Asian Journal of Chemistry; Vol. 23, No. 8 (2011), 3449-3453

ASIAN JOURNAL OF CHEMISTRY

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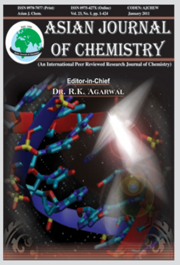

Potential for Manufacturing Unfired-Bricks Using Circulating Fluidized Bed Combustion Fly Ash

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(*Received*: 8 September 2010; *Accepted*: 20 April 2011) AJC-9824

The paper focuses on the manufacturing of the un-fired bricks using the circulating fluidized bed combustion fly ash by dry pressure molding method. The results show that: (1) The compressive strength of the brick reach the highest when it manufactured by cement 8 %, bottom ash 15 %, lime 12 %, gypsum 5 %, fly ash 60 % and water 15 %. The compressive strength can achieve 23.22 MPa. (2) NaCl, Na_2CO_3 and nuclei are better to improve the freeze-thaw resistance of the brick. (3) The drying shrinkage of the bricks added pp fiber can reach 0.69 mm/m which achieve the Chinese standard (JC239-2001). (4) The performance of the brick added the compound additive (NaCl 0.1 %, Na_2CO_3 0.1 %, Nuclei 0.5 %, PP fiber 0.1 %) is much better than the brick adding single additives. The drying shrinkage is 0.65 mm/m and the compress strength of 7d, 28d and after freeze-thaw circles are 19.47, 27.22 and 21.96 Mpa, respectively.

Key Words: CFBC fly ash, Bricks, Compress strength, Freeze-thaw resistnace, Drying shrinkage.

INTRODUCTION

Circulating fluidized bed combustion (CFBC) is considered as an environmentally-friendly coal-firing technology which has the potential to be a substitute for classic firing technology. Anthony and Granatstein[1] reported that the technology was noted for their ability to capture SO_2 *in situ via* direct reaction with Ca-based sorbents and Anthony *et al.*[2] also suggested that SO_2 was captured by limestone added *in situ*, which reacts *via* the following two-step process during the firing process:

$$CaCO_3 = CaO + CO_2$$
$$CaO + SO_3 = CaSO_4$$

Because of raised awareness of environmental-protection, CFBC technology has been spreading very quickly around the world especially in the developing countries like China which is in trouble with acid rain and other atmosphere problems. Xiao[3] presented that there were over 1000 CFBC boilers in operation up to 2004 in China and the number increased continuously.

On the other hand, fly ash which is a solid waste coming from power plant has been generally known as a recycle resource and applied to lots of areas. Magudeswaran *et al.*[4] studied the activated fly ash blended cement. Deshmukh *et al.*[5] analyzed the fly ash for agricultural use. Dakshene and Jain[6] advised that the alkali activated fly ash could be used for the adsorptive removal of tartrazin (E 102). Misran *et al.*[7] advised that mesoporous silica materials could be produced by F-fly ash. Yoon and Yun[8] suggested that F-fly ash could be used for preparing fly ash-glass-ceramic and Palomo *et al.*[9] synthesized fly ash based geopolymer materials. Cultrone and Sebastián[10] suggested that fly ash could be added to clayey materials to improve the quality of solid brick. Furthermore, Kumar[11] studied on the fly ash-lime-gypsum bricks and Chindaprasirt and Pimraksa[12] advised that the fly ash-lime granule bricks could be made without fired.

However, Li *et al.*[13] and Fu *et al.*[14] indicated that the properties of fly ash gained from CFBC boiler (CFBC fly ash) were different from F-fly ash because the combustion temperature of CFBC boiler (800-900 °C) is lower than typical coal boiler (1200-1500 °C) and the limestone is added to capture SO_2. The properties included chemical composition, mineral phases, morphology, *etc*. So the methods for utilizing F-fly ash should be unsuitable for CFBC fly ash and it gives us a new research area of solid waste treatment. Recently, Sheng *et al.*[15] reported the self-cementitious properties of CFBC fly ash and advised its potential for using as cement components. Li *et al.*[16] studied synthesizing zeolite using CFBC fly ash as main resources. Slavik *et al.*[17] prepared geopolymer from fluidized bed combustion bottom ash and Xu *et al.*[18] developed a new kind themerstable geopolymer material from CFBC fly ashes. Whereas, the paper concerning using CFBC fly ash to manufacture bricks was very few and only Shon *et al.*[19] discussed the potential use of stockpiled CFBC fly ashes in manufacturing compressed earth bricks. Even then, Shon's research only focused on the compress strength of the bricks and no results studied other important properties of brick like freeze-thaw resistance and dry shrinkage and no innovation in the manufacturing processes[19]. The aim of this paper is to evaluate the technical potential of unfired bricks added CFBC fly ash as the main component in building restoration. The bricks are made with CFBC fly ash, calcium oxide (CaO)/ calcium hydroxide ($Ca(OH)_2$), gypsum ($CaSO_4$), sand/bottom ash and cement. To replace the traditional molding method, the semi-dry molding method which is widely used in making ceramic materials was first applied to fly ash based-bricks manufacturing. The physical and mechanical properties including compress strength, freeze-thaw resistance and drying shrinkage referring to the Chinese standards (JC239-2001) were investigated. The results of the paper may give us an efficient way to recycle CFBC fly ash.

