



Synthesis of thermostable geopolymer from circulating fluidized bed combustion (CFBC) bottom ashes

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ABSTRACT

Circulating fluidized bed combustion (CFBC) bottom ashes (CBAs) are a class of calcined aluminosilicate wastes with a unique thermal history. While landfill disposal of hazardous element-containing CBAs poses serious challenge, these wastes have long been neglected as source materials for geopolymer production. In this paper, geopolymerization of ground CBAs was investigated. Reactivity of the CBAs was analyzed by respective dissolution of the ashes in 2, 5, and 10N NaOH and KOH solutions. Geopolymer pastes were prepared by activating the CBAs by a series of alkalis hydroxides and/or sodium silicate solutions. Samples were cured at 40 °C for 168 h, giving a highest compressive strength of 52.9 MPa. Of the optimal specimen, characterization was conducted by TG-DTA, SEM, XRD, as well as FTIR analyses, and thermal stability was determined in terms of compressive strength evolution via exposure to 800 or 1050 °C followed by three cooling regimes, i.e. cooling in air, cooling in the furnace, and immersing in water. The results show that CBAs could serve as favorable source materials for thermostable geopolymers, which hold a promise to replace ordinary Portland cement (OPC) and organic polymers in a variety of applications, especially where fire hazards are of great concern.

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1. Introduction

Geopolymers are a family of emerging synthetic compounds that were firstly proposed by Joseph Davidovits in the late 1970s and early 1980s [1]. As described by Davidovits, geopolymers are Si–O–Al three-dimensional inorganic polymeric materials containing a variety of amorphous to semi-crystalline phases. The framework of geopolymers consists of tetrahedral coordination of Si⁴⁺ and Al³⁺ cations linked by oxygen bridges, with the negative charges on AlO₄⁻ groups being balanced by alkalis cations (typically Na⁺ and/or K⁺) [2,3]. Nominally, the empirical formula of geopolymers can be referred to as



where M represents the alkalis cation; z, the molar ratio of Si to Al (1, 2 or 3); and n, the degree of polycondensation [3,4].

Compared with conventional ordinary Portland cement (OPC), geopolymers have demonstrated quite a few advantages, such as high mechanical strength, excellent chemical resistance, inherent fire and heat resistance, low thermal conductivity, no toxic fume emission when heated, low shrinkage and deleterious alkali aggregate effect, rapid controllable setting and hardening, as well as precise mouldability [3,5,6]. The intrinsic fire and heat resistances

of geopolymeric materials are of interests [7,8]. While most organic polymers soften and ignite at 400–600 °C [7], and OPC experiences decomposition of its Ca(OH)₂ content at around 500 °C [9], geopolymers are found to be nonflammable and heat resistant at high temperatures up to 1000 °C [5,10], making them a promising material for a variety of applications, such as commercial aerocrafts, marine ships and platforms, ground transportations, etc., where fire hazard and heat resistance are important design considerations due to restriction of egress.

Previous research [11] has shown that geopolymers synthesized from calcined source materials, e.g. fly ashes, blast furnace slags, and metakaolinites, generally show higher compressive strength than those derived from classic non-calcined ones, such as kaolinites, albites, stilbites, and mine tailings, suggesting that calcined source materials lead to higher geopolymerization degrees. Therefore, non-calcined aluminosilicate sources are usually subjected to calcinations at 500–750 °C for several hours prior to geopolymerization [8,12], which requires remarkable energy consumption. On the other hand, the calcined source materials, except for metakaolinites, are predominantly industrial wastes, whereas the non-calcined ones are largely natural minerals.

As the largest volume of calcined industrial wastes, coal fly ashes have been studied extensively as source materials for geopolymer synthesis, not only because of the sound properties of the obtained products, but also due to the significant environmental benefits derived from remarkably reduced CO₂ footprint and energy consumption in comparison with those of OPC [5,13]. However, other

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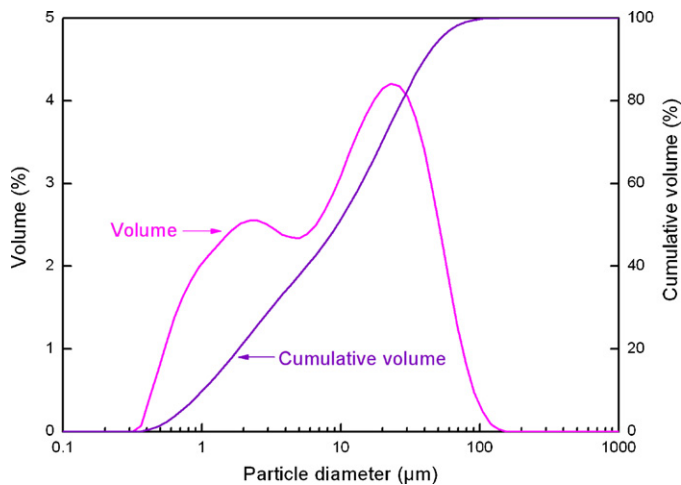


