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Sintering effect on cement bonded sewage sludge ash

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Abstract

Through foaming reaction, hydration reaction and pozzolanic effect, sewage sludge ash (SSA) was used as main material to produce a sewage sludge ash foamed lightweight material (SSAFLM). Firing tests were conducted at different temperatures. This was to study how the use of sewage sludge ash (SSA) improved the thermal properties and sintering effects of cement-base materials, and to evaluate the feasibility of using SSA to improve the soundness of cement-base materials under high temperature. The experimental results revealed that when the sintering temperature was lower than 600 °C, the engineering properties and microstructure of SSAFLM were mainly affected by dewatering and hydrates decomposition. However, when the temperature was over 600 °C, the results were chiefly affected by sintering effects. At high temperatures, the more SSA was used, less crack formation resulted. Moreover, after fired at 1093 °C for 4 h, the compressive strength was improved by 44%, and the total pore volume decreased by 30% in average.

Keywords: Sewage sludge ash (SSA); Lightweight material; Thermal conductivity; Firing test; Sintering effect

1. Introduction

High temperature sintering is usually applied in powder metallurgy and ceramic sintering. Solid-phase sintering is mostly applied in powder metallurgy, but liquid-phase sintering is used in ceramic production. The reaction process of liquid phase sintering is composed of three stages, i.e. rearrangement, precipitation after diffusion dissolving and enlarging of pores [1]. Cement paste or concrete can easily experience a rapid drop in strength and can even burst under high temperatures. This is because, under high temperatures, pore water and crystalline water that may exist in the dense materials will not evaporate but will be locked inside, which causes the accumulation of strong and ejective inner stress to destroy the structure [2]. Around 300 °C and above, high temperature effects can easily make cement paste or concrete explode. This explosion, mainly caused by steam pressure and heat stress, is a violent destructive behavior [3]. Elements in normal cement paste are decomposed in four stages under high temperature: (1) capillary and gel pore water evaporate between room temperature and 105 °C; (2) C–H–S gels are decomposed between 105 °C and 440 °C; (3) decomposition of $Ca(OH)_2$ happens between 440 °C and 580 °C; (4) $CaCO_3$ is decomposed between 580 °C and 1007 °C [4–6]. After fired, cement mortar has significant strength loss [7].

After sintered at high temperature, SSA has a 95% reduction in weight and in volume. SSA can be transformed into a stable inorganic material, which possesses porous properties and pozzolanic effects. In the past, SSA has been widely used to make bricks, clay tiles, lightweight aggregates and as an addition to cement [8,9]. Due to the high thermal sensitivity of cement-based materials, and the pozzolanic characteristics of SSA, it is therefore presumed that adding SSA can decrease the thermal sensitivity of specimens. Thus, in this research, at room temperature, foamed lightweight cement bonded material was made of SSA to investigate how temperature affected the macro/micro properties, and thus to establish the behavior of SSA at high temperatures.

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2. Experiment

2.1. Materials

Sewage sludge came as mixed sludge cakes from the primary, secondary and final settling tanks of the Ming-Shen Wastewater Treatment Plant, Taipei. The mixed sludge was fired in a pilot scale incinerator at 900 °C for 3 h and the ash was ground in a shredding machine for 2 h. The properties of SSA are shown in Table 1. The SSA is slightly acidic with a pH of 6.08 and a specific gravity of 2.29. The free chloride content of SSA was 4.35 ppm, which is far below the aggregate requirements listed in the Chinese National Standard (CNS 1240). From SEM micrographs shown in Fig. 1, it was seen clearly that the particle morphologies of SSA was irregular, which was different from the spherical particles of coal ash. The SSA toxicity characteristic leaching procedure (TCLP) met the standard requirements for hazardous industrial wastes, EPA, Taiwan. The TCLP-results and concentrations of heavy metals in raw sewage sludge and SSA are listed in Table 2. The resulting SSA was then used as the major compound in SSAFLM.

