

Manufacturing F-Fly Ash Based Geopolymer Mortars Using CFBC Bottom Ash as Fine Aggregates

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Summary: This paper presents a study on F-fly ash based geopolymer mortars using CFBC bottom ash as fine aggregates. The alkali activators were sodium silicate, sodium hydroxide and potassium hydroxide solutions. The study included the impact of aggregates addition amount, alkali activator, aggregate type on compressive as well as of flexural strength. The original materials and reaction products were analysed by XRD, FT-IR and SEM/EDS and a leaching system was conducted to measure the reactivity of CFBC bottom ash in alkaline solution. Best physics strength could be got when addition amount is 0.75-1.25 ($W_{CFBC\ bottom\ ash}: W_{fly\ ash}$). Sodium hydroxide solution shows better performance than potassium hydroxide in the gaining of strength. Sodium silica solution could greatly improve the strength and the best value was obtained when modulus is 1.2. The mortars prepared by CFBC bottom ash exhibited higher strength than the one by standard sand. The compressive and flexural strength of mortars were up to 60MPa and 10MPa. The main product of reaction was amorphous alkali aluminosilicate gel and denser microstructures could be obtained by using CFBC bottom ash as aggregates.

Keywords: CFBC, CFBC bottom ash, geopolymer, mortar, fly ash.

Introduction

Emission of NO_x and SO_2 bring many environment problems like acid rain and respiratory diseases. Coal firing plants are one of main emission resources of NO_x and SO_2 . As the fastest developing country, coal firing plants occupy an important place in Chinese energy structure and result in lots of serious atmosphere pollutions. To improve atmosphere quality, the Chinese government suggests that the classic coal firing technology should be replaced by Circulating fluidized bed combustion (CFBC) technology by which the emission of NO_x and SO_2 could be controlled [1-3]. So far, about 1000 CFBC firing boilers have been built around China and the number has been increasing [4]. However, because the properties of CFBC bottom ash are significantly different from these of conventional pulverized coal (PC) combustion fly ash [5, 6], the effective technologies to recycle CFBC bottom ash (CBA) are very few. Almost all of CBA is stored at local power plants or placed in landfills, which creates another enormous environment burden on China and seriously restricts firing technology innovation. After the first presentation of Davidovits's work [7], geopolymer, as an advanced "green" material, has attracted lots of attentions around world. Plenty of researchers have reported its potential of using to act as advanced material to be a classic Portland cement substitute [8, 9]. Now, most of published papers pay attention to manufacture geopolymer from industry solid wastes including fly ash, furnace slag and

normal bottom ash. Xu developed a new thermostable geopolymer from CBA [10]. Considering the huge amounts of un-used CBA, some more economic, simple, convenient recycle method must be found.

On the other hand, many solid wastes have been recycled as aggregates for Portland-cement based concrete. Torkittikul suggested that the ceramic waste be used as fine aggregates for Poland cement and fly ash concrete [11]. Akash Rao presented that the construction and demolition waste be recycled for concrete [12]. Partially hydrated old concrete was used as an aggregate by Amnon Katz [13]. Khaldoun Rahal reported that recycled coarse aggregate taken from old buildings be used as concrete aggregates [14]. Meanwhile, many solid wastes were used for preparing geopolymer concrete aggregates. Daniel L.Y. Kong prepared geopolymer concrete using crushed old basalt and river sand as the aggregates [15]. W.K.W. Lee synthesized geopolymer concretes using many siliceous aggregates. They include sand, basalt, marble and siltstone [16]. Hossein Rostami added sand and gravels to produce geopolymer materials and advised that it be much less expensive than comparable high-strength Portland cement concrete [17]. Hamzah Fansuri used geopolymerisation method to make coal fly ash aggregates [18]. Until now, no papers have been written about the feasibility of utilizing CBA as aggregate for geopolymer mortar or concrete.

This paper focuses on synthesizing geopolymer mortar using CBA as fine aggregates. The influencing factors studied included aggregates addition amount, alkaline type and composition of activator solutions. Some properties like compressive/ flexural strength and working flow were compared with Chinese standard sand. XRD, FT-IR and SEM were applied to investigate original CBA and reaction products. The results of this paper may give us a new efficient way to recycle CBA and a basic understanding of reaction mechanism.