Fig. 1. Particle size distribution of ground CFBC bottom ashes.

minor calcined wastes such as coal bottom ashes have received less attention. Only limited researches have been reported on synthesis, characterization, and application of bottom ash geopolymers [14–16]. This is partly because coal bottom ashes are much bigger in size (up to 10 mm) than their fly counterparts, which means that, instead of direct geopolymerization, coal bottom ashes must be ground to a proper fineness prior to the synthesis [16]. Moreover, to the authors' knowledge, no literature has been found on geopolymerization of the specific circulating fluidized bed combustion (CFBC) bottom ashes (CBAs), which in fact narrows the recycle and utilization of these industrial wastes.

It has been reported that the microstructures and properties of geopolymers depend greatly on the nature of initial source materials, even though the macroscopic characteristics may appear similar [3,11,17]. In addition to the chemical composition, the thermal history of source materials also plays a significant role on determining the geopolymerization behaviors as well as the final properties of the products [18]. As a 'young' member of bottom ash family, CBAs not only contain reasonable alumina and silica contents, but also possess a unique thermal history of heating at 800–900 °C, far lower than those of conventional bottom ashes (ca. 1200–1400 °C) [19,20]. Besides, CBAs have a retention time of several hours at the heating temperature, which represents an almost ideal condition needed for thermal activation of kaolinic source materials [8,12].

CFBC is an advanced and promising coal combustion technology for power generation, which has met environmental requirements for large reductions in SO₂ and NO_x emissions when burning high-sulphur fuels [21]. Ever since its commercialization in the 1970s, CFBC has gained common acceptance due to lots of advantages, such as low combustion temperature (ca. 850 °C), significantly reduced SO₂ and NO_x emissions, wide fuel flexibility, high combustion efficiency, as well as in situ SO₂ removal [21,22]. While the installation of CFBC units has grown steadily all over the world, the

sizes of CFBC boilers have also increased notably. In China, there are more than 1000 CFBC units in operation currently, with some others still under construction or design [23]. However, the expansion of CFBC capacity has led to significant discharging rates of resultant CBAs, and no efficient disposal of the CBAs other than landfill is available at present. Besides, these wastes usually contain certain heavy metals and hazardous elements, which may potentially contaminate ground and surface waters if not properly disposed.

The objective of this work is, therefore, to investigate the synthesis of geopolymers using CBAs as the source material. Reactivity of the CBAs as well as characteristics of the optimal geopolymer product will be discussed in detail. The thermal stability of selected geopolymer was also studied in terms of compressive strength gain or loss after exposure to high temperatures.

2. Materials and methods

2.1. Materials and sample preparation

CBAs used in this study were derived from combustion of a Chinese soft coal and collected from No. 5 CFBC boiler unit at Sinopec Jinling Petrochemical Power Plant (Nanjing, China). The as-received raw CBAs are coarse and irregular slags with particle dimensions up to 10 mm, much larger than typical coal fly ashes. Raw CBAs were dried at 110 °C for 2 h, followed by pulverization in a ball mill for 75 min. Particle size distribution of the ground CBAs was then measured on a Mastersizer 2000 laser analyzer (Malvern, UK), showing an average particle size (d₅₀) of 9.418 μm, and the result is shown in Fig. 1. Chemical composition of the CBAs was determined by an ARL 9800XP⁺ X-ray fluorescence (XRF), and the major and trace element contents are listed in Table 1.

An industrial grade solid sodium silicate (SiO₂, 60.3 wt%; Na₂O, 26.0 wt%; molar ratio of SiO₂/Na₂O, 2.38), sodium and potassium hydroxides (analytical reagents), as well as deionized water, were employed for making three groups of activating solutions, i.e. groups A, B, and C. Each group consists of three solutions, making a total of nine activators. Activators A1–A3 are sodium and/or potassium hydroxide solutions; B1–B3 are mixtures of sodium silicate and sodium hydroxide solutions; and C1–C3 are blendings of sodium silicate and potassium hydroxide solutions. Compositions of all the activating solutions are detailed in Table 2.