EXPERIMENTAL

The CFBC fly ash used in this investigation received from a 220 t/h Pyroflow CFBC boiler firing coal and high-sulphur petroleum coke and using limestone as the SO_2 sorbent in Power Plant at the Sinopec Jinling Petrochemical Corporation state in Jiangsu province. The ratio of coal to coke was 60:40 (cal %). The specific gravity was 2.29. The specific surface area (Blane) was 596.2 m^2/kg. The 45 μm sieve residue was 13.23 %. Table-1 shows the chemical composition of the CFBC fly ash. It could be seen that CaO of CFBC fly ash was 26.39 % and F-CaO (free calcium oxide) was 13.29 % which was much higher than normal F-fly ash. The mineral phases included quartz, anhydrite, calcite, lime, albite, hematite and portlandite but no mullite was found according to the XRD pattern (Fig. 1). Compared with the SEM images (Fig. 2A and 2B), almost all the CFBC particles were irregular while typical F-fly ash particles should be spherical.

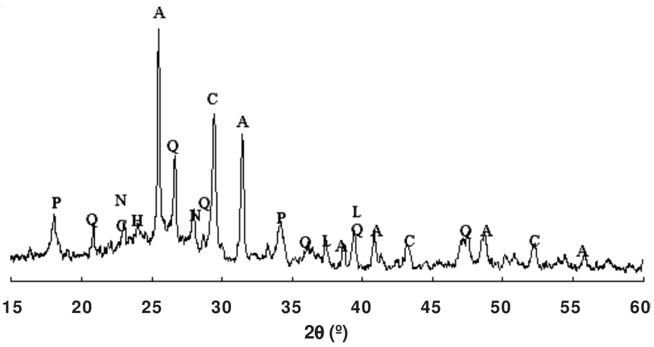
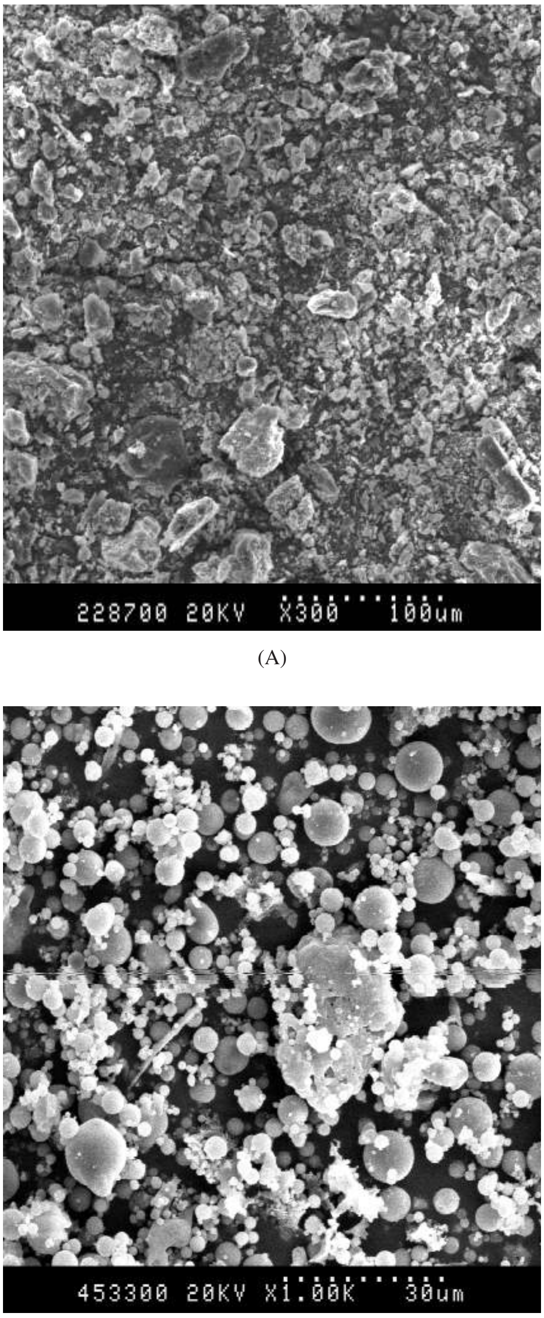


