Improving the mechanical characteristics and restraining heavy metal evaporation from sintered municipal solid waste incinerator fly ash by wet milling

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ABSTRACT

The milling process has a verified stabilizing effect on the leaching of heavy metals into the environment from municipal solid waste incinerator (MSWI) fly ash. The aim of this current study is to further improve and confirm the effectiveness of the process by exploring its effects on the evaporation of heavy metals and on the mechanical characteristics of the sintered MSWI fly ash. The chemical composition of the MSWI fly ash is first altered by the addition of water treatment plant sludge (WTS) and cullet, and then processed to produce sintered specimens suitable for reuse as an aggregate. In the experiments, fly ash, WTS and cullet (40%: 30%: 30%, respectively) were mixed and milled for 1 h. Samples were sintered for 60 min at temperatures of 850, 900, 950 and 1000 °C. Test results confirm that milling increased the compressive strength of the sintered specimens. The compressive strength of unmilled specimens sintered at 900 °C was only 90 kg/cm^2, but that of milled specimens was 298 kg/cm^2 when sintered at only 850 °C. There was also an improvement in the soundness ranging from 11.04% to 0.02% and a reduction in the evaporation rates of Pb, Cd, Cu, Cr and Zn from 54–64%, 43–49%, 38–43%, 30–40% and 14–35% (900–1000 °C) to 19–21%, 19–21%, 14–19%, 12–19% and 14–17% (850–1000 °C), respectively. The improvement in compressive strength was attained by the combination in the liquid sintering stage of powdered ash with the amorphous material. The amorphousness of the material also helped to seal the surface of the fly ash, thereby reducing the evaporation of heavy metals during the heating process.

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1. Introduction

In recent years, Taiwan has been actively promoting the recycling of municipal solid waste incinerator (MSWI) fly ash. Sintering technology has been adapted to modify the MSWI fly ash so that it can be recycled as a building material. Parameters of interest in this process generally include sintering temperature, sintering time, compressive force during pellet fabrication and the composition of the material itself. The characteristics of the municipal solid waste (MSW) affect the characteristics of the fly ash so the sintering parameters must be modified accordingly. Another problem that must be considered is the evaporation of heavy metals in the fly ash during the sintering process, especially under higher temperatures.

In past studies of the thermal treatment of MSWI fly ash, the powdered fly ash has been used without any pretreatment. Results

show that when sintering is carried out at 1000 °C, the evaporation rates of Pb, Cd, Cu, and Zn are around 83–95%, 48–95%, 70–80%, and 20–40%, respectively [1–4].

The effects of vitrification treatment (at 1400 °C) on both boiler ash and electrostatic precipitator (ESP) ash have also been investigated [5,6] with an obvious reduction in heavy metal leaching from melted slag after vitrification treatment. Results reveal that the heavy metals stabilized and became fixed in the melted slag. The problem is that the vitrification treatment at 1400 °C tends to cause a large amount of weight loss from the ash. This material loss contributes secondary flue dust particles that could contain volatile elements such as chloride, sulfate, Pb and Cd. Crystallization technology has been combined with vitrification treatment in a two-stage process for the generation of glass–ceramic or brick material from incinerator fly ash [7–9]. In the first stage, vitrification is carried out at 1400–1500 °C to melt the fly ash after which the molten sample is re-crystallized by annealing or sintering at 700–1050 °C. The mechanical properties of glass–ceramic material made from fly ash (such as bending, compressive strength and hardness) are good and the process does inhibit the leaching of heavy

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Table 1
The composition and heavy metal content of the experimental materials.

	Raw[a]	Extracted[b]	WTS[c]	Cullet
Composition (%)				
Ca	32.1 ± 0.75	40.89 ± 1.21	3.78 ± 1.07	6.35 ± 0.25
Si	2.57 ± 0.10	4.95 ± 0.38	26.81 ± 0.92	36.12 ± 1.80
Al	0.44 ± 0.06	0.90 ± 0.07	10.51 ± 0.80	1.55 ± 0.04
Na	3.83 ± 0.21	0.77 ± 0.09	3.13 ± 0.22	5.63 ± 0.15
K	4.44 ± 0.19	0.66 ± 0.04	5.05 ± 0.35	0.97 ± 0.02
Mg	0.72 ± 0.03	1.69 ± 0.06	1.46 ± 0.06	1.55 ± 0.09
Fe	0.40 ± 0.07	0.96 ± 0.05	4.56 ± 0.18	0.75 ± 0.03
Ti	0.09 ± 0.01	0.22 ± 0.01	0.39 ± 0.01	0.04 ± 0.00
Heavy metal content (mg/kg)				
Cd	246 ± 4	521 ± 61	119 ± 39	11 ± 1
Cr	288 ± 72	562 ± 63	184 ± 20	158 ± 3
Cu	1270 ± 80	3250 ± 70	242 ± 36	75 ± 2
Pb	5090 ± 90	5140 ± 220	613 ± 88	23 ± 1
Zn	$10,800 \pm 200$	$29,800 \pm 1500$	150 ± 43	206 ± 6

Mean $\pm$ standard deviation ($n = 3$).

[a] Raw reaction fly ash.
[b] Extracted fly ash.
[c] Water treatment sludge.

metals, however, the energy costs are high. The evaporation rate of heavy metals during the two-stage thermal treatment process itself is problematical as is the formation of secondary flue dust.

Additives can be utilized to affect the flux and reduce the operating temperature which helps to save on energy consumption during the melting and sintering processes. Polettini et al. [10] for example, used feldspar residue and cullet as additives which were mixed with fly ash in order to adjust the composition to the optimal range for sintering. The blend was sintered at 1100 and 1150 °C to obtain specimens with high compressive strength that also satisfied the requirements for the immobilization of some heavy metals although, the evaporation rates of Pb, Cd and Zn were still very high. Zhang et al. [11] used fly ash as an additive for the production of ceramic tile. Although they did not analyze the evaporation of heavy metals during thermal treatment, the compressive strength of sintered specimens did meet the required standard. Furthermore, when 20% fly ash was added before sintering at 960 °C, the leaching of the heavy metals could meet the horizontal vibration extraction procedure (HVEP) standard.

The main factor leading to a large amount of heavy metal evaporation is a high chloride content in the fly ash [1–4]. The presence of chloride and other soluble salts such as sylvite and sodium is also detrimental to the durability of sintered specimens. In short, the chemical composition of the fly ash is one of the critical parameters in sintering technology. Water extraction is a common method for the removal of easily soluble salts which is needed in order to avoid the development of an unstable structure in the sintered specimen [12–14]. However, it is necessary to increase the sintering temperature after water extraction because of the removal of soluble salts such as NaCl and KCl which produce flux that is good for reducing sintering temperature.