Portland cement (Type I) used met the CNS 61 "Portland Cement" specifications and its fineness was 300 m^2/kg as measured by Blaine Air Permeability Method (ASTM C204), with specific gravity of 3.15. The chemical composition of this cement is shown in Table 1. Reagent grade aluminum powder was used. The fineness was 6817 m^2/kg as measured by nitrogen adsorption method. The aluminum powder was used as a foaming catalyst in the alkaline environments.

2.2. Methodology

In the experiments, the water to solid ratio (W/S) was between 0.5 and 0.8, the ratio of weights of cement to that of SSA (C/SSA) were 20:80, 30:70 and 40:60 (It has been explained in the published paper that the mixture of C/SSA = 10:90 would not be studied because it was unable to fix and form.). Aluminum powder was used as foaming agent. The amounts of metallic foaming agent added was 0.5%, 0.9% and 1.3% of mass of the total solids.

Cement, SSA and metallic foaming agent were well mixed to give pastes of different W/S ratios. The fresh paste was cast into 25 mm cube-shaped steel molds and cured at room temperature for 24 h after casting. The specimens were then demolded and cured for 28 days at 25 ± 2 °C in saturated limewater according to ASTM 305 and ASTM C109 procedure. After curing, excess material over 25 mm due to foaming reaction was cut off and removed.

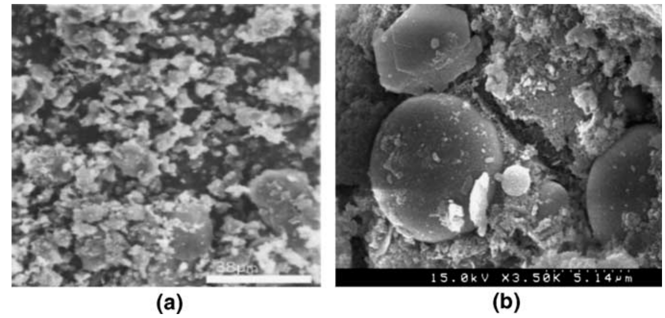

Fig. 1. Particle morphologies of sewage sludge ash (SSA) and coal ash (FA): (a) sewage sludge ash (×800) and (b) coal ash (×3500).

Specimens were placed in a high temperature furnace and fired at temperatures of either 25 °C, 200 °C, 400 °C, 600 °C, 800 °C, 1000 °C or 1093 °C for 4 h. The specimens were then cooled to room temperature to investigate the sintering effect and other properties.

Chemical analysis of samples was done by X-ray fluorescence analysis (XRF). The leaching test was based on toxicity characteristic leaching procedure (TCLP). SSAFLM characteristics were determined, including the ignition loss, bulk density, compressive strength (CNS 1232), volume change, pore size distribution (Mercury intrusion porosimetry, MIP), as well as SEM micrographs.

3. Results and discussion

3.1. Bulk density and water absorption

Due to effects of dehydration, hydrate decomposition and sintering, the bulk density of SSAFLM changed gradually. The bulk density of the SSAFLM became greater after fired at 1093 °C. From Table 3 and Fig. 2, it was found that when the temperature was between 25 °C and 600 °C, the ignition loss of SSAFLM was highly related to the volume shrinkage rate. This resulted in only slight variation in bulk density. When the temperature was between 600 °C and 800 °C, the bulk density of SSAFLM increased dramatically with the increase of SSA amount. This was probably because plastic flow happened between 600 °C and 800 °C to result in the material, becoming denser. After being fired at 1093 °C, the bulk density of the SSAFLM increased from 0.52 to 0.93 g/cm^3 (an average of 0.71 g/cm^3) to 0.88–0.99 g/cm^3 (an average of 0.91 g/cm^3). The most significant increase was 27.6%. The more SSA was used, the more significant was the bulk density and compressive strength increased. This was because the sintering effect at 1093 °C led to a significant volume

Table 1
Chemical compositions of cement and SSA (unit: %)

Materials	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3
Cement	20.5	6.50	3.20	1.90	62.5	0.40	0.78	–	2.20
SSA	43.6	16.6	10.4	1.40	5.61	0.82	2.34	12.1	0.24

Table 2
TCLP-results and concentrations of heavy metals in sewage sludge and sewage sludge ash (SSA)