Fig. 1. X-ray diffraction pattern of the CFBC fly ash, anhydrite (A), quartz (Q), calcite (C), lime (L), albite (N), portlandite (P), hematite (H)

The cement and gypsum were bought from NanJing Xiao Yetian Cement Corporation. The bottom ash was got from the Changxing power plant stated in Zhejiang province. The 0.25 mm sieve residue of the bottom ash is 39 %. Their chemical compositions were also shown in Table-1.The CaO, $Ca(OH)_2$ and all the other chemical reagents are analytically pure. The sand was normal sand and the specific gravity was 2.66, the moisture was smaller than 1 %.



(A)

(B)

Fig. 2. SEM microphotographs of the CFBC fly ash (A) and the F-fly ash (B)

TABLE-1
CHEMICAL COMPOSITION OF THE ORIGINAL MATERIALS (%)

Oxides	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	K_2O	TiO_2	P_2O_5	SO_3	LOI[a]
CFA[b]	43.23	26.16	13.29	3.09	0.34	0.56	0.53	1.12	0.14	3.79	7.52
Cement	21.44	4.95	64.3	3.52	0.29	1.39	0.69	0.22	0.06	2.38	1.59
Gypsum	9.37	1.93	28.91	0.72	0.15	2.45	0.39	0.10	0.08	32.05	22.23
BA[c]	52.37	25.85	2.89	8.46	0.48	0.85	1.06	0.92	0.22	0.30	6.45

[a]LOI loss on ignition at 960 ºC; [b]CFBC Fly ash; [c]Bottom ash.

Formulas and mixtures preparing: According to the former experiment results of our research group, the basic formulae were cement (4 to 8 %), sand (20 to 30%)/bottom ash (10 to 30 %), CaO (10 to 14 %)/$Ca(OH)_2$ (10 to 14 %) and $CaSO_4$ (3 to 6 %). The candidate additives to enhance the freeze-thaw resistance and improve the drying-shrinkage of the bricks were the water-glass, NaCl, triethanolamine, Na_2CO_3, nuclei (the powers from grounding the scraped bricks), PP fiber and comprehensive additives. The specific formulae and added ratio are given in Tables 1-5. All the components except sand/bottom ash were weighted as the Tables 1-5. Then the original mixtures were mixed by cement-mixer for at least 2 min (*ca.* 62 rpm). After it, the sand/bottom ash was added and mixed for another 2 min (*ca.* 125 rpm).

Molding process, curing condition and properties tests: After mixed, the mixtures were put into the brick mould (4 cm × 4 cm × 8 cm) (Fig. 3A) and made the mould full of it. Then an iron block (4 cm × 4 cm × 8 cm) was placed on the top of the mixtures and the 300KN-pressing machine was used to press the mixtures from its top through the iron block (Fig. 4A). The pressure used is 60KN and the time for keeping the pressure is 10 s. After the pressing process finished, the mould was blocked up for *ca.* 4 cm from the bottom and the pressing machine was also used to press the brick-samples out of the mould (Fig. 4B). Finally, the brick-samples (Fig. 3B) were stored in the open air and the water was spraying to its surface periodicity to keep humidity. The properties of the bricks including compress strength, freeze-thaw resistance and drying-