Results and Discussions

Stock paid much attention to the effect of aggregates on properties of concrete and suggested that the relation between them be non-linear and that the compressive strength not increase until the added ratio is more than 30% [19]. Meddah gained the similar results and showed that the coarse aggregates content growing from 44% to 47% could lead to an increase in the compressive strength [20]. Wu studied the optimum content of copper slag as a fine aggregate in high strength concrete and be concluded that less than 40% copper slag as sand substitution can achieve a high strength concrete that comparable or better to the control mix [21]. It could be seen that addition amounts of aggregates play an important role in the properties of concrete and it should be controlled in a reasonable range. The approximate results could be gained in our geopolymer mortars (Table-1). It is demonstrated by Table-1 that the highest physics strength was obtained when addition amount is 1 ($W_{CFBC \text{ bottom ash}} : W_{\text{fly ash}}$). The 7d and 28d compressive strength reached 50.3MPa and 57.5MPa, which were 249% and 230% higher than pure paste samples (No.1 in Table-1). Other moderate value could be gained when addition amount was 0.75 (7d, 46.3MPa and 28d 53.2MPa) and 1.25 (7d 47.5MPa and 28d 54.2MPa). Deviation from this optimum range (0.75-1.25) would lead to a serious decreasing of physics strength. The 28d compressive strength reduced to 31.7MPa, 21.9MPa and 17.8MPa when addition amounts increased to 2, 2.5 and 3.

No.13 to 16 in Table-1 showed how alkaline metal affect the compressive strength. There existed two views about the impact according to the literatures. Palomo suggested that the compressive strength of geopolymer samples manufactured by 12M NaOH solution be higher than ones of 18M KOH solution [22]. Komljenovi'c summarized Palomo's data and suggested the activation potential of NaOH be higher than KOH [23]. On the contrary, Xu studied the effect of alkali metals on the

stibnite/kaolinite and fly ash based geopolymer materials and advised that Na^+ enhance Al and Si dissolving from the raw material but the K^+ show better performance in the development of compressive strength [24]. Our experiments agreed with Palomo's and Komljenovi's findings. It could be seen that the sample prepared by NaOH exhibit excellent physical properties regardless of the concentration and curing time. The 7d and 28d compressive strength of 10M NaOH reached 50.3MPa and 57.5MPa respectively while the data of 10M KOH only achieved 21.9MPa and 47.5MPa. The similar results could be got in 5M alkaline solutions. The 28d compressive and flexural strength of 5M KOH were only 17.5MPa and 4MPa, which were 14% and 29.8% lower than 5M NaOH (No.16 in Table-3).

No.10, 11 and 12 in Table-3 indicated how the modulus of sodium silicate solution affected the compressive strength. It suggested that 1.2 modulus sodium silicate give higher compressive strength under all the curing times than 1.5 and 2.0 modulus. The 7d and 28d compressive strength of 1.2 were 38.1MPa and 60.1MPa, respectively (10.7% and 19.2% higher than 1.5 and 164% and 49.8% higher than 2.0). Escalante Garcia investigated the effect of modulus on the compressive strength of pulverized fuel ash and blast furnace slag blend geopolymer and suggested that 4% Na_2O and 1.5 modulus give the highest strengths for 100% BFS but for 50% blends, the strengths be best when modulus was 1-1.5 [25]. A more detailed exposition was performed by Silva and it was advised that the compressive strength of metakaolin based geopolymer be depend on the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of mixtures and optimum ratio be 3.0-3.8 ($\text{SiO}_2/\text{Al}_2\text{O}_3$) and 1($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) [26]. Table-2 showed the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratios of our mixtures. As Table-2, the excellent properties of our geopolymer mortar could occur when $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ were 4.39 and 0.88, respectively. This is different to the ratios suggested by Silva. It is easy to understand that optimum ratio should be changed when different raw materials were used. Among raw materials for geopolymer synthesizing, metakaolin is a highly responsive reactant and Silva claimed that SiO_2 and Al_2O_3 dissolve completely in a short time [26]. The reactivity of F-fly ash should be lower than metakaolin and longer time must be spent for the dissolving of SiO_2 and Al_2O_3 dissolving. On the other hand, SiO_2 and Al_2O_3 also could be dissolved from CFBC bottom ash (Fig. 3). These may lead to the optimum ratios for our geopolymer mortar is different to those of metakaolin.