According to sintering theory, the smaller the size of the particles the better the sintering action will be [15]. Milling can be used to decrease particle size and to facilitate the mixing process [9–11]. Particle size after milling is determined by sieving [13]. However, in past studies, milling has only been used as a pretreatment prior to sintering. The relationship between variations in particle characteristics and the effects produced by milling on sintering have not been investigated. De Casa et al. [14] did investigate the effects of milling on the physical–mechanical properties of sintered municipal incinerator fly ash processed by washing, dry milling and sintering to manufacture ceramic materials. They found that milling could reduce the firing temperature of milled-washed fly ash from 1210 °C to 1140 °C, as well as facilitate the immobilization of heavy metals. In recent years, milling technology has been used to help stabilize heavy metals in the fly ash. Both dry milling and wet milling can effectively decrease the release of heavy metals. For example, Nomura et al. [16] discovered that the dry milling (with a planetary ball mill) of a mixture of MSWI ash and calcium oxide can reduce heavy metal leaching. In another study they also found that milling could reduce the leaching effects of lead in simulated polluted soil [17]. These two studies are indicative of the potential of the milling technology for stabilizing heavy metals in solid phase materials. Li et al. [18] found that wet milling helped to stabilize Pb in MSWI ash. Sun et al. [19] found that milling increased the stabilization of Pb in a phosphoric acid MSWI fly ash solution.

In the present study, the chemical composition of the samples was adjusted by the addition of water treatment plant sludge (WTS) and cullet to improve the sintering characteristics. Wet milling was used to decrease the particle size and destroy the crystalline structure of the material so as to decrease the sintering temperature, for the manufacture construction materials. The crystalline
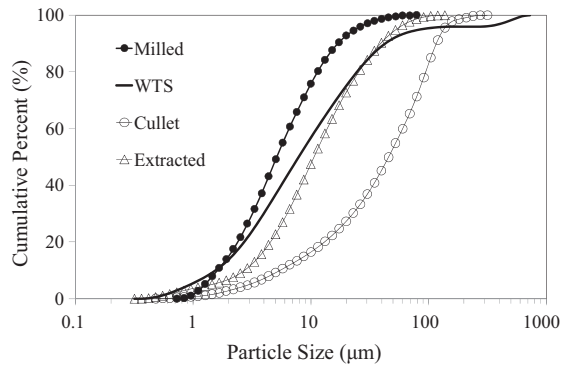
Table 2
The TCLP leaching concentrations of the experimental materials (Unit, mg/L).

	Reaction ash[a]	Extracted ash[b]	WTS[c]	Cullet	Milled ash	Regulation limits
Cd	0.01 ± 0.00	ND	0.02 ± 0.01	ND	0.07 ± 0.01	1
Cr	0.09 ± 0.00	0.16 ± 0.01	3.10 ± 0.01	ND	0.33 ± 0.01	5
Cu	1.49 ± 0.05	0.20 ± 0.19	0.28 ± 0.05	0.01 ± 0.01	0.43 ± 0.01	15
Pb	101.04 ± 1.12	6.85 ± 0.31	1.91 ± 0.61	0.01 ± 0.01	0.09 ± 0.01	5
Zn	3.93 ± 0.04	1.69 ± 0.55	1.72 ± 0.09	0.03 ± 0.02	0.99 ± 0.01	–
Final pH	$12.78 \pm .03$	12.76 ± 0.01	3.65 ± 0.08	7.88 ± 0.08	8.10 ± 0.01	

Mean $\pm$ standard deviation ($n = 3$). ND, not detectable, detection limit Pb = 5ppb, Zn = 0.3ppb, Cu = 0.6ppb, Cd = 0.35ppb, Cr = 0.5ppb.

[a] Raw reaction fly ash.
[b] Water-extracted fly ash.
[c] Water treatment sludge.

Fig. 1. Cumulative curve showing results for experimental materials and milled powder (milled: milled mixed fly ash; WTS: water treatment sludge; extracted: water-extracted fly ash).

structure, microstructure, heavy metal leaching and evaporation, and mechanical characteristics of the sintered specimens were studied in order to understand the effects of the recycling process and to explore the mechanism of heavy metal stabilization.

2. Materials and methods

2.1. Experimental materials

Fly ash was collected from a large MSW incineration plant in northern Taiwan. On average, 1350 metric tons are disposed of each day by this plant. Fly ash is generally comprised of boiler ash, cyclone ash or reaction ash depending on the air pollution control devices (APCD) position. Reaction ash sampled from the fabric baghouse filter behind the semi-dry scrubber system was used in these experiments.

The composition of the fly ash was adjusted by the addition of WTS and cullet. The WTS was collected from a water treatment plant, also in northern Taiwan. The sludge generation process included thickening and dewatering to form sludge cakes which were sun-dried in a field. The sludge cakes were then crumbled, dried and stored for future use. The cullet powder was produced from achromatic, transparent glass vessels which had been soaked in a strong nitric acid solution, washed in de-ionized water, broken into pieces, and finally crushed in a jaw crusher. The pieces were gathered and sifted through a No. 150 screen sieve.