2.2. Geopolymer synthesis

Geopolymers were synthesized by mixing ground CBAs with each activating solution, respectively, for 10 min to form nine homogenous slurries. For each slurry, a proper liquid/solid ratio around 0.5 was applied depending on an acceptable workability. The slurries were cast in triplet moulds of 20-mm cubes and vibrated for 5 min to remove entrained air bubbles. Subsequently, the moulds were sealed with polyethylene film and set in a standard curing box at 40 °C under ambient pressure. After 24 h of setting, the samples were demoulded and subjected to curing at 40 °C in sealed polypropylene boxes for further 120 h. The obtained spec-

Table 1
Major and trace element contents of CFBC bottom ashes.

Major elements as oxide (wt%)											
SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	SO ₃	LOI ^a	
61.17	26.78	2.05	4.35	1.54	0.34	0.95	0.05	0.07	0.09	1.69	
Trace element contents (μg/g)											
Ba	Zr	Sr	V	Cr	Zn	Rb	Cu	Ni	Ga	Y	Pb
408.2	217.3	190.9	118.4	143.0	66.8	74.1	62.6	47.7	31.8	22.4	24.7

^a LOI, loss on ignition at 960 °C.

Table 2
Composition of activating solutions (M, Na and K; R, molar ratio of SiO₂/Na₂O).

Activator ID	Activator type	Content (wt%)			
		NaOH	KOH	SiO ₂	H ₂ O
A1	15N NaOH	37.5	–	–	62.5
A2	15N KOH	–	45.7	–	54.3
A3	15N MOH ($N_K/N_{Na} = 1$)	17.5	24.4	–	58.1
B1	Na-water glass ($R = 1.5$)	19.0	–	22.6	58.4
B2	Na-water glass ($R = 1.2$)	21.0	–	20.3	58.7
B3	Na-water glass ($R = 0.9$)	23.8	–	17.4	58.8
C1	M-water glass ($R = 1.5$)	12.3	8.8	22.0	56.9
C2	M-water glass ($R = 1.2$)	10.1	12.3	18.4	59.2
C3	M-water glass ($R = 0.9$)	8.3	16.9	14.9	59.9

imens were then transferred in an electric blast drying oven for a last 24-h curing and drying at 40 °C before any testing was conducted. Mix designs for all geopolymers at liquid/solid mass ratio around 0.5 are summarized in Table 3.

2.3. Methods of analysis

The reactivity of the ground CBAs was examined by an alkaline dissolution experiment [17]. A sample of 0.50 ± 0.001 g of ground CBAs was immersed in 20 ml of NaOH or KOH solution (2, 5, or 10N) in a polyethylene beaker and stirred magnetically at room temperature. After 5 h of stirring, the solution was filtrated and diluted to 0.02N alkaline concentration, followed by neutralization by 37% HCl. A Perkin Elmer Optima 5300DV inductively coupled plasma optical emission spectrometer (ICP-OES) was employed to analyze the Al and Si concentrations in the neutralized solutions.

Compressive strengths of synthesized geopolymers of all mix designs were determined using a NYL-300 compressive strength testing apparatus (Wuxi Jianyi, China). Geopolymer of the optimal mix design, which led to the highest compressive strength, was selected and subjected to thermal stability test. Six selected specimens were respectively heated in a muffle furnace from ambient temperature to 850 or 1050 °C at a heating rate of 5 °C min⁻¹. After heating treatment at 850 or 1050 °C for 2 h, the specimens were cooled under three cooling regimes, i.e. cooling in the furnace, cooling in air, and immersing in cool water, respectively. The compressive strength gains or losses of the cooled specimens were then determined.

Simultaneous TG-DTA was carried out on a Netzsch STA 449C thermal analyzer to determine the mass loss history of the selected geopolymer at elevated temperatures. The sample was heated in an alumina crucible from 25 to 1350 °C in an inert nitrogen environment. The heating and nitrogen purging rates were kept constant at 10 °C and 25 ml min⁻¹, respectively.

Ground CBAs as well as the selected geopolymer before and after the thermal exposures were characterized via SEM, XRD, and FTIR. The SEM photomicrographs were observed on a Hitachi S-3400N scanning electron microscope. The XRD patterns were obtained by

Table 3
Mix design and calculated molar ratios for CFBC bottom ash geopolymers (M, Na and/or K).