Table-1: Compressive and flexural strength of geopolymer mortar.

No.	Alkali System	Ratio (BA:FA)	Compressive strength/MPa				Flexural strength/MPa				
			3d	7d	14d	28d	3d	7d	14d	28d	
1		0	-	14.4	-	17.4	-	2.16	-	3.4	
2		0.5	-	21.9	-	30.4	-	2.36	-	3.8	
3		0.75	-	46.3	-	53.2	-	3.74	-	4.9	
4		1	-	50.3	-	57.5	-	7.75	-	9.1	
5	10M NaOH	1.25	-	47.5	-	54.2	-	7.39	-	8.5	
6		1.5	-	29.7	-	38.6	-	7.08	-	8.0	
7		2	-	23.1	-	31.7	-	6.75	-	7.3	
8		2.5	-	15.9	-	21.9	-	4.15	-	6.8	
9		3	-	12.2	-	17.8	-	3.66	-	5.3	
10		1.2 ^a	1	34.3	38.1	55.6	60.1	5.15	6	6.35	7.1
11	Sodium Silica	1.5	1	21.3	34.4	37.8	50.4	4.75	5.72	7.19	7.75
12		2.0	1	9.1	14.4	14.6	40.1	3.34	4.73	5.75	6.2
13	10M KOH	1	1	6.3	21.9	33.1	47.5	1.43	2.52	5.00	7.3
14	10M NaOH	1	1	15.4	50.3	51.9	57.5	4.52	7.75	8.15	9.1
15	5M KOH	1	1	5.1	8.9	12.9	17.5	1.8	2.7	3.9	4
16	5M NaOH	1	1	10.5	12.9	15.8	20.4	2.1	2.9	4.8	5.7
17	10M KOH	1/Sand	1	4.1	13.9	23.7	35.6	1.2	2.3	3.4	5.7
18	10M NaOH	1/Sand	1	9.25	21.3	37.5	41.7	3.1	4.56	5.3	6.15

Modulus of sodium silica solution

Table-2: Relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of mixtures and compressive strength.

Modulus.	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	Compressive strength/MPa	
			7d	28d
1.2	4.92	0.880	38.1	60.1
1.5	5.08	0.774	34.4	50.4
2.0	5.28	0.647	14.1	40.1

van Deventer suggested that there be three stages during the geopolymerisation process: the dissolution of solid reactants, transferring of the dissolved species from the solid surface into a gel phase, nucleation and condensation of the gel phase. Since the geopolymerisation process always occurred in an environment with insufficient solution and space to react with (the liquid to solid ratio applied in geopolymer manufacturing often ranges from 0.3-0.4), the reaction products were amorphous “gel” other than crystalline zeolite [27]. Fig1 showed the XRD patterns of the geopolymer mortars. All of crystalline peaks belonged to quartz (including 2 θ : 26.74°, 20.96°, 50.26° et al) and mullite (including 2 θ : 26.24°, 25.98°, 35.26° et al), which came from original CBA and F-fly ash. Since almost all the mineral of standard sand is crystalline quartz, the peak of quartz become much stronger in the patterns of mortar prepared by standard sand (Fig1-a). The results of XRD patterns proved that there be no new crystalline forming during the reaction and the reaction products should be a semi-crystalline amorphous “gel”, which has been generally accepted.