2.2. Experimental methodology

The fly ash was extracted with deionized water before the addition of the WTS and the cullet. For a description of the process refer to Chuang [20]. The process was carried out twice, with a liquid to solid ratio of 5 and an extraction time of 5 min. After the water extraction process the fly ash becomes extracted fly ash. The ratios of extracted fly ash, WTS and cullet in the mixture were 40%, 30% and 30%, respectively [21]. The mixed ingredient is called the mixed fly ash.
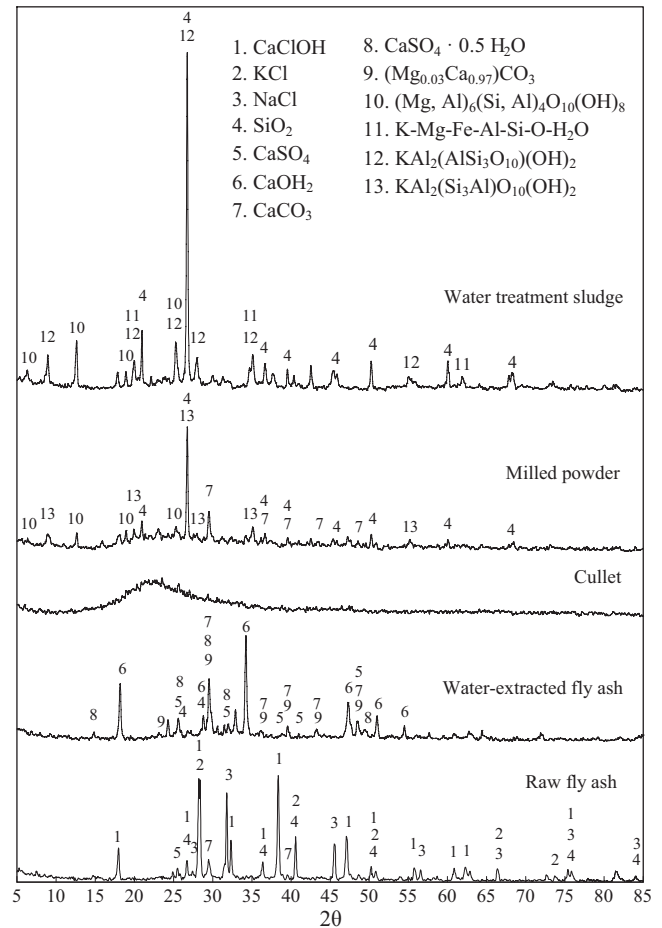

Fig. 2. XRD patterns for water-extracted fly ash, water treatment sludge, cullet and milled blend.

The liquid to solid ratio during the wet milling of the mixed fly ash was 9, the rotational speed was 93 rpm and the milling time was 1 h; for further details please refer to Li et al. [18]. After milling, the thick mixed fly ash liquid was filtered, then dried and pelleted at 34,474 kPa (5000 psi). The pellets were cylindrical in shape with a diameter of 20.5 mm and about 22.0–27.7 mm high. An electro-thermal rectangular furnace was used in the experiments. The heating rate was 20 °C/min. The sintering times for specimens processed without and with milling were 900, 950 and 1000 °C and 850, 900, 950 and 1000 °C, respectively. The sintering time was 1 h.

The evaporation rate of heavy metals during the sintering process can be calculated using the formula below

$$E(\%) = \frac{(W_1 \times C_1) - (W_2 \times C_2)}{W_1 \times C_1} \times 100\% \quad (1)$$

where E (%) is the evaporation rate; W_1 (kg) is the weight of the specimen before sintering; W_2 (kg) is the weight of the specimen after sintering; C_1 (mg/kg) is the concentration in the specimen

Table 3
Heavy metal concentration of the milling solution (Unit: mg/L).

Elements	1 h of milling time	96 h of milling time
Pb	2.86 ± 0.03	0.05 ± 0.01
Zn	2.07 ± 0.05	0.06 ± 0.01
Cd	0.05 ± 0.01	0.01 ± 0.00
Cu	0.02 ± 0.01	0.07 ± 0.01
Cr	0.04 ± 0.01	0.01 ± 0.00

Ave ± SD sample number: 3.

Table 4
Heavy metal content in the experimental samples (Unit: mg/kg).

Elements	Before milling	After 1 h of milling
Pb	1100 ± 41	1100 ± 76
Zn	7400 ± 260	8100 ± 430
Cd	74 ± 0.95	93 ± 5.4
Cu	590 ± 15	590 ± 26
Cr	260 ± 9.3	260 ± 28

Ave ± SD sample number: 3.

Table 5
The TCLP results of the sintered specimens for different sintering temperatures with and without milling (Unit, mg/L).

Element	850 °C	900 °C		950 °C		1000 °C		Regulation limits
	With milling	Without milling	With milling	Without milling	With milling	Without milling	With milling	
Cd	0.14 ± 0.01	0.27 ± 0.01	0.13 ± 0.01	0.47 ± 0.02	0.13 ± 0.01	0.95 ± 0.03	0.10 ± 0.01	1
Cr	0.80 ± 0.00	0.76 ± 0.03	0.57 ± 0.00	0.48 ± 0.01	0.55 ± 0.03	0.49 ± 0.01	0.32 ± 0.06	5
Cu	0.16 ± 0.00	0.10 ± 0.00	0.26 ± 0.00	0.14 ± 0.01	0.25 ± 0.03	0.17 ± 0.00	0.19 ± 0.00	15
Pb	0.39 ± 0.00	0.11 ± 0.01	0.38 ± 0.00	0.22 ± 0.02	0.37 ± 0.02	0.24 ± 0.03	0.34 ± 0.03	5
Zn	1.36 ± 0.06	1.82 ± 0.01	1.23 ± 0.00	1.49 ± 0.07	1.21 ± 0.01	1.63 ± 0.19	1.13 ± 0.21	–
pH	5.07 ± 0.01	5.40 ± 0.02	4.81 ± 0.02	5.21 ± 0.02	4.70 ± 0.01	4.94 ± 0.02	4.43 ± 0.02	–

Mean ± standard deviation ($n = 3$), ND, not detectable, detection limit Pb = 5ppb, Zn = 0.3ppb, Cu = 0.6ppb, Cd = 0.35ppb, Cr = 0.5ppb.

before sintering; C_2 (mg/kg) is the concentration in the specimen after sintering.

2.3. Analysis

The size of the particles was analyzed with a laser particle size analyzer (Honeywell Microtrac X-100). The leaching concentration of heavy metals was extracted using the toxicity characteristic leaching procedure (TCLP) USEPA method 1311. After digestion of the samples using the alkali fusion method, the heavy metal content and chemical composition were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; JOBINYVON JORIBA, Ultima-2000). X-ray diffraction (XRD; Bruker D8A) was used to identify the crystallographic structure of the fly ash during the different stages. The microstructure of the surface of the fly ash particles was observed by scanning electron microscopy (SEM; Leo 1530). The water absorption rate, soundness test, and compressive strength of the sintered specimens were analyzed by the CNS 488, CNS 1167 and NIEA R206.20T methods, respectively.

