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Restrain the Evaporation of Heavy Metals during Sintering of MSWI Fly Ash by Milling with Proper Additives

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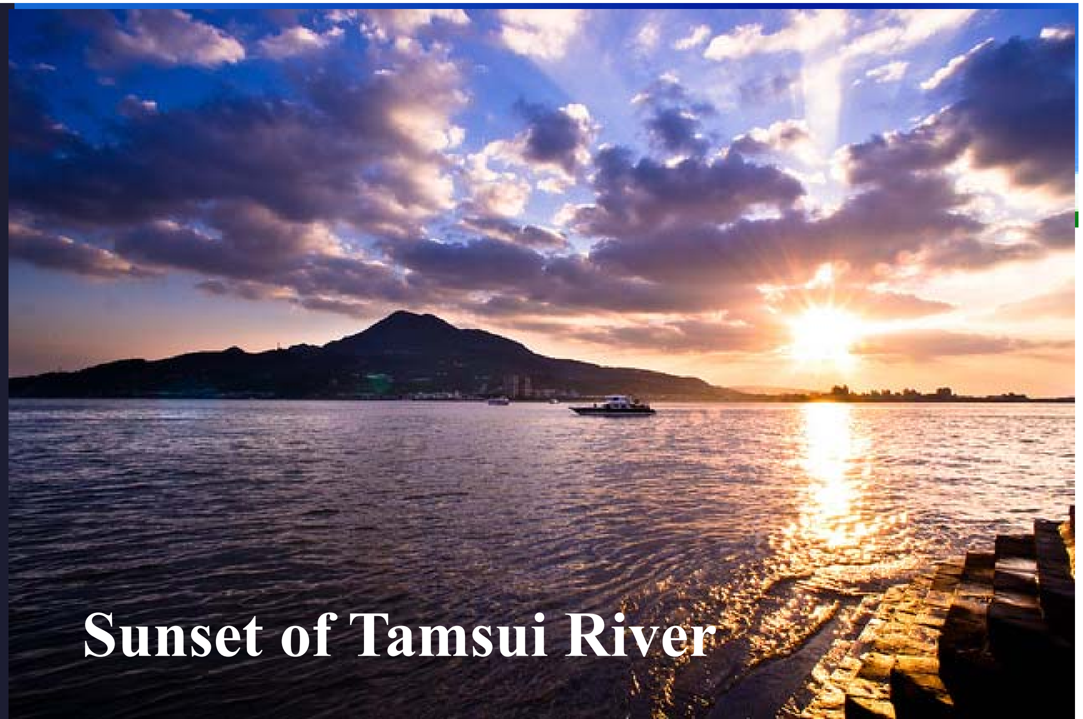

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Outline

1 Introduction

2 Literature Review

3 Methods

4 Results and Discussion

5 Conclusions

Introduction

Introduction

- Taiwan has been actively promoting the recycling of municipal solid waste during past 20 years.
- At present, the recovery of MSW has exceeded 60%.
- The diverted MSW is 95% treated by incineration.
- 70% of the bottom ash is recovered, 30% is landfilling.
- Most of the fly ash is solidified or stabilized followed by designated landfilling (similar to secured landfill).

Introduction

- In recent years, Taiwan has been actively promoting the recycling of municipal solid waste incinerator (MSWI) fly ash, in order to compliance with the policy of zero waste or zero landfill.
- Some of the fly ash is recovered as the cement kiln feedstock after washing, but the heavy metals, especially for Pb, will be evaporated totally during the high temperature in the kiln, they don’t have any mechanism of treatment or stabilization.

Introduction

- Sintering technology has been adapted to modify the MSWI fly ash, it is not so high temperature as cement kiln, the product can be recycled as building material.
- Parameters should be considered in this process generally include sintering temperature, sintering time, compressive strength during the pellet molding and the proper composition of the material itself.

Introduction

- The characteristics of the municipal solid waste (MSW) affect the characteristics of the fly ash, it is not suitable for sintering directly, so the sintering parameters must be modified.
- Another problem that must be considered is the evaporation of heavy metals in the fly ash during the sintering process, especially for Pb under higher temperatures.

Literature Review

Literature Review – evaporation of heavy metals

- In past studies, MSWI fly ash has been used without any pretreatment. When sintering at 1,000 ^{o}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 1,400 ^{O}C) with an obvious reduction in heavy metal leaching from melted slag. Nevertheless, vitrification cause a large amount of weight loss, it contributes secondary flue dust contain volatile elements such as chloride, sulfate, Pb and Cd.

Literature Review – additives

- Additives can reduce the operating temperature which helps to save on energy consumption. Polettini et al. used feldspar residue and cullet as additives mixed with fly ash, sintered at 1,100 and 1,150 ^{o}C obtained specimens with high compressive strength that immobilized some heavy metals, but the evaporation rates of Pb, Cd and Zn were very high.
- Zhang et al. used fly ash as an additive for the production of ceramic tile. the compressive strength met the standard, when 20% fly ash was added and sintering at 960 ^{o}C, the leaching of the heavy metals could meet the standard of TCLP.