Fig. 2 showed SEM micrographs of geopolymer mortars. Compared with original F-fly ash, almost all the spherical glass particles disappeared and only few small ones could be found. The main product was an amorphous aluminosilicate “gel” phase (Fig. 3-A and B). With the help of EDS, we know that composition of “gel” is 3.84% Na, 10.75% Al, 21.7% Si and 62.2% O. The microstructure and composition were typical for fly

ash based geopolymer and were obtained by many researchers [28-30]. The mortars prepared by CBA gained much denser microstructures and almost all of particles were pasted together. On the contrary, Fig. 2-B exhibited looser microstructures and many small irregular particles could be observed. It is clear to understand that denser microstructures bring higher physics strength. 28d compressive strength adding CBA were 57.5MPa (10M NaOH) and 47.5 MPa (10M KOH) respectively (37.8% and 33.4% higher than standard sand). More details about microstructures could be found in Fig. 2-C and D. Lee investigated the reaction products of geopolymer used natural mineral aggregates including sand and natural rocks and suggested that there be some porous interface between aggregates and geopolymer binders [16]. The approximate observations are shown in Fig. 2-D and there exists a considerable porous void in the boundaries between sand and geopolymer binders. However, CBA particle tightly insert in geopolymer binders and no distinct crack and porous void was found (Fig. 2-C). Lee told us that denser microstructures could be gained through adding more soluble silicate into original solutions [16]. It is demonstrated in Fig. 3 that Si and Al could be dissolved under strongly alkaline environment and we speculated that the similar efficiency of adding silica be got when CBA aggregates used. The additional Si and Al dissolved from CBA should effectively accelerate the “gel” forming process, which improve the compactness of microstructures. Furthermore, because the dissolving tends to occur on the contact surface, the binding capacity of aggregates should be greatly enhanced, which causes porous voids disappear. Based on our results, many further studies must be carried out to improve our understanding of the positive effective of CBA on microstructure of geopolymer mortars.

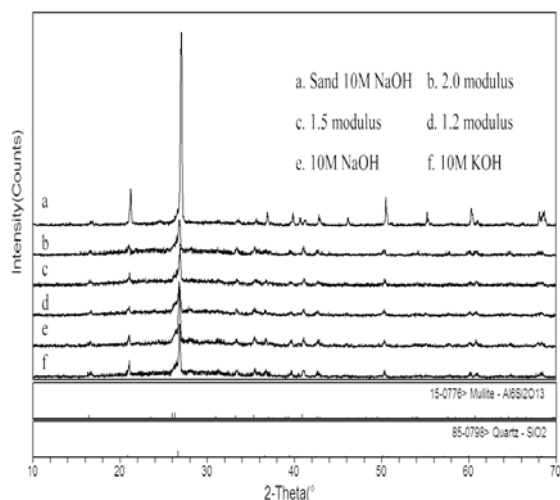


Fig. 1: XRD patterns of reaction products.

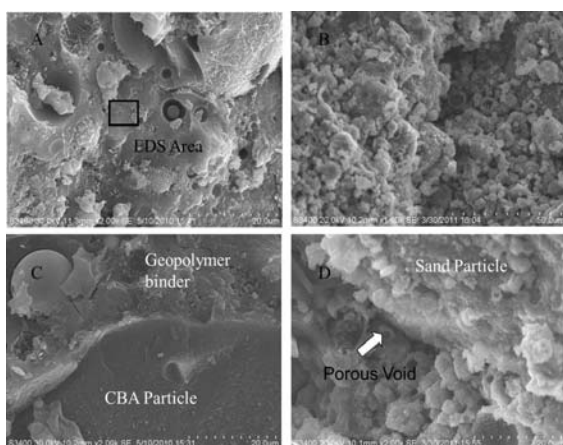


Fig. 2: SEM micrographs of reaction products after 14 d (A and C. CBA system, B and D. Sand system).

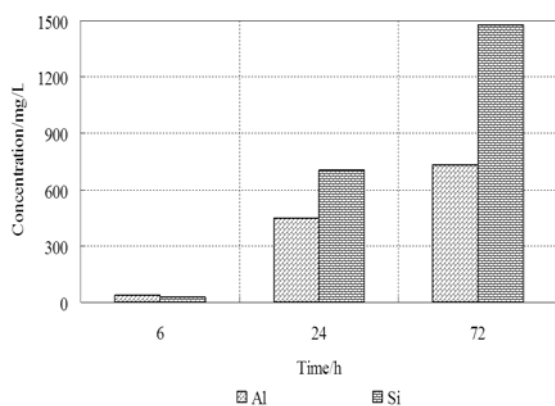


Fig. 3: Concentration of alkaline leaching solution.