TABLE-2
COMPRESS STRENGTH OF BRICKS OF DIFFERENT FORMULAE

No.	Cement (%)	Sand /bottomash (%)	CaO/$Ca(OH)_2$ (%)	$CaSO_4$ (%)	Fly ash (%)	H_2O (%)	Compress strength (7d)/Mpa	Compress strength (28d)/Mpa
A1	4	25 (s)^a	10(c)^b	5	56	15	10.28	15.25
A2	6	25 (s)	10(c)	5	54	15	10.97	18.13
A3	8	25 (s)	10(c)	5	52	15	12.97	20.41
A4	8	20 (s)	10(c)	5	57	15	11.78	18.81
A5	8	25 (s)	10(c)	5	52	15	12.97	20.63
A6	8	30 (s)	10(c)	5	47	15	11.72	17.69
A7	8	10 (b)^c	10(c)	5	67	15	14.38	20.34
A8	8	15 (b)	10(c)	5	62	15	15.44	21.63
A9	8	20 (b)	10(c)	5	57	15	13.56	19.66
A10	8	25 (b)	10(c)	5	52	15	13.28	17.63
A11	8	30 (b)	10(c)	5	47	15	11.69	17.41
A12	8	15 (b)	10(c)	5	62	15	14.44	20.63
A13	8	15 (b)	12(c)	5	60	15	16.69	23.22
A14	8	15 (b)	14(c)	5	58	15	14.28	19.75
A15	8	15 (b)	10(h)^d	5	62	15	12.72	17.88
A16	8	15 (b)	12(h)	5	60	15	12.94	18.69
A17	8	15 (b	14(h)	5	58	15	12.69	16.50
A18	8	15 (b)	12(c)	3	62	15	11.50	18.41
A19	8	15 (b)	12(c)	4	61	15	14.00	20.38
A20	8	15 (b)	12(c)	5	60	15	14.69	21.22
A21	8	15 (b)	12(c)	6	59	15	12.75	18.50

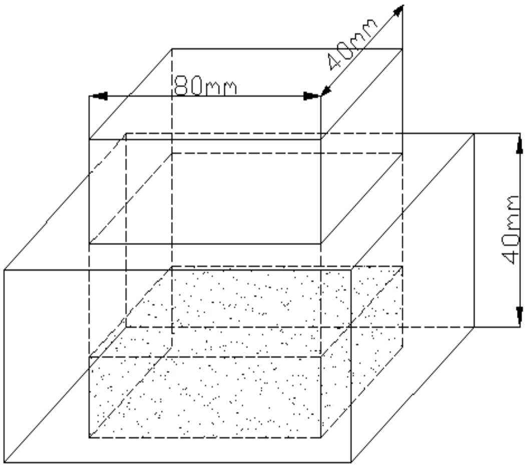
^{a}Sand; ^{b}CaO; ^{c}Bottom ash; ^{d}$Ca(OH)_2$

TABLE-3
FREEZE-THAW RESISTANCE AND COMPRESS STRENGTH OF THE BRICKS ADDED DIFFERENT ADDITIVES

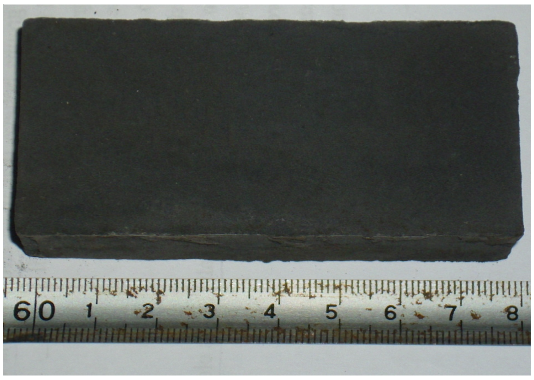
No.	Additives	Ratio (%)	Density (g/cm^3)	Freeze-thaw resistance		Water absorption for 24 h (%)	Compress strength (MPa)	
				Loss of mass (%)	Compress strength (MPa)		7d	28d
B0	–	–	1.33	0.39	17.83	31.23	14.69	21.22
B1	Na_2SiO_3	0.10	1.35	0.35	20.13	32.01	13.78	19.44
B2	Na_2SiO_3	0.50	1.35	0.36	18.54	31.47	12.16	19.31
B3	Na_2SiO_3	1.00	1.37	0.31	18.51	31.02	12.38	19.41
B4	NaCl	0.10	1.33	0.35	21.41	31.66	15.66	23.91
B5	NaCl	0.50	1.30	0.34	20.60	31.57	14.84	22.38
B6	NaCl	1.00	1.34	0.34	20.97	30.88	14.61	22.06
B7	Triethanolamine	0.01	1.34	0.30	15.83	32.39	14.16	20.50
B8	Triethanolamine	0.05	1.34	0.30	15.20	31.59	15.34	22.50
B9	Triethanolamine	0.10	1.34	0.35	13.16	33.54	10.94	18.81
B10	Na_2CO_3	0.10	1.32	0.37	18.09	31.40	15.84	22.19
B11	Na_2CO_3	0.50	1.33	0.37	18.41	30.73	15.31	21.44
B12	Na_2CO_3	1.00	1.31	0.38	18.09	31.07	15.34	21.88
B13	Nuclei	0.50	1.38	0.31	20.64	30.2	15.78	23.84
B14	Nuclei	1.00	1.33	0.33	19.18	29.6	15.22	22.03
B15	Nuclei	2.00	1.35	0.35	18.13	29.2	15.08	22.09