Literature Review – milling

- Recently, milling has been used in many studies to stabilize heavy metals in the fly ash. Both dry milling and wet milling can effectively decrease the release of heavy metals.
- Nomura et al. found that the dry milling of a mixture of MSWI ash with calcium oxide reduced heavy metal leaching.
- Li et al. found that wet milling helped to stabilize Pb in MSWI ash, Sun et al. found that milling increased the stabilization of Pb of MSWI fly ash in a phosphoric acid solution.

Methods

Methods-materials

- Fly ash was collected from a 1,350 ton/d MSW mechanical grate incinerator operated around 950 ^{o}C, with semi-dry and bag-filter system.
- The fly ash was adjusted by water treatment sludge (WTS) and cullet.
- WTS was collected from a water treatment plant in northern Taiwan.
- The cullet was collected from waste clear glass vessels in the lab, washed and crushed in a jaw crusher and sieved through No. 150 mesh.

Methods-milling

- Water extraction was carried out twice with a liquid to solid ratio 5 for 5 minutes.
- Conventional ball-milling machine were used, the liquid to solid ratio was 9 during the milling of the mixed ash, the ball miller were operated at 93 rpm for 1 h.

Methods- Adjustment condition

WFA[1] (%)	WTS[2] (%)	Cullet (%)	Identification code
80	10	10	811
60	20	20	622
40	40	20	442
40	30	30	433
40	20	40	424
30	30	40	334
30	60	10	361
20	40	40	244

[1]washed fly ash. [2]water treatment sludge.

Methods-
pelletized and sintering

- After milling, the liquid was filtered, then dried and pressed at 34,474 kPa (5,000 psi), to form a cylindrical shape pellet with diameter of 20.5 mm and 22.0-27.7 mm high.
- An electro-thermal rectangular oven was used in the experiments. The temperature programming were 20^{o}C/min, and the sintering time 1 h. The sintering temperature of the pellets processed without and with milling were 900, 950 and 1,000 ^{o}C and 850, 900, 950 and 1,000 ^{o}C, respectively.

Methods- evaporation rate

- The evaporation rate of heavy metals during the sintering process were calculated as below
- $$E\,(\%) = \frac{(W_1 \times C_1) - (W_2 \times C_2)}{W_1 \times C_1} \times 100\% \qquad (1)$$

E (%): evaporation rate;

W_1(kg): weight of the specimen before sintering;

W_2(kg): weight of the specimen after sintering;

C_1(mg/kg): concentration in the specimen before sintering;

C_2(mg/kg): concentration in the specimen after sintering.

Methods-analysis

- Particles size distribution of fly ash was analyzed with a laser particle size analyzer (Honeywell Microtrac X-100).
- Leaching concentration of heavy metals was extracted using the toxicity characteristic leaching procedure (TCLP) USEPA method 1311.
- Samples digestion using the alkaline fusion method,
- Heavy metals and chemical composition were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES; JOBINYVON JORIBA, Ultima-2000).

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Methods-analysis

- X-ray diffraction (XRD; Bruker D8A) were used to identify the crystallographic structure during the different stages.
- The microstructure of the surface of the samples were 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.
- Soundness test (weathering)：Immerse the sintering samples in saturated solution of sodium sulfate 16-18 h, and then drying, repeat the cycles of immersion and drying(5 times). The final weight loss should not greater than 12 %.

Results and Discussion

Table 1 The element composition of washed fly ash

element		WFA
Al		0.90±0.07
Ca		40.89±1.21
Fe		0.96±0.05
K		0.66±0.04
Mg		1.69±0.06
Na		0.77±0.09
Si		4.95±0.38
Ti		0.22±0.01
ave±SD, Sample number：3, unit：wt%		

Table 2 The heavy metals content of WFA

element		WFA
Cd		521.2±60.7
Cr		561.5±63.2
Cu		3,251±67.9
Pb		5,136±223
Zn		29,772±1,524
ave±SD, Sample number：3, unit：mg/kg		

Table 3 The TCLP leaching concentration of WFA

element	Leaching concentration	Regulation Limits of hazardous waste
Cd	ND	1
Cr	0.16±0.01	5
Cu	0.20±0.19	15
Pb	6.85±0.31	5
Zn	1.69±0.55	-
Leachate pH	12.76±0.01	-

ave±SD, Sample number：3, unit：mg/L

Table 4 The element composition of WTS and Cullet

Oxidation state	WTS(%)	Cullet(%)
SiO_2	59.41	75.69
Al_2O_3	20.67	2.73
Na_2O	1.43	4.80
K_2O	4.57	0.01
MgO	2.26	2.27
CaO	4.15	6.21
TiO_2	0.68	0.04
Fe_2O_3	6.76	0.97