Sample ID	Liquid/solid (mass ratio)	Si/Al	Al/M	H ₂ O/M
GA1	0.50	1.94	0.54	3.54
GA2	0.50	1.94	0.61	3.52
GA3	0.51	1.93	0.53	3.54
GB1	0.50	2.65	1.02	6.26
GB2	0.50	2.58	0.93	5.74
GB3	0.62	2.84	0.52	5.26
GC1	0.50	2.63	1.04	6.25
GC2	0.50	2.52	1.02	6.40
GC3	0.50	2.41	0.95	6.03

an ARL X'TRA high-performance powder X-ray diffractometer with Cu K α radiation generated at 40 mA and 40 kV. Samples were step scanned from 10 to 60° 2 θ at scanning step of 0.02° and scanning rate of 10° min⁻¹. A Nicolet 6700 FTIR Spectrometer was used to record the FTIR spectra.

3. Results and discussion

3.1. Alkaline dissolution

Dissolution of Si and Al from aluminosilicate source materials plays a crucial role in geopolymerization reactions. Although XRD in combination with XRF can provide an estimate of the amorphous components of the source material, they do not reveal how readily these components are available for dissolution [24]. Besides, the extent of dissolution of source materials in alkaline mediums at low solid/solution ratios could be used to predict their behavior at high solid/solution ratios [17]. Therefore, an alkaline dissolution test at solid/solution ratio of 0.025 g/ml was conducted to examine the reactivity of the CBAs for geopolymerization. The results of the test are presented in Fig. 2. As shown in the figure, the CBAs contain reasonable reactive silica and alumina contents [17], suggesting that the ground CBAs may be a favorable source material for geopolymer synthesis.

3.2. Compressive strength

The compressive strengths of geopolymers of all mix designs range from 5.5 to 52.9 MPa, as illustrated in Fig. 3. It is evident that the mechanical properties of synthesized geopolymers depend significantly upon their mix designs. As shown in Fig. 3, the series GB geopolymers, prepared from group B activating solutions and the CBAs, show compressive strengths higher than 35.5 MPa, with specimen GB2 giving the maximum of 52.9 MPa. The series GC geopolymers, activated by group C solutions, also exhibit high compressive strengths ranging from 27.9 to 48.6 MPa. However, the series GA geopolymers, using group A activators, reveal poor compressive strengths in the range of 5.5–8.8 MPa. The results indicate that the geopolymers activated by silicate solutions exhibited higher compressive strength than those activated by hydroxide solutions, suggesting that the presence of a proper amount of soluble Si in the activation solution benefits the development of the compressive strength.

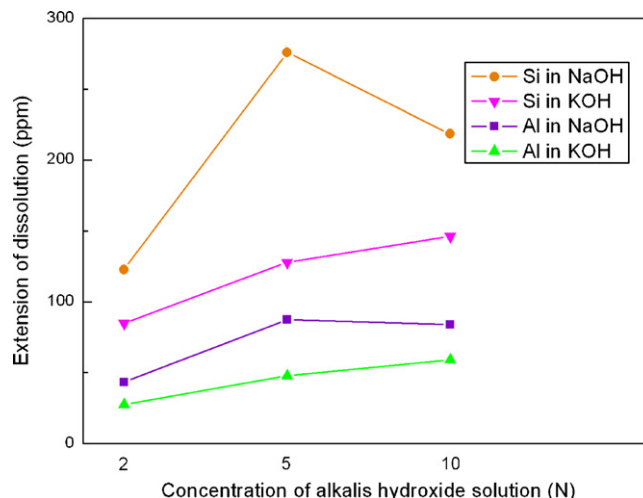


Fig. 2. Dissolution extents of Si and Al from CFBC bottom ashes in alkaline solutions.

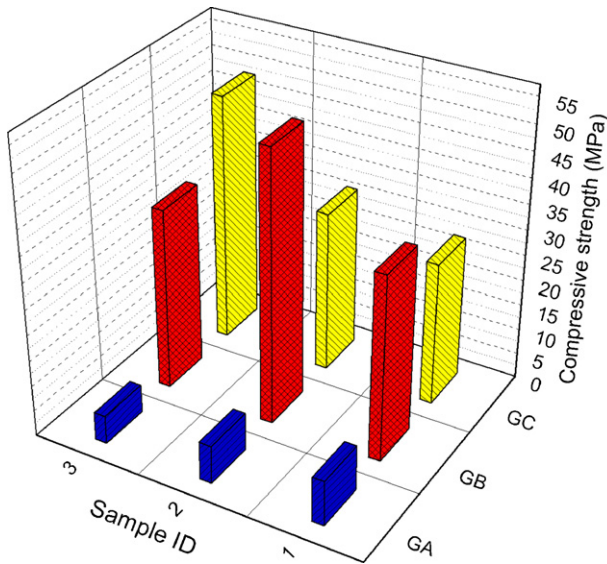


Fig. 3. Compressive strengths of CFBC bottom ash geopolymers of all mix designs.

