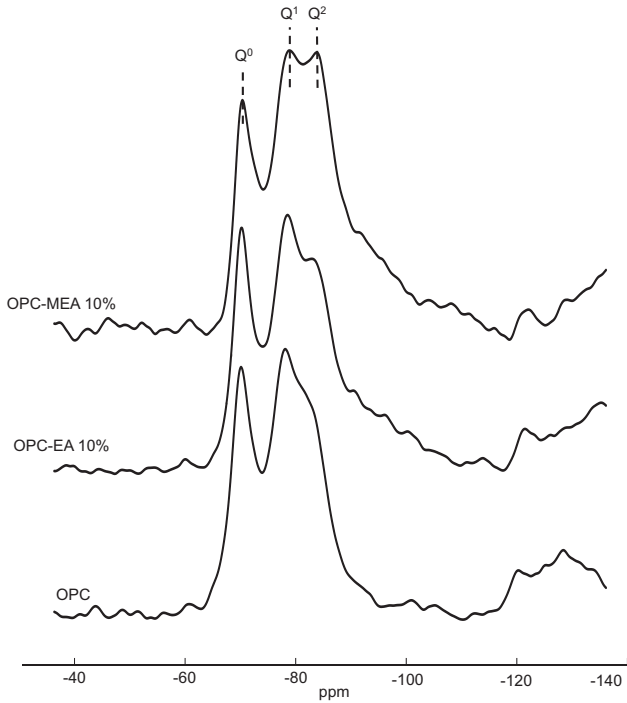


Fig. 5. ^{29}Si NMR spectra of the OPC-MEA 10%, the OPC-EA 10%, and OPC cement paste at W/B = 0.38 after curing for 28 days.

can also accelerate the pozzolanic reactions that started earlier. Moreover, the early strength of the cement has developed rapidly, perhaps because the specific surface area of the MEA was higher than the OPC one. If the specific surface area is higher and the particle size is lower, the generated hydraulic activity would react more rapidly. When the W/B was low, the compressive strength of the MEA paste was higher than the OPC one after 28 days of curing. Even when the W/B was raised, the compressive strength of the added MEA paste was still higher than the OPC one after 7 days of curing. It can be seen from this that the paste with the added MEA had a high water content, probably because of the higher specific surface area of the MEA, which would induce water adsorption to increase. Frequently, in normal constant water addition, the higher specific surface area will shorten the setting time and decrease the workability, which makes for poor fluidity. To monitor this situation, the initial and final setting times were tested during the experiments.

The addition of the MEA decreased the initial and final setting times. It can be seen in Table 7, that when the W/B of the OPC exceeded 0.45, the final setting time became too long, as much as 555 min. In addition, when the substitution ratio was 10%, the final setting time decreased to 360 min. On the other hand, when the W/