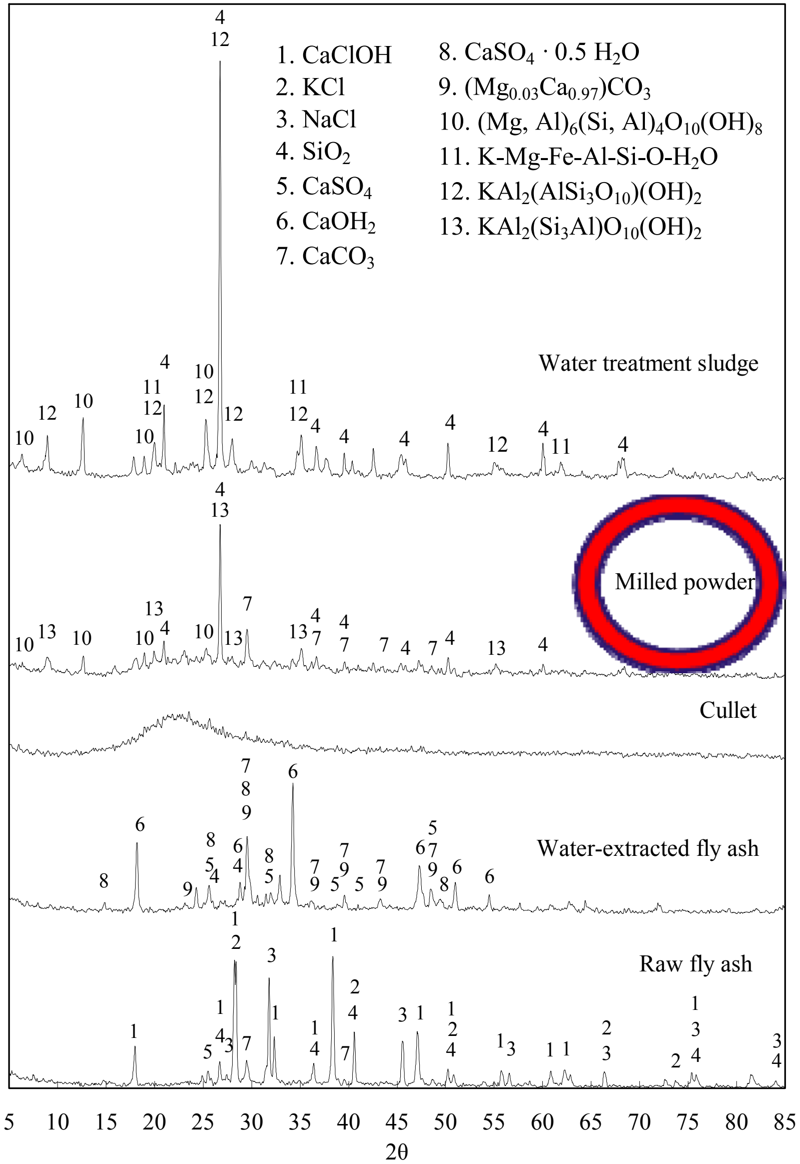
Table 5 The TCLP leaching concentration of WTS and Cullet

element	WTS	Cullet	Regulation limits
Cd	0.02±0.01	ND	1
Cr	3.10±0.01	ND	5
Cu	0.28±0.05	0.01±0.01	15
Pb	1.91±0.61	0.01±0.01	5
Zn	1.72±0.09	0.03±0.02	
Leachate pH	3.65±0.08	7.88±0.08	-

ave±SD, Sample number：3, unit：mg/L

ND：below the limit of detection(Pb=5ppb、Zn=0.3ppb、Cu=0.6ppb、Cd=0.35ppb、Cr=0.5ppb)

Fig. 1 XRD patterns



- ❖ Raw fly ash: soluble salt compound
- ❖ WFA: $Ca(OH)_2$, $CaSO_4$
- ❖ WTS: SiO_2
- ❖ Cullet: amorphous state
- ❖ Milled powder (433): The whole crystalline degree was decreased

Fig. 2 The compression strength of sintered specimen without milling.