3.3. Thermal stability

Thermal stability of the selected geopolymer (GB2) was investigated in terms of compressive strength evolution after exposure to elevated temperatures. Fig. 4 presents the photographs of geopolymer GB2 before and after the thermal exposures and cooling treatments. After the heating and cooling processes, the selected geopolymer specimens generally evolved their compressive strengths to certain extents up to 65 MP, with that exposed to 1050 °C and quenched in water as the only exception, which exhibited a little strength loss of 4.1 MP, as shown in Fig. 5. It is believed [9] that two opposing processes are responsible for the strength gain or loss of geopolymers after exposure to elevated temperatures: (1) further geopolymerization and/or sintering leading to strength gain; (2) the damage caused by thermal incompatibility due to non-uniform temperature distribution. The final strength evolution depends on the dominant process.

As shown in Fig. 4, geopolymer specimens subjected to thermal exposure at 800 °C all exhibited only very slight fissures on the surfaces. However, the ones heated at 1050 °C developed slight but distinct crackings under all cooling regimes. The formation of the fissures is possibly due to the accumulated effects of volume expansions derived from dehydration reactions [7], as further discussed in Section 3.4 (TG-DTA analysis). Besides, thermal incompatibili-

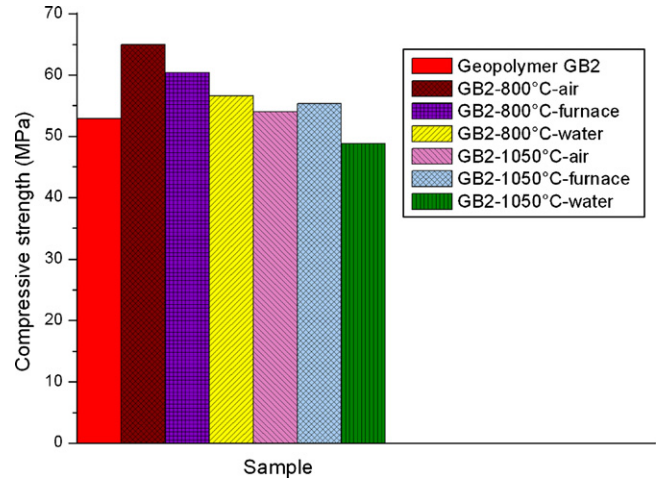


Fig. 5. Compressive strength evolutions of selected geopolymer after thermal exposures.

ties arising from non-uniform temperature distribution may also be responsible for the crackings [9].

Since no significant cracking is found on the surfaces of all the six specimens in this study, the strength evolution of each specimen may mainly attribute to the effect of viscous sintering at higher temperatures, whereas the completion of geopolymerization at lower temperatures might also be responsible for the strength gain. Similarly, the more strength gains of the specimens exposed to 800 °C, in comparison with those of the specimens heated at 1050 °C, are possibly due to the fewer and slighter fissures developed in the heating and cooling processes. The selected geopolymer specimens showed distinct fissures after exposure to 1050 °C. However, compared with the unheated specimen GB2, the ones heated at 1050 °C still gave compressive strength gains of 1.1 and 2.4 MPa after cooling in air and in the furnace, respectively.

It is known that, based on its unique inorganic polymeric nature, geopolymers are nonflammable materials with low heat conductivity [10]. Therefore, the strength gain or retention of geopolymeric materials at high temperatures is of significance.

3.4. TG-DTA analysis

The TG-DTA and DTG (the first derivative of the residual mass versus temperature) curves of the selected geopolymer are presented in Fig. 6. It is shown that a 9% mass loss occurred over the temperature range of 100–1050 °C, implying that the geopolymer specimen cured and dried at 40 °C retains about 9% water, of which