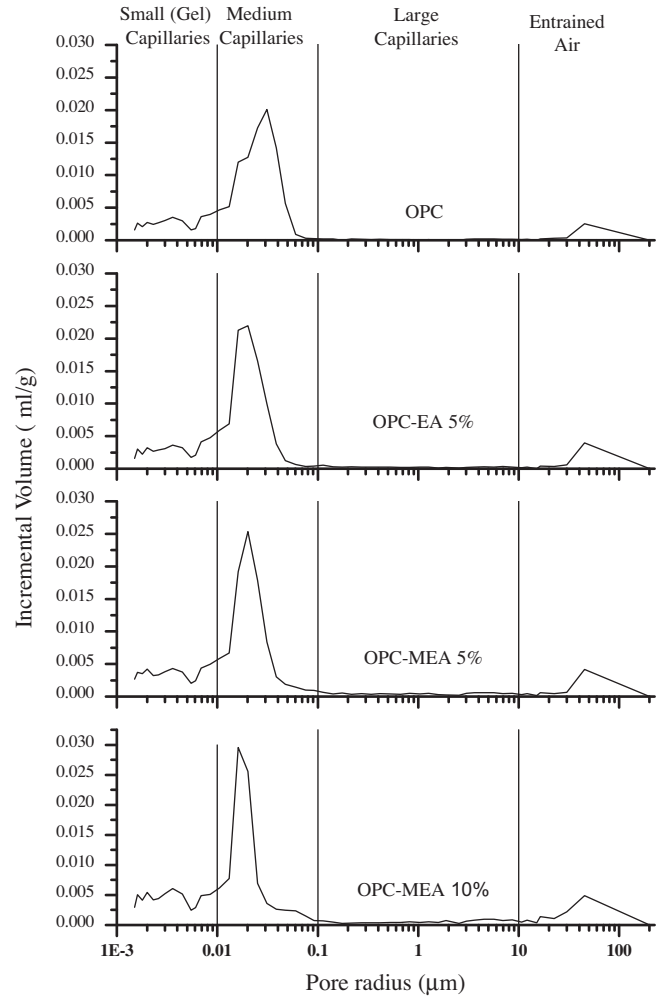


Fig. 6. MIP diagram of the OPC-MEA 10%, OPC-MEA 5%, OPC-EA 5%, and OPC cement paste at W/B = 0.38 after curing for 28 days.

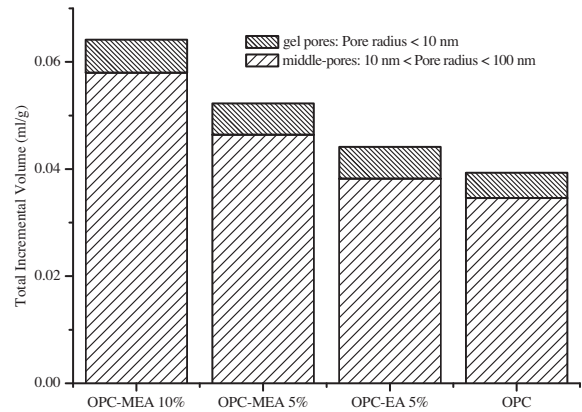


Fig. 7. Total incremental volume of the gel pores and middle pores in different cement pastes with 0.38 of W/B and 28 days of curing time.

B was decreased to 0.29, the setting time became too short and the workability appeared deficient. From the above statement, it can be seen that a substitution ratio of 10% and a W/B of 0.38 led to the highest compressive strength.