3. Results and discussions

3.1. Characteristics of the material

Details about the composition of the materials are shown in Table 1. The largest elementary component in the reaction fly ash is calcium (Ca) followed by are potassium (K) and sodium (Na). A water extraction process was used to remove soluble salts such as KCl and NaCl from the MSWI fly ash, which could be helpful in long-term stabilization of the structure of the sintered specimens but also caused the ratio of some elements in the fly ash to increase. For example, the Ca content reached 40%. The change in the composition of the extracted fly ash necessitates the raising of the sintering temperature to obtain specimens with the same mechanical characteristics. The sintering temperature can be reduced by adjusting the composition of the fly ash, with the addition of cullet and WTS. Since the major elements in the cullet and the WTS are silicon and aluminum they can increase the Si and Al concentration and decrease the Ca concentration for suitable sintering of the material.
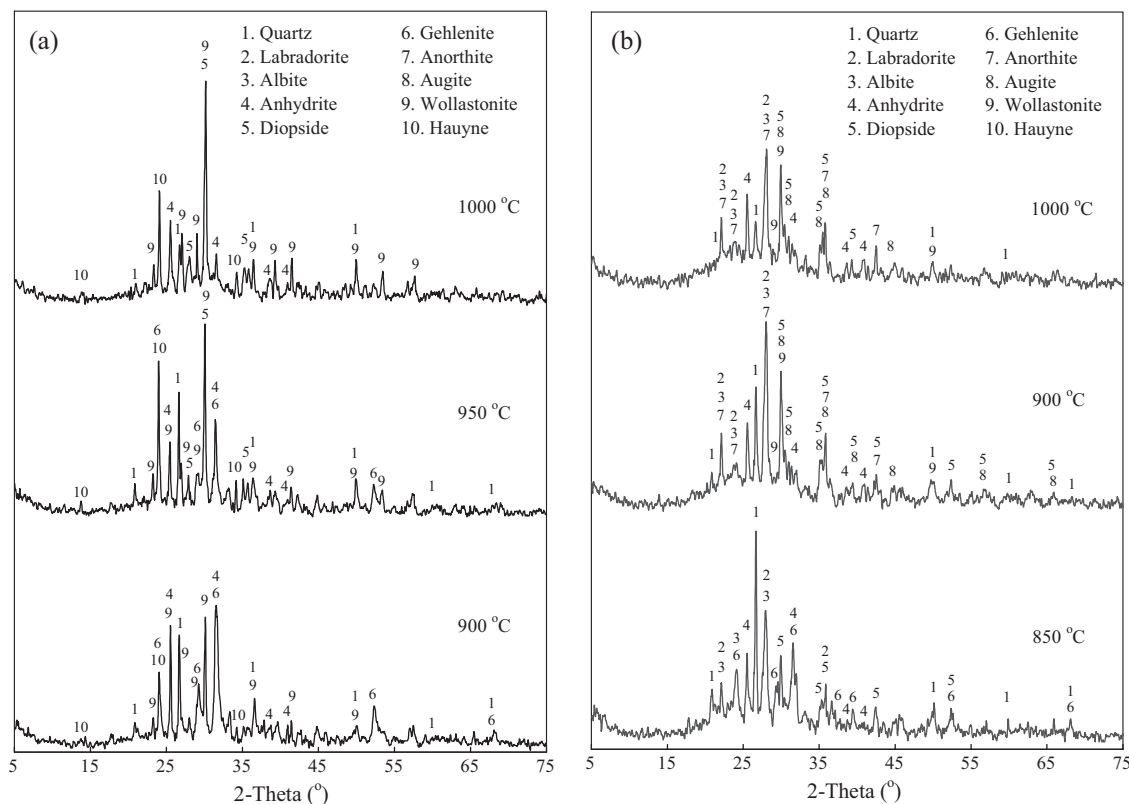

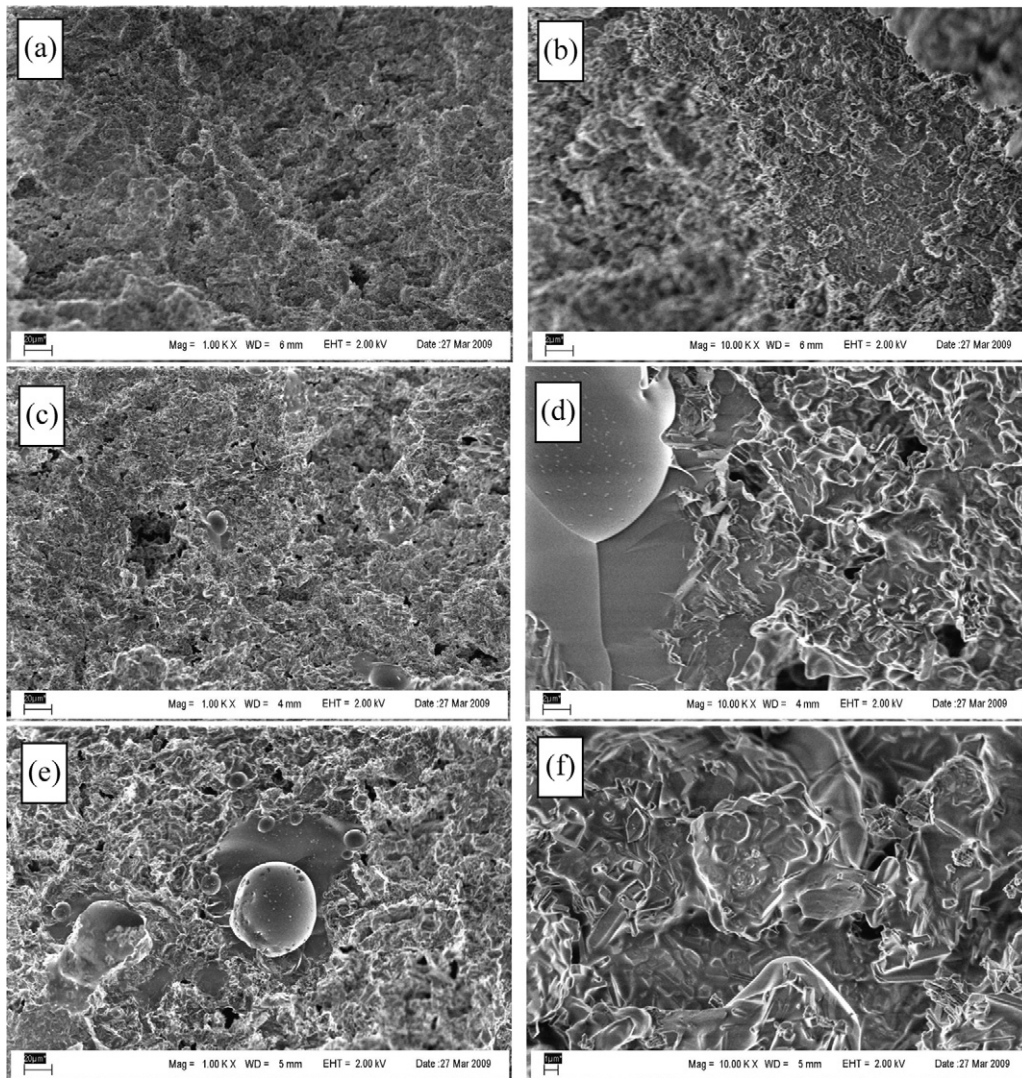**Fig. 3.** XRD patterns for sintered specimens: (a) without milling; (b) with milling.