Materials	Heavy metals	Pb	Cd	Cr	Cu	Zn
Raw sludge	Total weight (mg/kg)	0.28 ± 0.09	1.6 ± 0.13	9.51 ± 0.11	33.32 ± 1.28	176.57 ± 2.97
SSA	Total weight (mg/kg)	1.2 ± 0.013	4.81 ± 0.03	21.96 ± 1.84	89.64 ± 3.77	567.3 ± 4.85
	TCLP (mg/L)	0.017 ± 0.006	ND	0.1 ± 0.05	3.81 ± 0.13	–
	Regulation TCLP (mg/L)	5	1	5	15	–

ND: not detected.

Table 3
Properties of SSAFLM at 1093 °C

C:SSA	A/S (%)	W/S	Bulk density		Water absorption (%)		Compressive strength (MPa)	
			Before fired	After fired	Before fired	After fired	Before fired	After fired
40:60	0.5	0.5	0.91	1.02	56.82	44.26	10.73	13.98
		0.6	0.77	0.88	71.79	54.27	9.58	12.71
		0.7	0.65	0.84	87.53	57.59	9.17	12.46
	0.9	0.5	0.86	0.96	60.73	48.89	10.57	12.41
		0.6	0.74	0.87	73.47	58.07	9.58	12.13
		0.7	0.62	0.71	92.89	70.41	9.04	11.30
	1.3	0.5	0.82	0.93	64.15	50.36	9.95	12.28
		0.6	0.67	0.81	86.60	68.85	9.51	11.27
		0.7	0.62	0.70	89.90	70.75	8.98	10.88
30:70	0.5	0.5	0.93	1.11	57.01	37.74	9.87	17.55
		0.6	0.77	0.96	74.21	53.28	8.86	13.78
		0.7	0.67	0.89	89.68	67.71	8.73	12.96
	0.9	0.5	0.88	1.10	63.35	39.78	9.17	16.65
		0.6	0.73	0.91	76.98	55.81	8.86	13.48
		0.7	0.61	0.75	101.2	78.63	8.60	12.25
	1.3	0.5	0.86	1.06	63.46	45.44	8.94	15.05
		0.6	0.74	0.89	78.10	58.13	8.85	13.28
		0.7	0.62	0.70	96.03	74.23	8.53	12.19
20:80	0.5	0.6	0.76	1.06	74.68	42.19	8.77	19.34
		0.7	0.66	0.90	89.77	53.59	8.72	15.37
		0.8	0.58	0.73	106.72	70.76	8.67	12.21
	0.9	0.6	0.73	0.99	78.15	45.25	8.76	18.38
		0.7	0.61	0.84	100.1	60.86	8.71	15.35
		0.8	0.53	0.69	116.9	79.96	8.65	11.90
	1.3	0.6	0.72	0.93	79.93	49.96	8.72	14.57
		0.7	0.60	0.72	97.24	62.91	8.71	12.37
		0.8	0.52	0.63	113.5	82.86	8.58	11.14

A = ash, W = water, S = solids, C = cement, SSA = sewage sludge ash.

shrinkage and denser structure. Thus, sintering makes SSAFLM have enhanced compressive strength, but still retain lightweight characteristics.

To analyze the relation between three variables (i.e. cement to sewage sludge ash (C/SSA), water-to-solid ratio (W/S) and aluminum powder amount to solids (A/S), and bulk density (γ) before and after the specimen was heated to 1093 °C, Eqs. (1) and (2) were developed by multiple regression analysis.

$$\gamma \text{ (before fired)} = -0.042\text{C/SSA} - 0.977\text{W/S} - 0.215\text{A/S}, \text{ with } R^2 = 0.97, \tag{1}$$

$$\gamma' \text{ (after fired)} = -0.356\text{C/SSA} - 0.997\text{W/S} - 0.347\text{A/S}, \text{ with } R^2 = 0.95. \tag{2}$$

The results showed that under both room (before firing) and high temperatures (after firing), the effect of the water to solid ratio on bulk density of SSAFLM was the most pronounced, compared to all the other parameters.