Experimental

The CFBC bottom ash used in this investigation came from a 220 t/h Pyroflow coal firing CFBC boiler using limestone as the SO_2 sorbent in Power Plant at the Sinopec Jinling Petrochemical Corporation state in Jiangsu province. The $45\mu\text{m}$ residual is 95%. The density is about $2.4 \times 10^3 \text{ kg/m}^3$. The F-fly ash used for synthesizing geopolymer mortar was gained from a normal coal firing boiler in Huaneng Nanjing power plants state (Jiangsu province). The $45\mu\text{m}$ residual was 5%. Al_2O_3 and SiO_2 of CBA and F-fly ash were both higher than 80% (Table-3). The standard sand (GB/T17671-1999) was bought from Jiangsu Research Institute of Building Science co. ltd. The CBA and standard sand possess similar particles size distributions except for the range from 0.15-0.5mm (Fig. 4). To be an inhomogeneous solid waste, the particles of CBA could be divided by color into three varieties (Fig. 4). The peak of quartz (including 2θ : 26.74° , 20.96° , 50.26° etc.) could be found in all 3 XRD patterns and margarite ($\text{CaAl}_2(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$, including 2θ : 28.04° , 35.64° , 42.56° etc.) only exit in particle B (Fig. 4). Because margarite forms preferentially along with the dark graphite during the geological activities, the mineral should resource from raw firing coal. The FT-IR spectra of CBA includes bands at about 3443 cm^{-1} (due to O-H stretching vibration), 1634 cm^{-1} (due to O-H bending vibration), 1432 cm^{-1} (due to molecular and hydroxyl water/carbonate bond), 1093 cm^{-1} (due to asymmetric stretching vibration of Si-O-Si group), 798 cm^{-1} (due to Si-O-Si stretching vibration quartz), 781 cm^{-1} (due to Si-O-Si stretching vibration quartz) and 470 cm^{-1} (due to in plane O-Si-O bending vibration) (Fig. 5) [31-33].

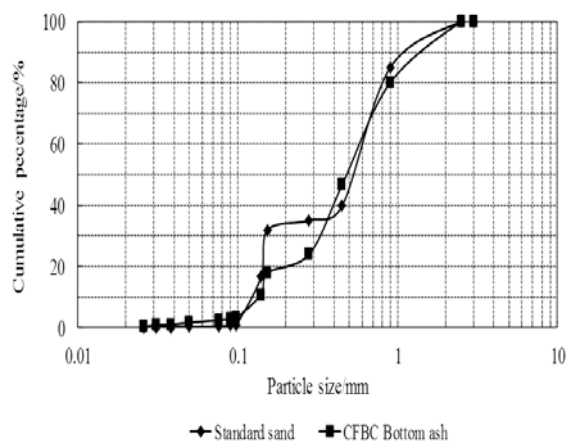


Fig. 4: Particle size distribution of CFBC bottom ash and Standard sand.

Table-3: Chemical composition of CFBC bottom ash (%).

Oxides	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	Na ₂ O	MgO	K ₂ O	TiO ₂	P ₂ O ₅	LOI*
F-Fly ash	56.71	28.9	2.34	4.02	0.46	0.04	1.32	1.07	0.12	4.81
Bottom ash	61.2	26.8	2.1	4.4	0.34	0.61	1.54	0.94	0.07	1.7

*LOI = loss on ignition at 960 °C.



Fig. 5: Photograph and XRD patterns of CFBC bottom ash particles.

The alkaline solutions used for manufacturing geopolymer mortars were sodium silicate solution (Modulus, SiO₂/Na₂O: 1.2, 1.5 and 2.0), sodium hydroxide solution (5M, 10M), potassium hydroxide solution (5M, 10M). The mass ratio between activator liquid and F-fly ash was 0.5. The addition amount of aggregates ($W_{CFBC \text{ bottom ash}}/standard \text{ sand} : W_{fly \text{ ash}}$) was from 0.5-3. Fly ash and alkaline solution were mixed by planet cement-mixer for 4 min (2 min under 62 R/ min and 2 min under 125 R/min). Then aggregates were added to mixtures and mixed for additional 2 min under 125 R/min. Next, the mixtures were casted into an standard mold (4cm×4cm×16cm) (GB/T17671-1999) and the mold were stored with mixtures in 40°C and 100%