Fig. 4. SEM observations of sintered specimens without milling treatment: (a) 900 °C, 1 k×; (b) 900 °C, 10 k×; (c) 950 °C, 1 k×; (d) 950 °C, 10 k×; (e) 1000 °C, 1 k×; (f) 1000 °C, 10 k×.

The TCLP concentrations of the three materials are shown in Table 2. Water extraction has removed some of the easily releasable Pb from the fly ash, which causes a steep decrease in the leaching concentration from 101.04 to 6.85 mg/L. However, this leaching concentration still does not conform to Taiwan's regulatory limits (5 mg/L). Further treatment of the fly ash for stabilization of the Pb is thus necessary. The leaching concentrations of heavy metals from the cullet and the WTS all do fall within the regulatory limits.

3.2. Change in the characteristics after milling

The cumulative curves of the particle size for the extracted fly ash, cullet, WTS and milled mixed fly ash are shown in Fig. 1. The d_{50} of the extracted fly ash, WTS and cullet are 10.65, 7.87 and 45.84 μm, respectively. The extracted fly ash and WTS can be classified as fine powders. After 1 h of milling, the d_{50} of the mixed fly ash decreases to 5.11 μm. Smaller sized particles have higher surface energies which affects the heat needed for sintering. The milling process has the benefit of making the size of the mixed fly ash particles uniform thereby helping to produce stable sintered specimens.

The XRD spectra of the reaction fly ash, extracted fly ash, cullet, WTS and milled mixed fly ash are shown in Fig. 2. The main compounds in the reaction fly ash are CaClOH, $CaSO_4$, KCl, NaCl and SiO_2. After water extraction, the CaClOH, NaCl and KCl became dissociated so that the chlorine (Cl), sodium (Na), potassium (P) and some of the calcium (Ca) can be extracted into the solution. The rest of the calcium combines with carbonates or hydroxyls to form calcium carbonate or calcium hydroxide which then precipitates. The lower solubility of $CaSO_4$ makes water extraction difficult which is why it can be identified in the extracted fly ash. The main mineral found in the WTS is quartz. The extraordinarily obvious main peak in the XRD spectrum is indicative of the crystalline phase. The other main minerals, mica, chlorite and serpentine, are silicate minerals, commonly found in Taiwan. Examination of the cullet spectrum shows no obvious peak, but rather the gently rising curve typical of the XRD spectra of amorphous material. Comparison of the three materials shows no identifiable compounds in the XRD spectra of the milled mixed fly ash. The identifiable compounds are calcium carbonate from the extracted fly ash, mica from the water treatment plant sludge, and mineral quartz from both the extracted fly ash and the WTS. However, after milling the mixed fly ash for 1 h, the height of all of the peaks decreased. For example, the peak for
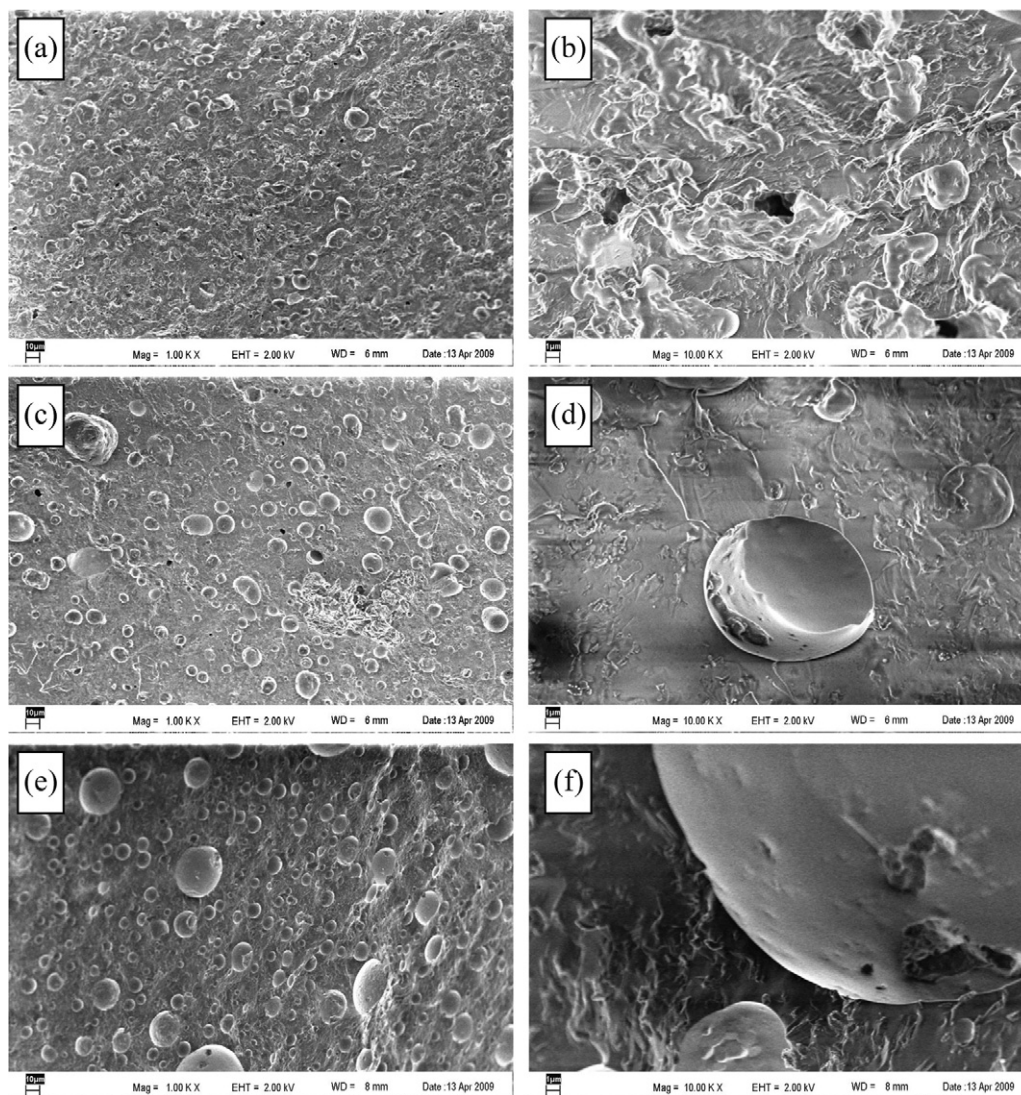
Fig. 5. SEM observations of sintered specimens with milling treatment: (a) 900 °C, 1 k×; (b) 900 °C, 10 k×; (c) 950 °C, 1 k×; (d) 950 °C, 10 k×; (e) 1000 °C, 1 k×; (f) 1000 °C, 10 k×.