From Table 3 and Fig. 3, it was found that after being fired at 1093 °C, the water absorption of the SSAFLM decreased from 57.01–116.9% (an average of 82.96%) to 37.74–82.86% (an average of 58.46%). The more SSA was used, the more significant was the water absorption decreased.

To analyze the relation between three variables (i.e. C/SSA, W/S, A/S) and water absorption (w) before and after the specimen was heated to 1093 °C, Eqs. (3) and (4) were developed by multiple regression analysis.

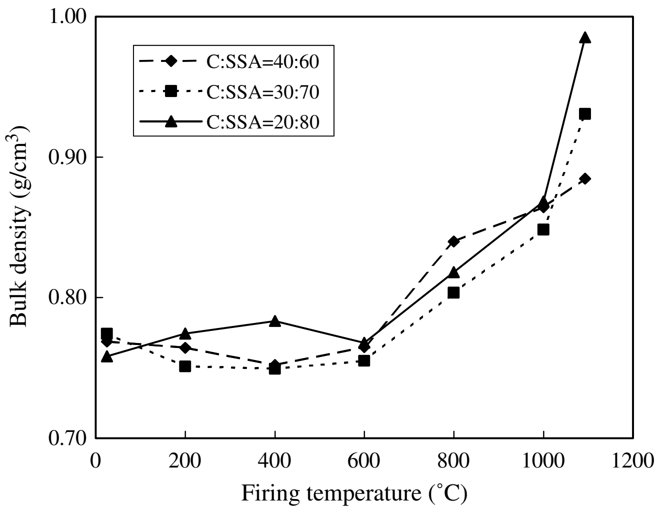

Fig. 2. Relationship between firing temperature and bulk density of SSAFLM (A/S = 0.5%; W/S = 0.6).

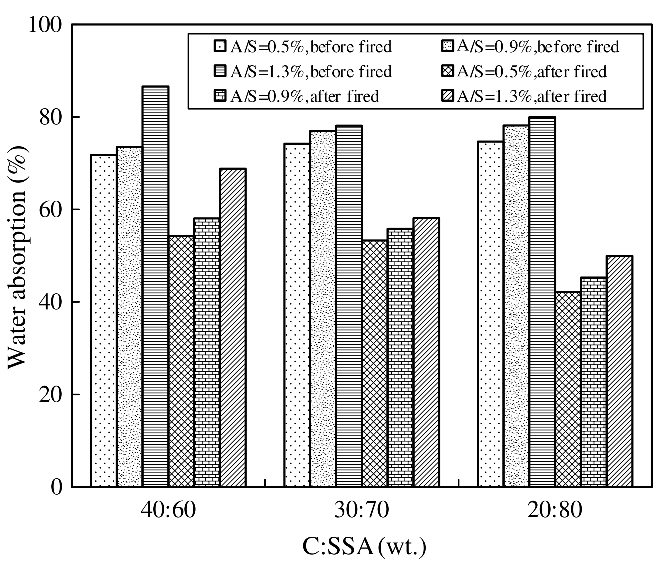

Fig. 3. Water absorption of SSAFLM at 1093 °C (W/S = 0.6).

$$w \text{ (before fired)} = -0.070\text{C/SSA} + 0.167\text{W/S} + 0.938\text{A/S}, \quad \text{with } R^2 = 0.97, \tag{3}$$

$$w' \text{ (after fired)} = -0.320\text{C/SSA} + 0.296\text{W/S} + 0.974\text{A/S}, \quad \text{with } R^2 = 0.88. \tag{4}$$

3.2. Volume change and compressive strength

Volume change and crack growth of pure cement paste and SSAFLM samples with the same consistency, but burnt at different temperatures were compared. Fig. 3 shows that the volume of SSAFLM shrank by 22–37% evenly, with no twisting or cracking. This was quite different from the significant twisting and bursting in the pure cement paste. Due to porous properties of foamed lightweight materials, the thermal stress generated during burning could be released through pores, which acted as an energy scattering medium and as an deformation buffer zone. The thermal conductivity of cement paste was 0.567 W/m K, which was significantly higher than 0.185 W/m K and 0.074–0.151 W/m K of SSA and SSAFLM. As well, it was found from SEM micrograph that the SSA particle was irregular, adding SSA can thus increase more pore volume of specimens. Obvious visual cracks initiated in pure cement paste at 400 °C. At burning temperature up to 1000 °C, extensive cracking resulted cracks. After burning at 1093 °C followed by cooled to room temperature, pure cement paste specimens showed serious signs of distress.