TABLE-4
PHYSICAL PARAMETERS OF THE PP FIBER

Type of fiber	Single-wire bundle	Density	0.91 g/cm^3
Equivalent diameter	18-20 μm	Length	3 mm
Tensile strength	≥ 400 MPa	Elastic modulus	≥ 3500 MPa
Elongation at break	8-30 %		

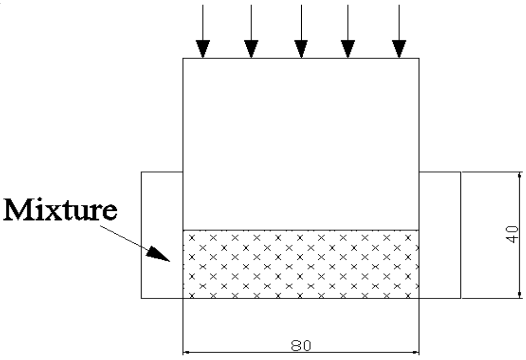


(A) Brick mould

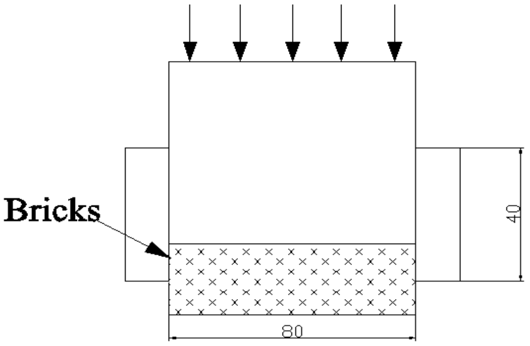


(B) Brick sample

Fig. 3. Brick mould and brick sample



(A) Pressing brick



(B) De-mold brick

Fig. 4. Schematic diagram of manufacturing process

shrinkage were tested referring to the Chinese standard for fly ash based bricks (JC239-2001).

RESULTS AND DISCUSSION

Compress strength: Table-2 shows the formula and compress strength results of every experiment systems. From the system A1 to A3, it suggests that the compress strength is positive correlation with the ratio of cement. When the ratio of cement growing from 4 to 8 %, the compress strength of 7d and 28d increase from 10.28 to 12.97 MPa and 15.25 to 20.41 Mpa, respectively. Both the sand and bottom ash could be used as light aggregate. Systems A4 to A11 compare the effect of them on compress strength. The results suggest that there exists an optimum added ratio for both sand and bottom ash. More or less than the optimum added ratio leads to decrease of the compress strength. For sand systems, the compress strength reaches the highest 12.97 Mpa (7d) and 20.63 Mpa (28d) when the ratio is 25 % while for bottom ash system, the compress strength comes to the highest 15.44 Mpa (7d) and 21.63 Mpa (28d) when the added ratio is 15 %. Considering that the bottom ash is also a type of solid wastes from the power plant, it should be a more economical light aggregates material than the normal sand. System A12 to A21 show how the ratio of CaO, $Ca(OH)_2$ and $CaSO_4$ effect the compress strength. From them, it could be seen that the compress strength reaches the highest data when the ratio is 12 % for both CaO and $Ca(OH)_2$ and 5 % for $CaSO_4$. Summarizing the results from all systems, the formula of highest compress strength is 8 % cement, 15 % bottom ash, 12 % CaO, 5 % $CaSO_4$, 60 % CFBC fly ash and 15% water and the data excess the Chinese standards for fly ash basic-bricks.