quartz in $2\theta = 26.7$ decreased 40% after 1 h of milling. Clearly, the mechanical energy from the milling was not sufficient to allow the formation of new compounds, but did increase the surface energy of the particles which acted to increase defects in the crystalline structure, which in turn allowed for a decrease in the energy required for sintering and led to the easier formation of different compounds after sintering.

Table 3 shows the concentration of the heavy metals in the milling solution. The results indicate that the concentration of heavy metals decreased to less than 2.86 mg/L and 0.07 mg/L after 1 h and 96 h of milling time, respectively. It can be seen that little heavy metal leached into the milling solution. Table 4 shows an increase in the concentration of the heavy metals in the milled fly ash, because of the dissolution of some materials into the milling solution. The TCLP concentration of Pb in the fly ash could be reduced by milling, as shown in Table 2. This result has been described in previous studies [18,19]. In this study, it is found that the TCLP concentrations of heavy metals, with the exception of Cu, were less than one tenth the regulatory limits, as shown in Table 2. This confirms that the milling process is an effective method for stabilizing Pb, Cr, and Zn present in the fly ash.

3.3. Crystalline phase and microstructure of the sintered specimens

XRD patterns of sintered specimens produced with and without milling are shown in Fig. 3. The intensity of the XRD patterns of the quartz crystal decrease with increasing sintering temperature. After sintering at 900 °C and 1000 °C, the main peaks were from 153 to 88 without milling and from 124 to 78 with milling, respectively. At a high sintering temperature, the quartz will react with other elements (such as Ca and Si) to produce other minerals, as indicated by the lessening of the main quartz peak. Wollastonite, a calcium inosilicate mineral, and diopside, a monoclinic pyroxene mineral were the major minerals that formed in the specimens without milling. All of these materials have a simple chain-like structure, as shown in Fig. 3a. The next most common mineral to form from the Na, Al and Ca was hauyne, of the tectosilicates, and gehlenite, of the sorosilicates. In milled specimens sintered at temperatures above 900 °C, we see the formation of albite, anorthite and labradorite of the feldspar group of tectosilicates (see Fig. 3b) followed by augite and diopside of the inosilicate group.
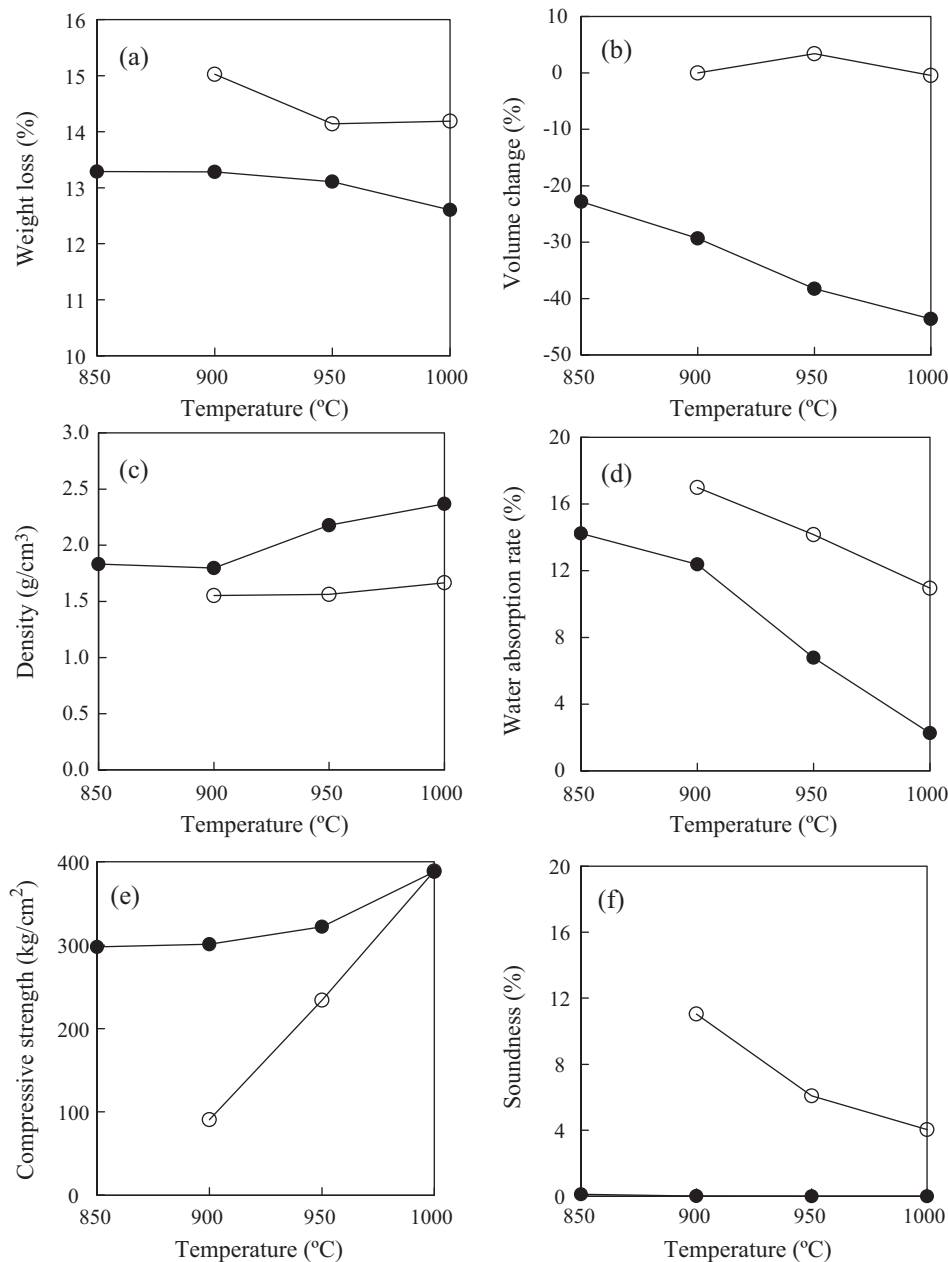
Fig. 6. The physical and mechanical properties of sintered specimens produced with and without milling treatment, where hollow circles indicate non-milled, full circles indicate milled: (a) weight loss; (b) volume change; (c) density; (d) water absorption rate; (e) compressive strength; (f) soundness.