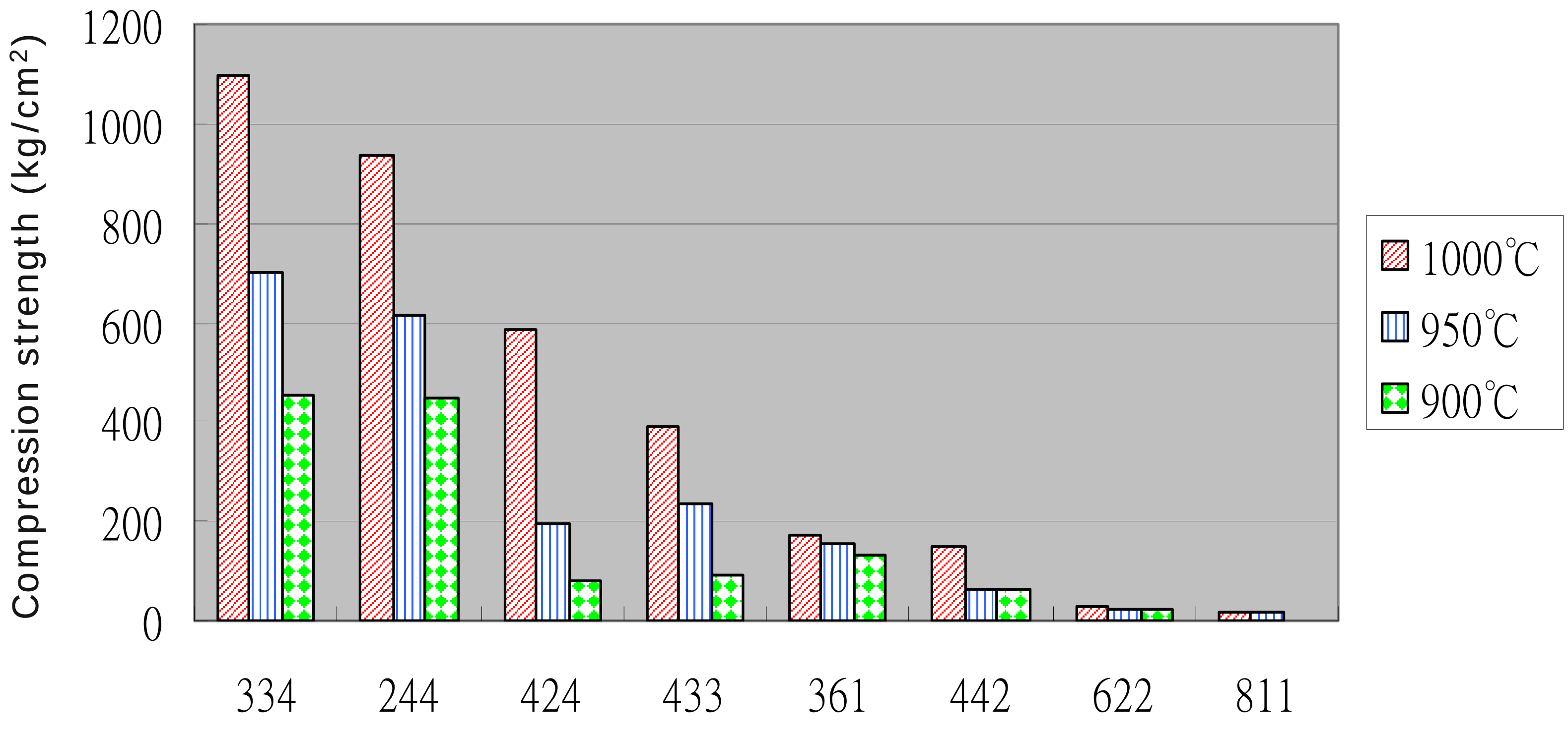


Fig. 3 The comparison of compression strength between milled and non-milled

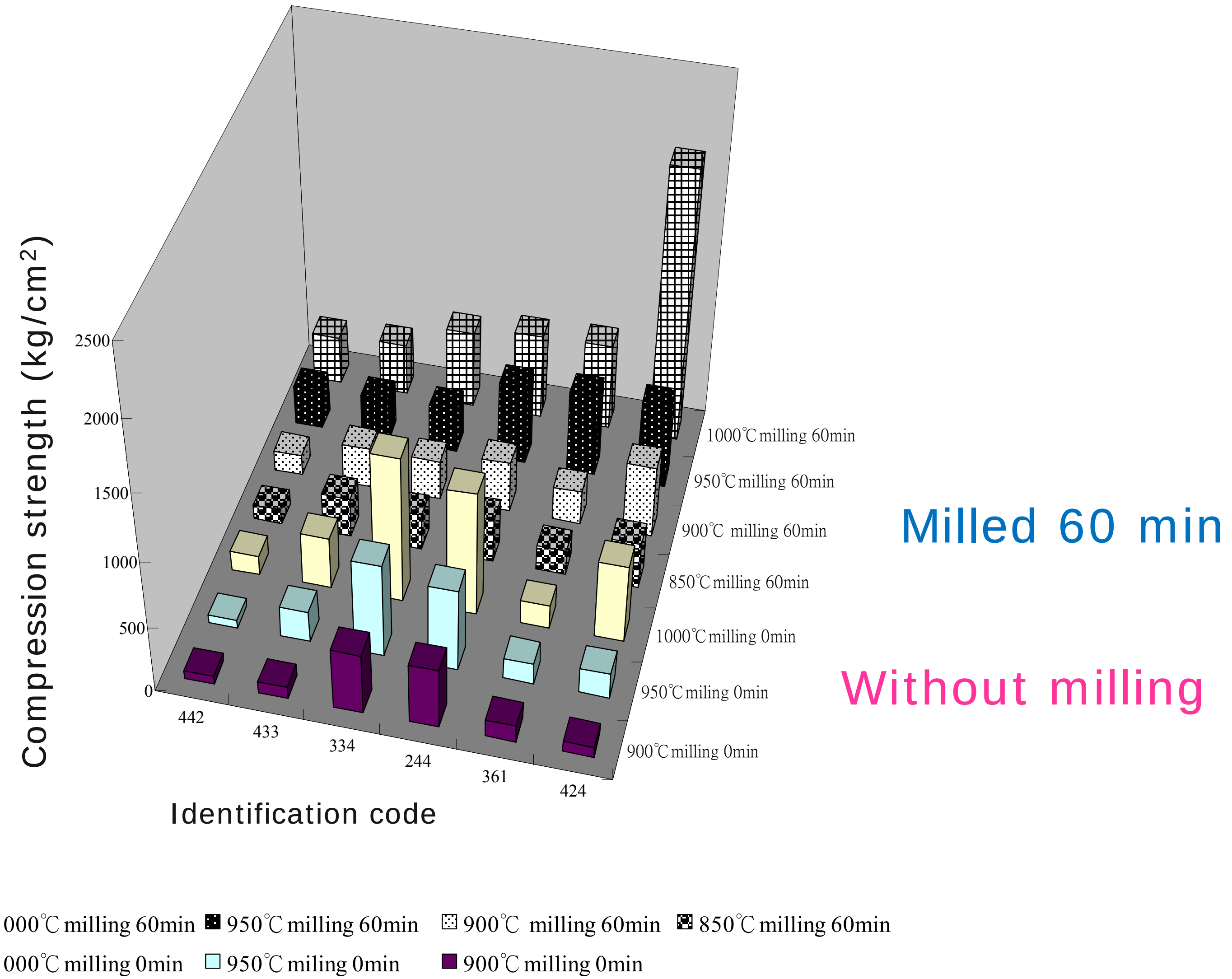


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Table 6 The soundness of sintered specimen without milling treatment

Identification code	1000 °C	950 °C	900 °C