Figs. 4 and 5 indicate that due to high temperature effects, the volume shrinkage rate of SSAFLM increased as the amount of SSA increase. When temperature was over 600 °C, the volume shrinkage rate increased significantly. As lower than 1000 °C, the volume shrinkage rate went up with the increase of cement amount. This was because that cement was the key factor affecting volume change. Of which, cement paste shrank due to hydrates decomposition and moisture evaporation. However, when exceeding 1000 °C, volume shrinkage rate raised with the

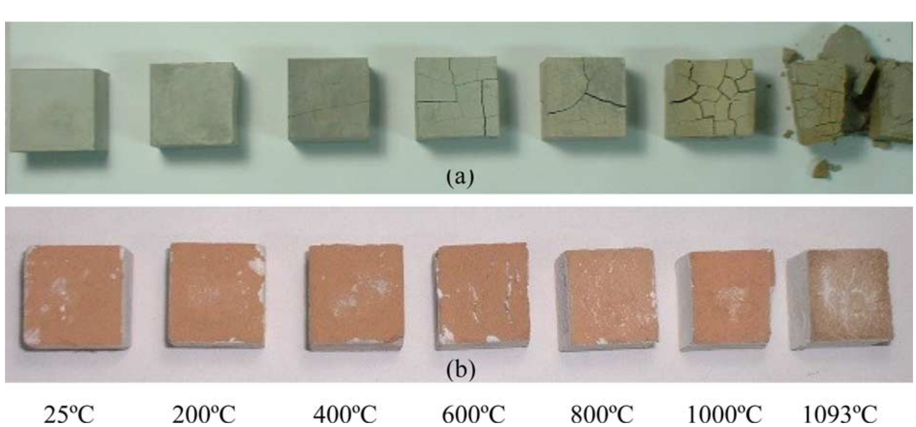

Fig. 4. Appearance changes of SSAFLM after fired at different temperatures: (a) pure cement paste (W/S = 0.35) and (b) SSAFLM (C/SSA = 30:70; W/S = 0.6).

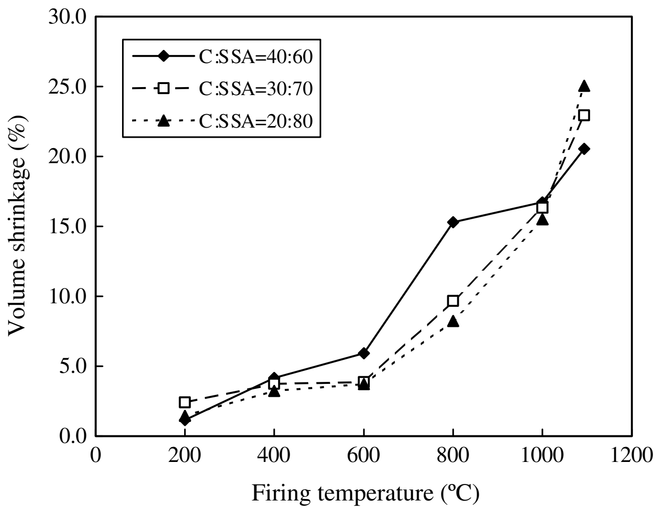

Fig. 5. Relationship between firing temperature and volume shrinkage of SSAFLM (A/S = 0.5%; W/S = 0.6).