In other words, the milling process affected the type and hardness of the material that formed in the sintered specimens. All of the aforementioned minerals are important rock-forming silicate minerals. Albite, labradorite and anorthite belong to the tectosilicate group, having a hardness rating of between 6 and 6.5, comprising the most important rock-forming minerals on earth. The hardness of the augite and dispside ranges from 5 to 6 and that of the wollastonite from 4.5 to 5. Fig. 3 shows that, with suitable adjustment, milling and sintering could produce mineral substances with the potential to form specimens with high compressive strength.

SEM examination of the microstructure of the sintered specimens shows an obvious difference between those produced with and without milling, for a variety of sintering temperatures (Figs. 4 and 5). Fig. 4 shows the microstructure of sintered specimens produced without milling. At magnifications of 1 k and 10 k,

the temperature effect is obvious. At a sintering temperature of 900 °C, the particles in the mixed fly ash are basically pushed together, not displaying the characteristics of the sintered state. In the specimens sintered at 950 °C (Fig. 4c), it can be seen that the particles have gradually become connected and bound together, but that pores still exist inside the specimens. Multiple zoom images of the specimens shown in Fig. 4d confirm the appearance of the liquid sintering state in some places and some imprinted crystalline shapes on the fractured particle surfaces, indicative of the generation of some crystals at this temperature. When the sintering temperature is 1000 °C, the liquid sintering state around the powdered particles grows to form larger particles, although there are still some pores between these large particles. Fig. 5 shows the microstructure of the milled and sintered specimens. It is very clear that liquid sintering has occurred. The fractured particle surfaces
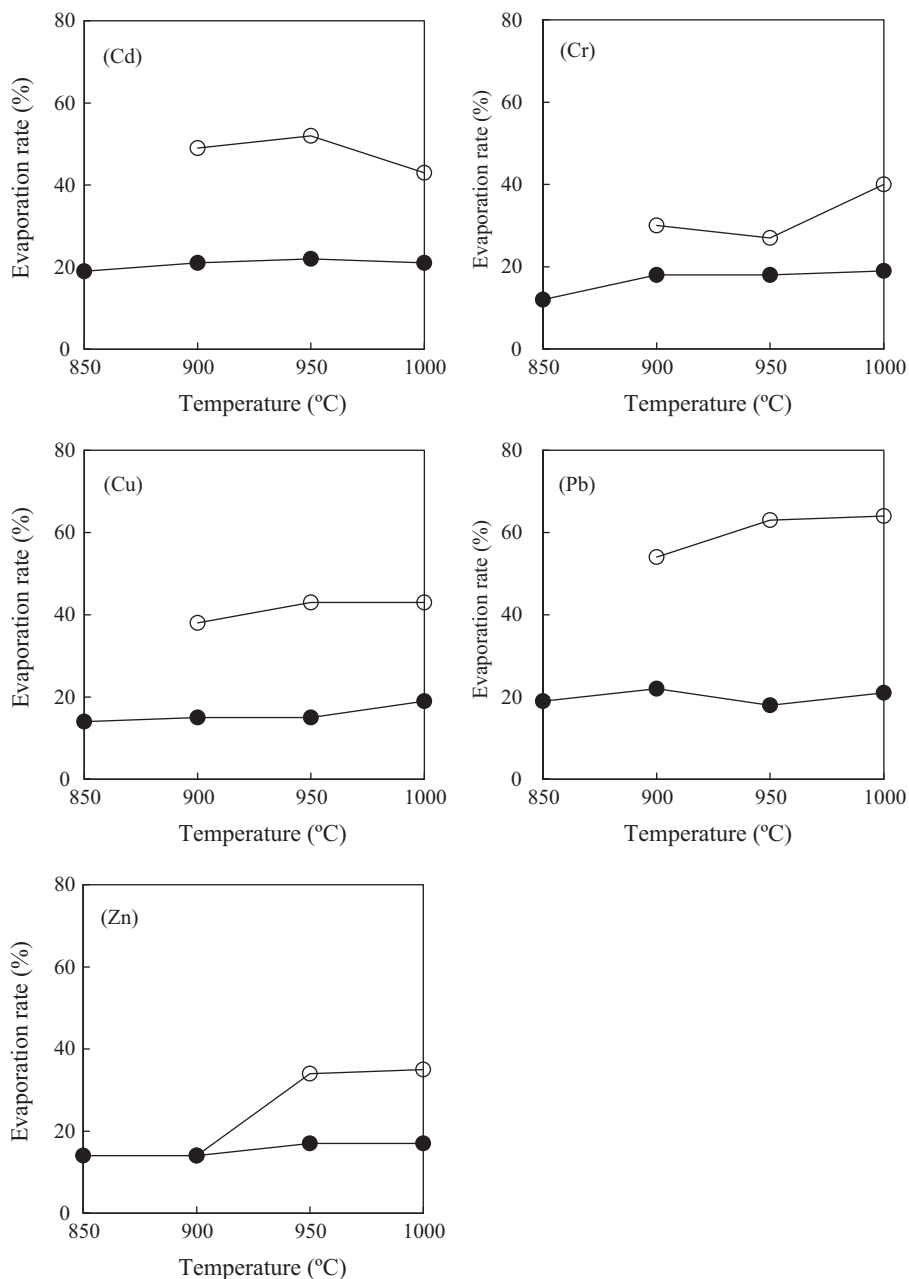
Fig. 7. Evaporation rate of heavy metals from sintered specimens produced with and without milling treatment where hollow circles indicate non-milled and full circles indicate milled.

are smoother than was the case without milling (Fig. 5a). It can be seen in Fig. 5b that the particles have moved together and are covered with amorphous material. In this liquid sintering stage, it is not easy to discriminate between single particles. This does not mean that all the particles have become completely amorphous; it simply shows that the space between the particles is now filled with amorphous material. Surface fracturing always occurs where particles in the specimen are cracked by force. When the sintering temperature reaches 950 °C and 1000 °C, the amount and dimensions of the amorphous material and closed pores in the specimens will increase.