244	3.854	5.409	5.724
433	4.04	6.078	11.04
334	0.002	0.928	17.02
424	2.112	6.727	19.01
361	7.785	13.21	52.16
442	17.81	19.32	27.1
Ceiling limit：12%		unit：%	

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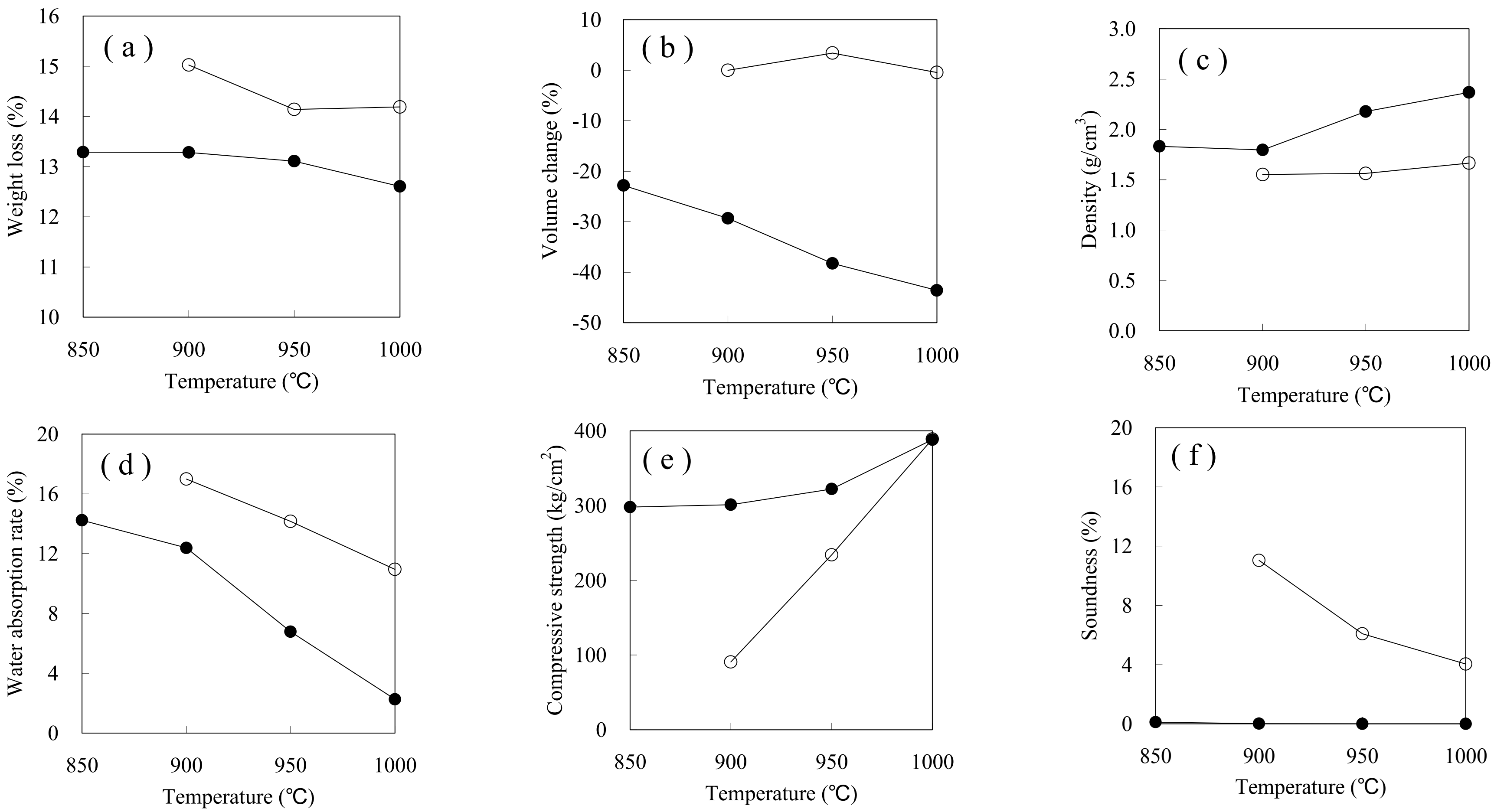
Table 7 The soundness of sintered specimen with milling