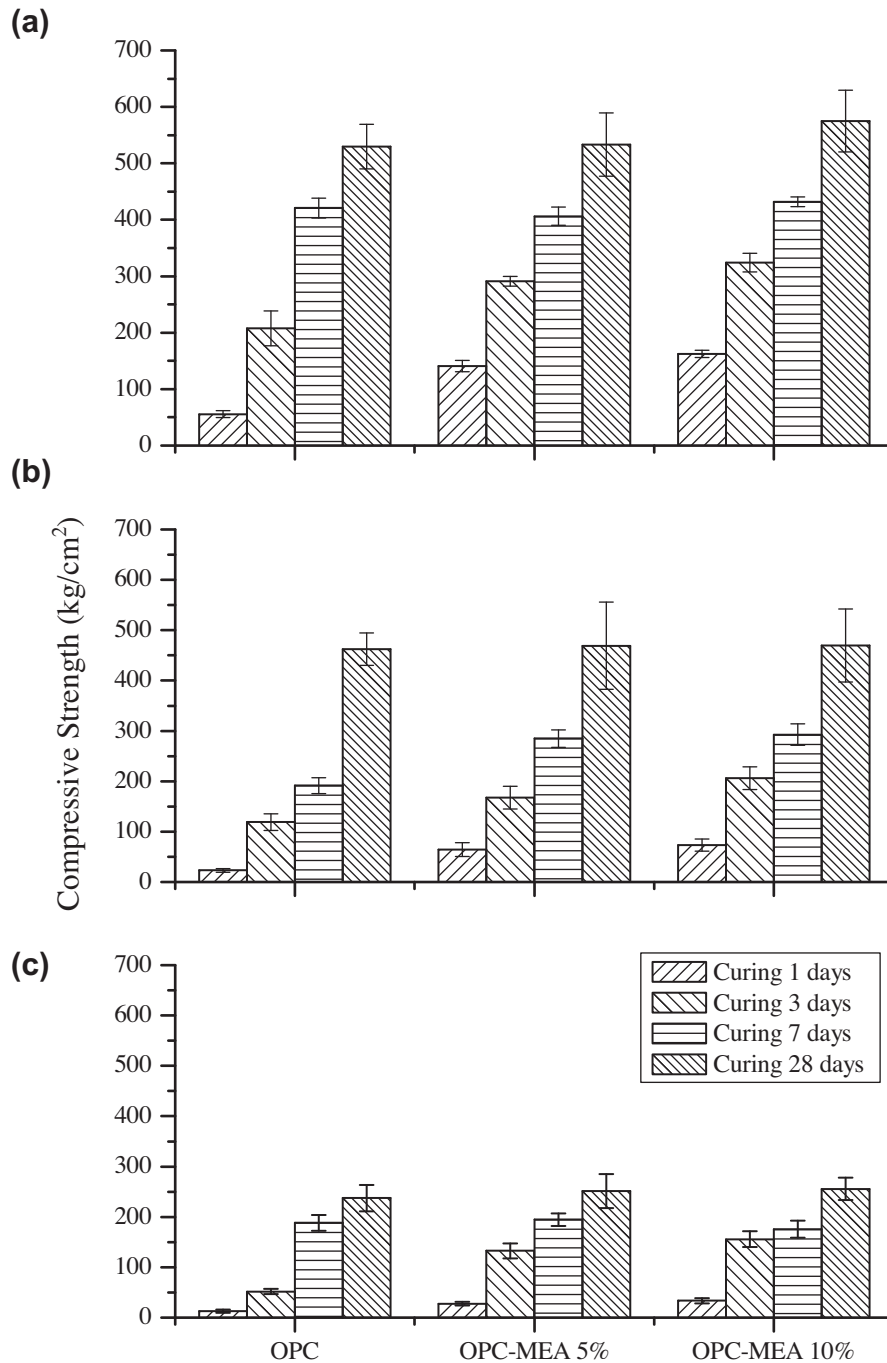


Fig. 8. Compressive strength of different cement pastes and curing days at (a) 0.38 W/B, (b) 0.45, and (c) 0.55.

Table 7
Initial and final setting times for different W/B ratios and substitution ratios.

W/B	OPC		OPC-EA 5%		OPC-MEA 5%		OPC-MEA 10%	
	IST ^a	FST ^b	IST	FST	IST	FST	IST	FST
0.29	211	385	204	340	94	265	ND ^c	ND
0.38	261	375	274	390	126	255	101	170
0.45	365	555	525	700	353	540	220	360
0.55	753	915	778	910	509	695	374	555

^a IST: Initial Setting Time.

^b FST: Final Setting Time, Unit: min.

^c ND: not detectable.

4. Conclusions

The milling process can stabilize the heavy metals present in the MSWI fly ash with the exception of Cr. The milling process decreased the particle size and destroyed the structure of the EA, especially the crystalline texture. After milling for 96 h, the surface morphology of the MEA was like the melting state. The MEA has a higher specific area and smaller particle size that may fill in the cement paste at early ages. The addition of MEA can decrease the Ca(OH)₂ content during the pozzolanic reactions and increase the C–S–H in the cement more than for OPC. The results of NMR and MIP also indicate that the Psi value increased as well as the middle-size and/or gel pores, which improves the densification of the

cement paste. Therefore, the MEA can increase both the hydration and pozzolanic reactions. From the above, we can see that a partial substitution of OPC by MEA should enhance both the early and later compressive strength of the cement paste. In addition, the initial and final setting times would be decreased but are still in the acceptable range.

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