Comparison of specimens produced with and without milling shows that the milling process can increase the quantity of amorphous material during sintering. This occurs because of the destruction of particles in the powder allowing for redistribution of the crystalline structure [18]. Milling reduces the elementary binding forces and increases the surface energy of the particles, which tends to increase the formation of amorphous material at lower temperatures, and enhance the mechanical characteristics of the sintered specimens. This contributes to the early formation of more complex structures (e.g., tectosilicates), as shown in the XRD patterns discussed above. In other words, a suitable amount of amorphous material is helpful for the formation of suitable sintered specimens, however, if the amount of amorphous material is too great, the strength of the specimen is insufficient and the original shape of the sintered specimen will collapse. In this study, when the sintering temperature reaches 1050 °C, the milled and sintered specimen are not no longer cylindrical in shape.

3.4. Effect of milling on the sintered specimens

The characteristics of the sintered specimens are shown in Fig. 6. The weight loss of sintered specimens, with and without milling was 13% and 14–15%, respectively (see Fig. 6a). The data show the weight loss to be very similar possibly due to the decomposition of some of the calcium carbonate and calcium hydroxide in the extracted fly ash at high sintering temperatures (see Fig. 2). The shrinkage of the milled specimens increased considerably when the sintering temperature reached 1000 °C (see Fig. 6b). When the temperature rose to 1050 °C, the shape of the milled sintered specimens collapsed. In Fig. 5, it can be seen that the amount of amorphous material increases with the temperature, indicating that a surfeit of liquid phase material would be harmful for recycling. The amorphous material eliminates open pores between the particles in the milled and sintered specimen. Thus, the density increases and the water absorption rate decreases with an increase in temperature as well (see Fig. 6c and d).

The compressive strength is an important factor affecting the mechanical characteristics of sintered specimens. As shown in Fig. 6e, the compressive strength of specimens produced without milling and sintered at 900 °C is less than 100 kg/cm^2. The compressive strength increases with the sintering temperature, reaching 389 kg/cm^2 (38.2 MPa) when the temperature reaches 1000 °C. However, if the powder is treated by milling, the compressive strength rises to 300 kg/cm^2 (29.4 MPa) at 850 °C, and 389 kg/cm^2 at 1000 °C. Comparison of the results shows that milling can help to produce suitable specimens at lower sintering temperatures. The formation of complex tectosilicates and amorphous material are the main factors leading to the increased compressive strength, firmly binding the particles together; see Figs. 3 and 5. Clearly, milling can improve the soundness of sintered specimens, as shown in Fig. 6f.

Table 5 shows the TCLP leaching concentrations of sintered specimens produced with and without milling as well as the pH of the final extraction solution. The pH decreases with both sintering temperature and milling. The TCLP leaching concentrations of Cd, Cu, and Pb increase slightly with increased temperature in the specimens produced without milling. However, in the milled specimens, the amount decreases slightly with increased temperature, although in all cases, amounts are lower than the regulatory limits. The pH ranges between 4.43 and 5.40, an interval where heavy metals are easily released, but the TCLP concentrations of all the sintered specimens (especially the milled specimens) fall within the regulatory limits.

3.5. Restraining heavy metal evaporated by milling

As noted above, the evaporation of heavy metals is affected by the composition of the fly ash. For example, chlorides combine easily with heavy metals during the sintering process, which could lead to an increase in their evaporation rate. Water extraction is an efficient method to remove these chlorides from the fly ash. However, the main chloride compounds, KCl and NaCl, also produce good flux during sintering, which could improve the sintering characteristics. How to restrain heavy metal evaporation from the fly ash during sintering or other types of thermo-treatment while keeping the temperature as low as possible is an important question.

Fig. 7 shows the evaporation rates of the heavy metals, Cd, Cr, Cu, Pb and Zn, from sintered specimens, fabricated with and without milling. For specimens sintered at 900–1000 °C without milling, the evaporation rates of Pb, Cd, Cu, Cr and Zn are 54–64%, 43–49%, 38–43%, 30–40% and 14–35%, respectively. The specimens in these experiments were produced through a pelleting process, so the evaporation rate was lower than that of powdered fly ash without pelleting. The demands for the compressive strength and heavy

metal evaporation are often in conflict. For example, although increasing the sintering temperature will improve the compressive strength, the heavy metal evaporation rate will also increase, which raises the environmental risk of secondary pollution by heavy metals. On the other hand, although a lower sintering temperature can reduce the evaporation rate of the heavy metals, the mechanical characteristics of the sintered specimens might not meet the standards required for recycled building materials. In this respect, our results show the heavy metal evaporation rate of sintered specimens produced with milling to be better than those produced without. For example, after sintering at 850–1000 °C, the evaporation rates of Pb, Cd, Cu, Cr and Zn are 19–21%, 19–21%, 14–19%, 12–19% and 14–17%, respectively. Obviously, the addition of milling to the recycling process could efficiently reduce the evaporation of heavy metals from the specimens. When the sintering temperature reached 1000 °C, there was a decrease in the amount of Pb, Cd, Cu, Cr and Zn evaporation of 43%, 22%, 24%, 21% and 18%, respectively. In this study, it is found that the liquid phase in milled and sintered specimens was generated at 900 °C (see Fig. 5). At this time, the surface of the fly ash powder was covered by amorphous material, sealing the heavy metals within the samples. The evaporation rate of the milled sintered specimens increased little with the sintering temperature, as shown in Fig. 7. This reveals that the amorphous material helped to seal the heavy metals within the sintered specimens, and was not affected by the sintering temperature. Therefore, the milling process can effectively restrain heavy metal evaporation during sintering.

4. Conclusions

The milling process acts to destroy crystalline structures in the fly ash. Compounds recombine to form new ones during the sintering process, as evidenced by the formation of the tectosilicates, albite, labradorite and anorthite in the experiments. Such compounds offer a structural foundation to the sintered specimens. Our experimental results show that amorphous materials are more easily generated at lower temperatures during the liquid sintering stage in milled sintered specimens than in specimens produced without milling. The amorphous material helps to combine the particles in the fly ash together which affects the mechanical characteristics of the sintered specimens, leading to increased compressive strength, soundness, density, and shrinkage, and decreased water adsorption rate and weight loss. If the material generated is sufficient to cover the surfaces of the particles, it can also restrain the evaporation of heavy metals from the fly ash during the heating process. Therefore, the milling process can help to stabilize heavy metals in the fly ash, improve the compressive strength, and restrain heavy metal evaporation from sintered specimens.

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