Identification code	1000 °C	950 °C	900 °C
244	0.00	0.00	0.00
433	0.00	0.01	0.02
334	0.08	0.17	0.04
424	0.07	0.17	1.21
361	0.03	0.12	3.52
442	1.97	2.18	5.58
Ceiling limit：12%　　unit：%			

The choice of Adjustment condition

- Sample 433 was chosen for the further research since the compression strength of sintered specimens produced with and without milling treatment was similar on 1,000 ^{o}C .
- Other physical and mechanical properties of sintered specimens produced with and without milling treatment could be compared.
- The evaporation rate of heavy metals from sintered specimens was the important matter of environmental pollution.

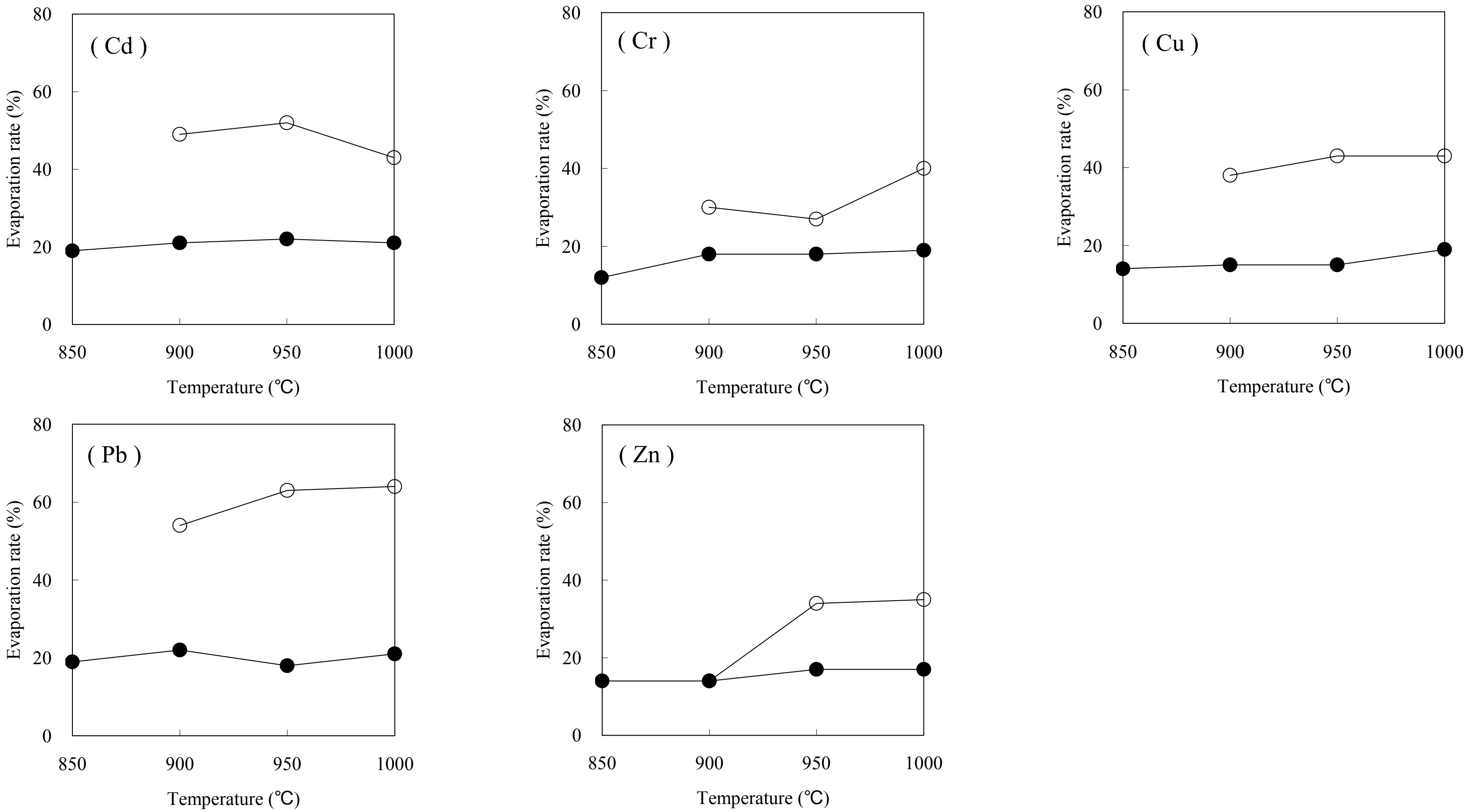
Fig. 4 The physical and mechanical properties of sintered specimens (433) produced with and without milling