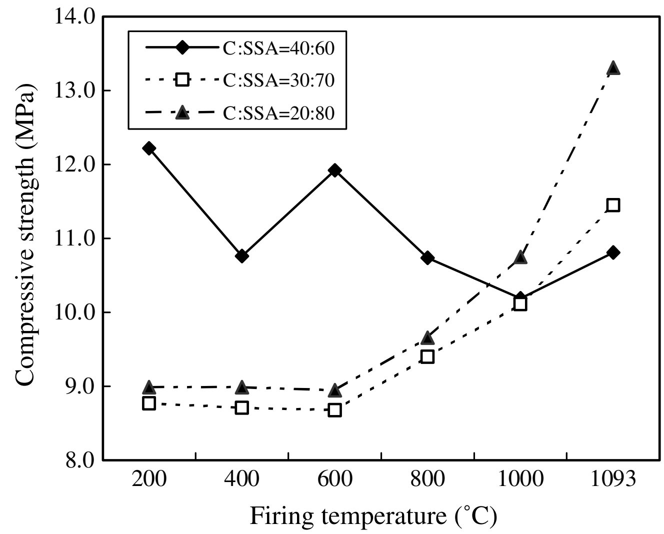

Fig. 6. Relationship between firing temperature and compressive strength of SSAFLM (A/S = 0.5%; W/S = 0.6).

increase of SSA amount. At this stage, the shrinkage rate was mainly affected by the sintering effect of SSA. As a whole, volume shrinkage rate due to the sintering effect of SSA was much higher than that due to substance decomposition of cement paste.

Table 3 and Fig. 6 show that after fired at 1093 °C, the compressive strength of SSAFLM was apparently higher than before firing. Comparing the compressive strength of SSAFLM before and after fired, it was found that

Table 4
Pore size distribution of SSAFLM at 1093 °C

C:SSA (wt.%)	A/S (wt.%)	W/S (wt.%)	Before fired		After fired	
			Total pore volume (mL/g)	Capillary pore volume (%)	Total pore volume (mL/g)	Capillary pore volume (%)
40:60	0.5	0.5	0.601	88.59	0.554	95.89
		0.6	0.607	84.77	0.645	100.0
		0.7	0.911	90.10	0.789	97.06
	0.9	0.5	0.634	91.30	0.660	98.11
		0.6	0.791	91.76	0.650	100.0
		0.7	1.030	96.42	0.878	97.19
	1.3	0.5	0.607	92.74	0.680	96.31
		0.6	0.792	94.39	0.835	96.81
		0.7	1.051	86.49	0.932	93.23
30:70	0.5	0.5	0.654	94.16	0.350	94.75
		0.6	0.837	88.82	0.585	99.81
		0.7	1.030	95.78	0.629	97.88
	0.9	0.5	0.752	95.13	0.414	99.81
		0.6	0.948	95.37	0.585	96.61
		0.7	1.105	94.30	0.656	98.26
	1.3	0.5	0.834	94.75	0.488	97.07
		0.6	0.911	94.47	0.535	98.45
		0.7	1.128	94.85	0.711	96.65
20:80	0.5	0.6	0.876	92.03	0.511	96.96
		0.7	1.135	87.68	0.516	96.59
		0.8	1.150	94.26	0.763	99.63
	0.9	0.6	0.902	93.64	0.499	99.36
		0.7	1.236	92.74	0.644	99.38
		0.8	1.469	94.79	0.782	98.75
	1.3	0.6	0.969	93.06	0.453	100.0
		0.7	1.266	93.28	0.915	84.40
		0.8	1.606	95.13	0.962	93.29

A = ash, W = water, S = solids, C = cement, SSA = sewage sludge ash.

specimens, with 60%, 70% and 80% of SSA, had their compressive strengths increased by 18–35%, 42–77% as well as 37–120% respectively. This meant that the more SSA amount was used, the more significantly the compressive strength gain of SSAFLM. On the other hand, the compressive strength of SSAFLM was inversely proportional to water-to-solid ratio, whether before or after fired. Specimens with a lower water-to-cement ratio always had a higher compressive strength.