humidity for 24h before being de-molded. The curing condition was also 40°C and 100% humidity after de-molding. The compressive and flexural strength were tested after 3d, 7d, 14d and 28d by a 300KN compressive testing machine and 6KN electric flexure testing machine. The flow of mortar was tested according to Chinese standard (GB/T176-2008) and results were shown in Fig. 7. Mortars added CBA achieved a litter lower value than standard sand under every addition amounts. X-ray diffraction patterns for the powder samples were taken on a Shimadzu XD-3A diffractometer, using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$). The morphologies of the composites were observed on X-650 scanning electron microscope (SEM). FT-IR spectras were recorded on a Bruker VECTOR 22 Fourier transform spectrometer model VECTOR 22 using KBr pressed discs. An Optima 5300DV inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin Elmer, USA) was used to detect the composition of leaching solutions.

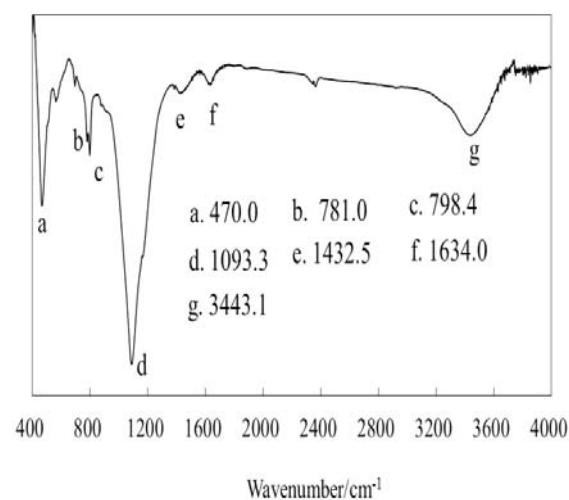


Fig. 6: FT-IR spectra of CFBC bottom ash.

The alkaline leaching experiments were conducted with 2.5g aggregates sample (CFBC bottom ash/ standard sand) (after being milled for 60min) with 100g NaOH (10M) solution. The sample and alkaline solutions were mixed in a 250ml Teflon bottles. The bottles were fixed in a water-base which had a shaking instrument to keep the sample particles suspended in the alkaline solution. The reaction time was 6h, 24h and 36h. The temperature was 40°C.

After leaching, the mixture solutions were filtered by 0.6 μ m filter membrane with a vacuum pump and the concentrations of silica and aluminum in the solution were detected by ICP-OES.

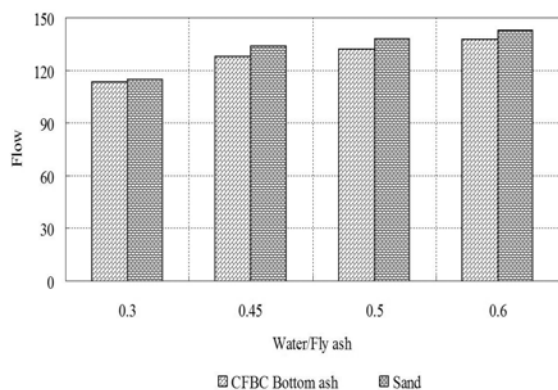


Fig. 7: Flow of F-fly ash mortars (mortars prepared according to GB/T176-2008).

Conclusions

The present study explored the use of CBA as fine aggregates for F-fly ash based geopolymer mortars. Certain aggregates addition amount (0.75-1.25 BA: FA) can introduce give better compressive and flexural strength of mortars, with values up to 57.7MPa and 9.1MPa. NaOH solution yielded a higher physics strength than KOH. The mortars prepared by silica solution with 1.2 modulus exhibited highest compressive and flexural strength (60.1MPa and 7.1MPa). Typical geopolymerisation reaction was occurred and the main reaction products were aluminosilicate amorphous “gel”. The mortars prepared by CBA showed higher compressive and flexural strength than the one by standard sand and denser microstructures could be obtained by using CFBC bottom ash as aggregates.

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