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.

Fig. 5. Evaporation rate of heavy metals from sintered specimens (433) produced with and without milling



Hollow circles indicate non-milled, full circles indicate milled

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Fig. 6. SEM of sintered specimens without milling : (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×.

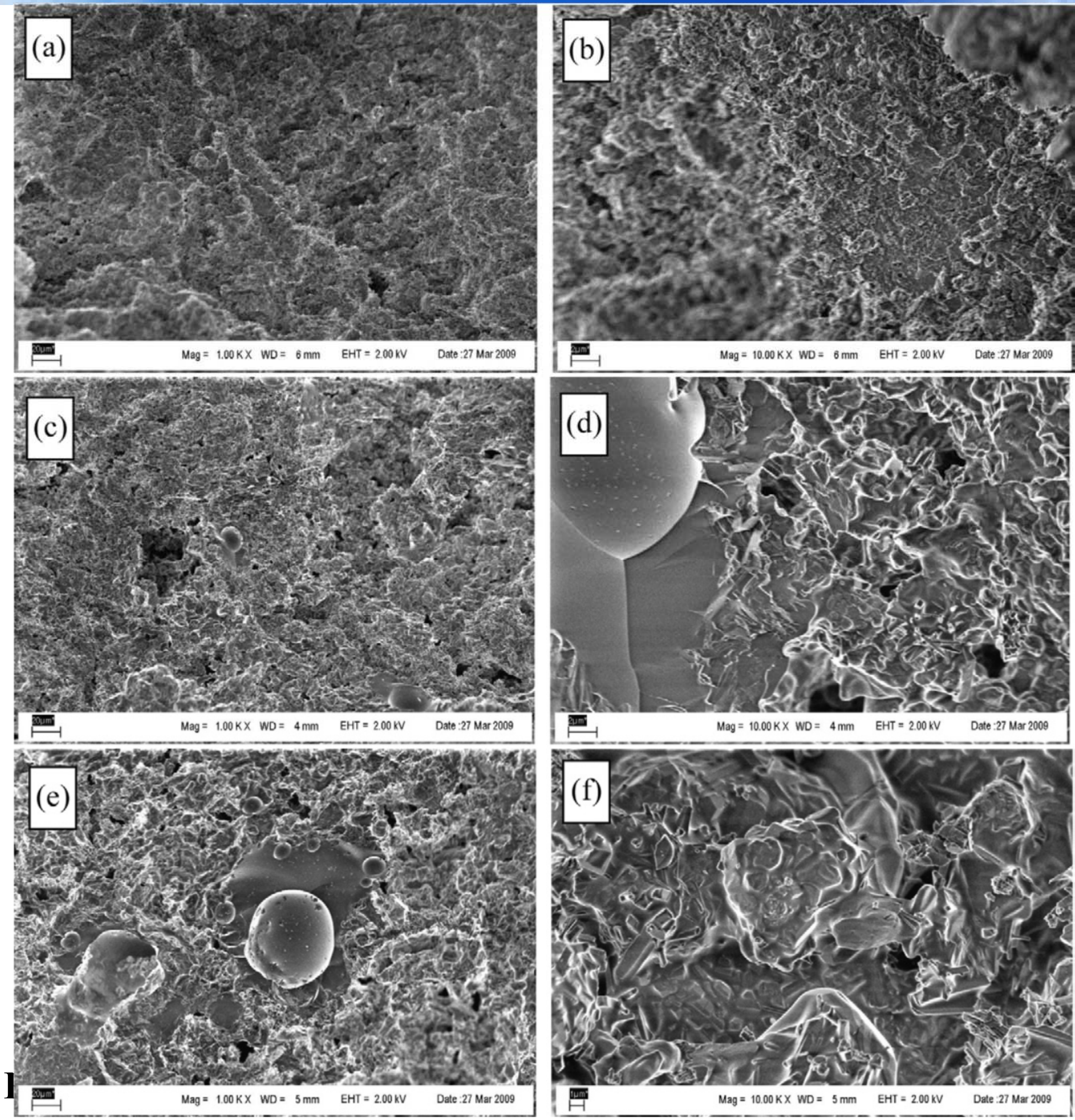
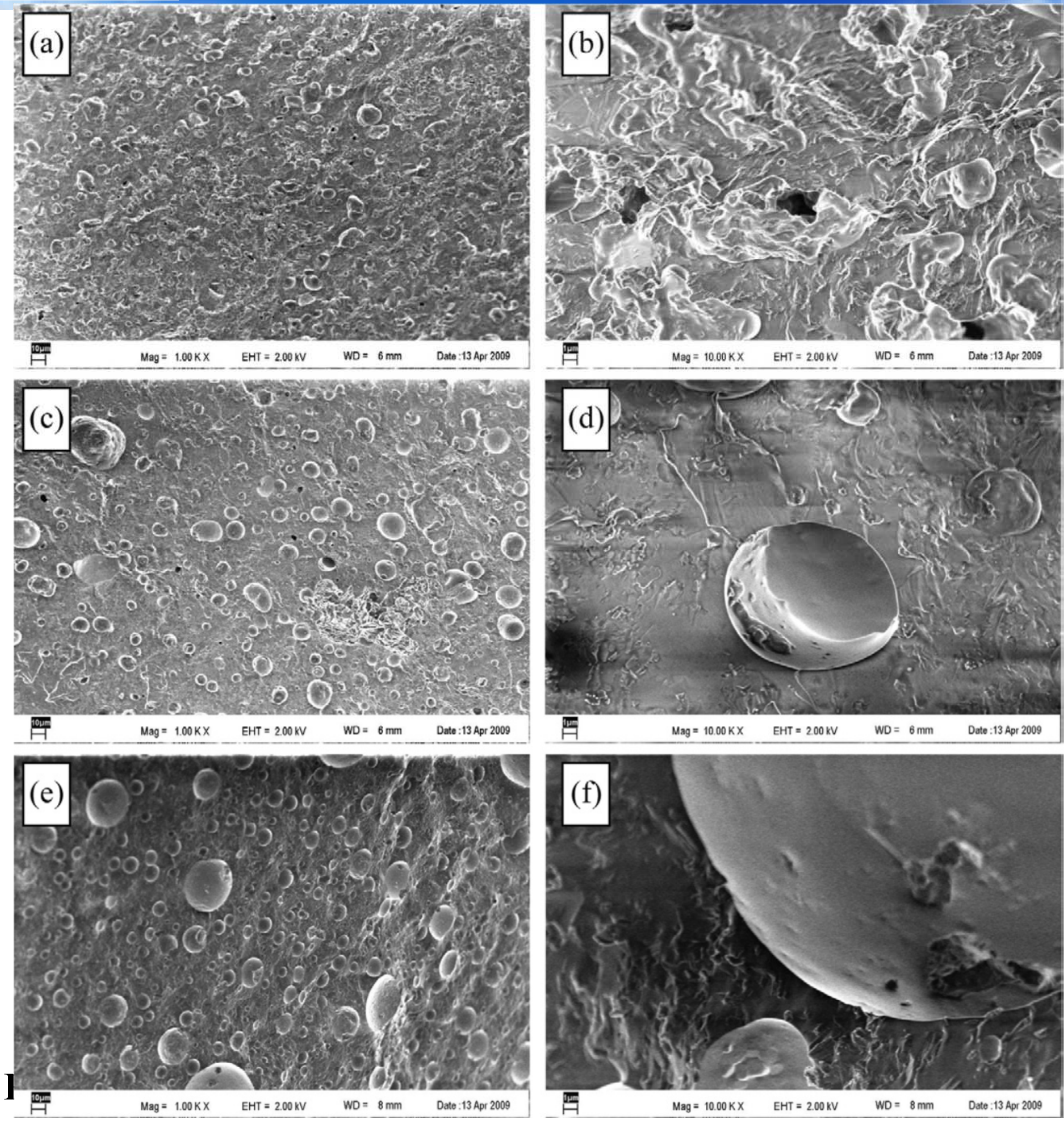


Fig. 7. SEM of sintered specimens with milling : (a) 900 ◦C, 1 k×; (b) 900 ◦C, 10 k×; (c) 950 ◦C, 1 k×; (d) 950 ◦C, 10 k×; (e) 1000 ◦C, 1 k×; (f) 1000 ◦C,10 k×.



Conclusions

Conclusions(1/2)

- The milling operation acts to destroy crystalline structures of the fly ash.
- Compounds recombine to form new ones during sintering. Such compounds offer a good structural foundation to the sintered specimens.
- Amorphous materials are more easily generated at lower temperatures during the liquid sintering stage in milled sintered specimens than without milling.

Conclusions(2/2)

- The material generated is sufficient to cover the surfaces of the particles, it can restrain the evaporation of heavy metals during sintering.

- The milling process can help to stabilize heavy metals in the fly ash, improve the mechanical characteristics includes compressive strength, and restrain heavy metal evaporation from sintered specimens.

Thank you for your Attention

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