To analyze the relation between three variables (i.e. C/SSA, W/S, A/S) and the compressive strength (σ) of SSAFLM both before and after burning at 1093 °C, Eqs. (5) and (6) were developed by multiple regression analysis. At room temperature, the compressive strength of SSAFLM was in directly proportional to the cement amount, but inversely proportional to water-to-solid ratio and the amount of aluminum powder. However, at 1093 °C, the amount of cement became an inverse factor. This meant that cement was more sensitive to temperature than SSA. Hence, SSA was a better material with respect to compressive strength than cement under high temperature environments.

$$\sigma \text{ (before fired)} = 0.481\mathrm{C/SSA} - 0.477\mathrm{W/S} - 0.184\mathrm{A/S}, \quad \text{with } R^2 = 0.69, \tag{5}$$

$$\sigma' \text{ (after fired)} = -0.769\mathrm{C/SSA} - 0.771\mathrm{W/S} - 0.355\mathrm{A/S}, \quad \text{with } R^2 = 0.80. \tag{6}$$

The compressive strength before sintering was in a positive correlation with C/SSA. That meant the compressive strength increased with the increase of the cement amount. However, after fired at 1093 °C, the compressive strength displayed a negative correlation with C/SSA. This was because SSAFLM had countless open and connected pores, the accumulated thermal stress and steam pressure inside the specimen were easily released. Therefore the internal stress that would normally make specimens crack or burst was relieved.

3.3. Pore structure and SEM micrographs

The total pore volume of pure cement paste, made with a water-to-solid ratio of 0.38, was 0.12 mL/g, and its capillary pore volume (>0.01 μm) and gel pore volume (0.01 μm) was 0.10 mL/g and 0.02 mL/g respectively. Total pore volume of SSAFLM before fired was between 0.601 mL/g and 1.606 mL/g. However, after fired at 1093 °C, the pore volume ranged between 0.554 mL/g and 0.962 mL/g, as shown in Table 4. This showed that pore volume decreased by 7.8–40.1% (an average of 29.71%), capillary pore volume decreased by 28.98% and gel pore volume by 0.73%. Comparing the variation of pore size distribution, it was found that before fired, capillary pore volume was between 85% and 96% of total pore volume, and gel pore volume between 4% and 15%. After fired at 1093 °C, capillary pore volume increased to 94.8–100% of total pore volume, and gel pore volume decreased to zero to 5.3%. It was probably because the enlarging stage of liquid phase sintering in SSAFLM had been achieved after fired at 1093 °C for 4 h. Therefore, larger pores became larger, but the quantity of smaller ones decreased.

In Fig. 6, the pore size distribution of SSAFLM was analyzed. It shows that, before fired, the accumulative volumes of pores larger than 0.01 μm, 0.5 μm as well as 0.05 mm were respectively between 85% and 96%, 47.8%

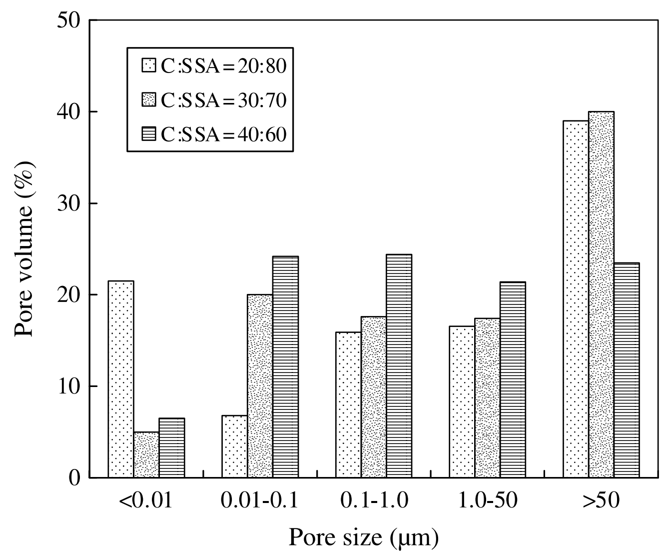

Fig. 7. Effect of SSA amount on the pore distribution of SSAFLM (A/S = 0.5%; W/S = 0.7).