Freeze-thaw resistance: Besides the compress strength, the freeze-thaw resistance is another important property of the fly ash basic-bricks. In order to improve the property of the bricks, the water-glass ($SiO_2/Na_2O = 3.75$), sodium chloride, triethanolamine, sodium carbonate and nuclei are used as

TABLE-5
PROPERTIES OF THE BRICKS ADDED PP FIBER AND COMPREHENSIVE ADDITIVES

Additives	Compress strength (7d)/Mpa	Compress strength (28d)/Mpa	Dry shrinkage	Density (g/m^3)	Freeze-thaw resistance		Water absorption for 24h (%)
					Weight loss (%)	Compress strength (MPa)	
PP fiber	18.56	25.28	0.69	1.32	0.35	21.46	31.41
Comprehensive admixtures	19.00	27.22	0.65	1.46	0.17	21.96	27.20

additives. Table-3 shows the added ratio and results of freeze-thaw experiments. It is clear that the water-glass, NaCl, Na_2CO_3 and nuclei take a positive effect to the property. As it showed, before they are added, the compress strength of the bricks after freeze-thaw circles is 17.83 Mpa. And then, the compress strength increase to 20.13 Mpa (0.1 % water-glass), 18.54 Mpa (0.5 % water-glass), 18.51 Mpa (1 % water-glass), 21.41 Mpa (0.1 % NaCl), 20.60 Mpa (0.5 % NaCl), 20.97 Mpa (1 % NaCl), 18.09 Mpa (0.1 % Na_2CO_3), 18.41 Mpa (0.5 % Na_2CO_3), 18.09 Mpa (1 % Na_2CO_3) and 20.64 Mpa (0.5 % nuclei), 19.18 Mpa (1 % nuclei), 18.13 Mpa (2 % nuclei). On the other hand, the effect by the triethanolamine is negative because the compress strength after freeze-thaw circles reduces to 15.83, 17.20, 13.16 Mpa when 0.01, 0.05, 1 % triethanolamine is added. Meanwhile, Table-3 tells us how the additives influence the 7d and 28d compress strength of the samples. As the Table-3, the effect by water-glass to compress strength is negative, although it could enhance the freeze-thaw resistance of the bricks. For example, the 7d compress strength reduce to 13.78 Mpa, 12.16 Mpa and 14.38 Mpa and the 28d compress strength decline to 19.44, 20.44 and 20.41 Mpa when 0.1, 0.5 and 1.0 % water-glass is added, respectively. In addition, the losses of mass of all the bricks are from 0.30 to 0.39 % which reaches the Chinese standards (2 %). Taking the results of Table-3 into account, the Na_2CO_3, NaCl and nuclei are the most suitable additives for improving the freeze-thaw resistance of the CFBC-basic bricks and the optimum added ratio is 0.1 % for NaCl and Na_2CO_3, 0.5 % for nuclei.

Drying shrinkage: According to Chinese standards for fly ash basic bricks, the drying shrinkage of the bricks must be smaller than 0.75 mm/m. For optimizing the property of the bricks, the PP fiber is added to the formula. Table-4 shows the physical parameters of the PP fiber and Table-5 shows the results of all the properties after pp fiber added. As the Table-5, adding the PP fiber does not decrease the drying shrinkage from 0.80 mm/m to 0.69 mm/m only, but the compress strength of 7d, 28d and after freeze-thaw circles grows to 18.56, 25.28 and 21.46 Mpa, respectively also.

Table-5 also shows the results of all the additives added at the same time (NaCl 0.1 %, Na_2CO_3 0.1 %, nuclei 0.5 %, PP fiber 0.1 %). It shows that the properties of the bricks reach the highest when the comprehensive additive is added. The drying shrinkage decreases to 0.65 mm/m, meanwhile, the compress strength of 7d, 28d and after freeze-thaw circles grows to 19.47, 27.22 and 21.96 Mpa, respectively.

Conclusion

The CFBC could be used for manufacturing unfired-bricks through drying pressure molding method. The optimum formula for compress strength is 8 % cement, 15 % bottom ash, 12 % CaO, 5 % $CaSO_4$ 60 % CFBC fly ash and 15 % water. The 7d and 28d compress could come to 16.69 Mpa and 23.22 Mpa, respectively. The bottom ash is an effective and economical substitute to the normal sand as the light aggregates. The Na_2CO_3, NaCl and Nuclei are the suitable additives for improving the freeze-thaw resistance of the bricks. The PP fiber could enhance the drying shrinkage and the optimum property of the bricks could be gained when the comprehensive additives (NaCl 0.1 %, Na_2CO_3 0.1 %, nuclei 0.5 %, PP fiber 0.1 %) are used. Therefore, the CFBC fly ash has the potential to manufacture unfired-bricks when using the dry pressing molding method, although the chemical compositions, mineral phases and morphology are very different from typical F-fly ash.

ACKNOWLEDGEMENTS

This work was financially supported by the Natural Science Foundation of China (Grants 51008154), State Key Laboratory of Pollution control and Resource Reuse of China and Sinopec Jinling Petrochemical Corporation.

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