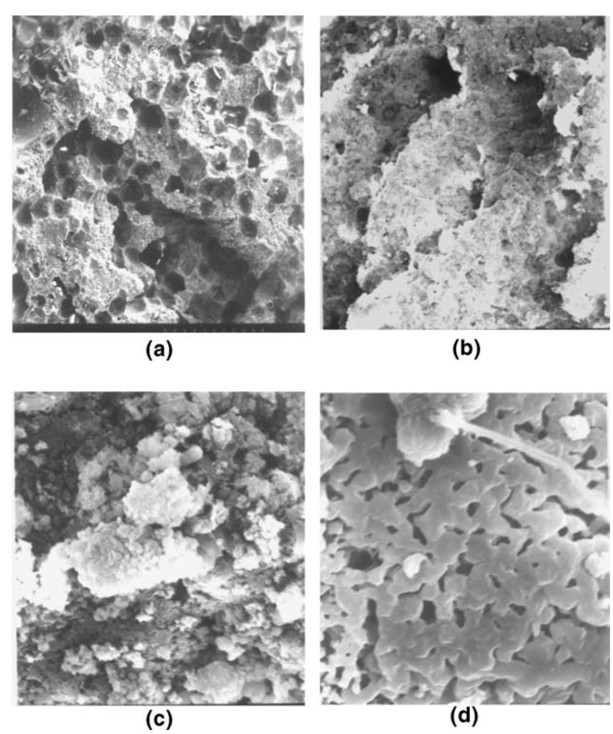

Fig. 8. SEM micrographs of SSAFLM (A/S = 0.5%; W/S = 0.7; C:SSA = 30:70): (a) before fired; ×40, (b) after fired; ×40, (c) before fired; ×3000 and (d) after fired; ×3000.

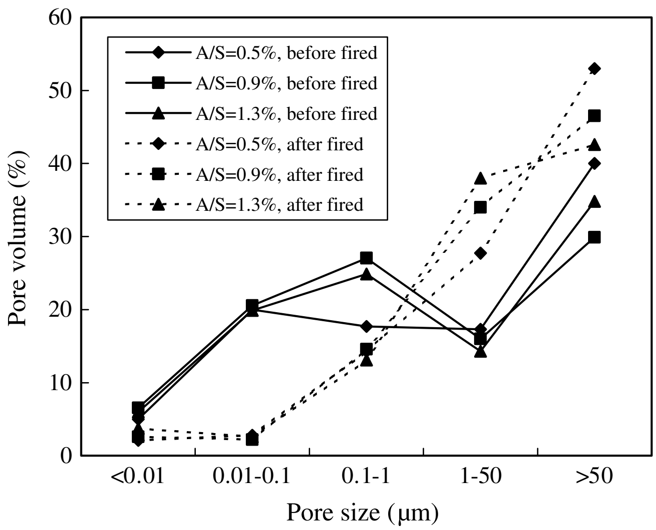

Fig. 9. Pore distribution of SSAFLM at 1093 °C (W/S = 0.7; C:SSA = 30:70).

and 63.9% as well as 23.5% and 40.0% of total pore volume. However, after fired at 1093 °C, the pore volume distributions of these three sizes changed to 94.8–100%, 82.5–90.3% and 27.7–46.5% respectively. Fig. 7 shows the volume of pores larger than 1.0 μm in SSAFLM increased significantly after fired at 1093 °C. In addition, because of the melting flow effect after high temperature, those smaller pores were filled up, and those larger ones became larger.

SEM micrograph in Fig. 8(a) and (c) shows the porous structure of SSAFLM before fired. After fired at 1093 °C, specimens became denser because of sintering effect. However, the amount of the plastic flow generated after sintering was not sufficient to fill up all the pore volume in specimens, and thus made specimens still porous, as shown in Figs. 8(b), (d) and 9.

4. Conclusions

- The disadvantages of low strength and high water absorption of SSAFLM at room temperature could be improved through sintering.
- Between 1000 °C and 1093 °C, the compressive strength of SSAFLM was in an inverse relationship with the amount of cement, and an increase in the amount of SSA would enhance the strength significantly. The result at room temperature was just the reverse.
- After fired at 1093 °C for 4 h, SSAFLM completed the enlarging stage of liquid phase sintering, and thus decreased total pore volume by 30% than before fired.

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