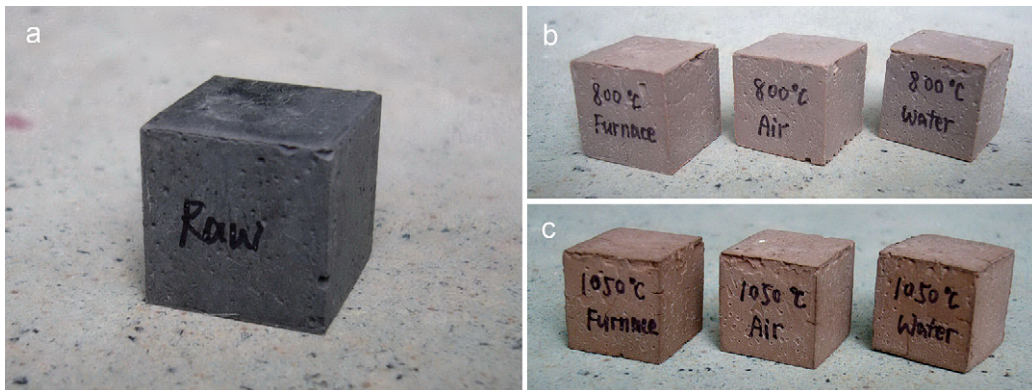


Fig. 4. Photograph of selected geopolymer (a) before thermal exposure; (b) after exposure to 800 °C and cooling in air, in the furnace, and in cool water; and (c) after exposure to 1050 °C and cooling in air, in the furnace, and in cool water.

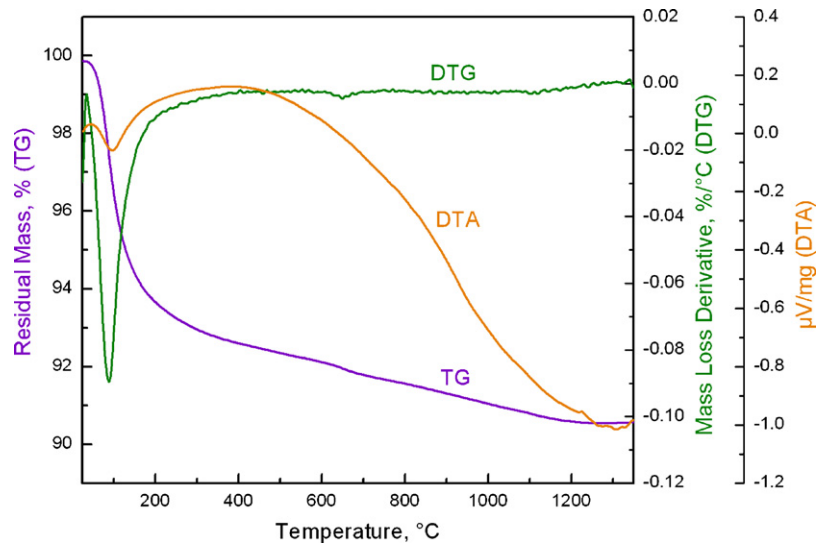
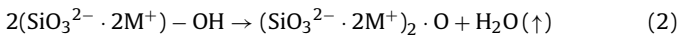


Fig. 6. Thermogravimetric-differential thermal analysis curves of selected geopolimer.

7% is lost at temperatures below 250 °C. The remainder was either bound tightly or less able to diffuse to the surface [8], and continued to evolve at temperatures higher than 250 °C in a dehydration reaction [7], which yields gaseous H₂O according to



The steam produced in this reaction results in an unconstrained volume expansion at high temperatures, which is presumably responsible for the cracks developed at temperatures higher than 250 °C. Besides, the sintering effect at high temperatures may also be responsible for the crack development due to possible phase changes that result in an increased volume.

3.5. Scanning electron microscopy

The SEM images of ground CBAs as well as the selected geopolimer before and after thermal exposures are shown in Fig. 7. As shown in Fig. 7a, ground CBAs exhibit an appearance far different

from those of conventional pulverized coal combustion fly ashes (PFAs). While typical PFAs largely contain glassy spheres of small sizes, the ground CBAs consist exclusively of irregular, coarse, and angular particles. This is obviously due to the significant differences between the combustion conditions under which the CBAs and PFAs are formed. Fig. 7b presents a well-formed geopolimer matrix of specimen GB2, demonstrating that CBAs could be utilized as alternative source materials for geopolimer production. It can also be seen in Fig. 7b–d that the microstructure of geopolimer GB2 remained almost unchanged after the heating and cooling treatments, with Fig. 7e show traces of the formation of some new crystalline phases, which is further supported by Fig. 8 in Section 3.6.

3.6. XRD diffractography

As shown in Fig. 8, the XRD patterns of raw CBAs as well as the selected geopolimer before and after exposure to 800 °C are

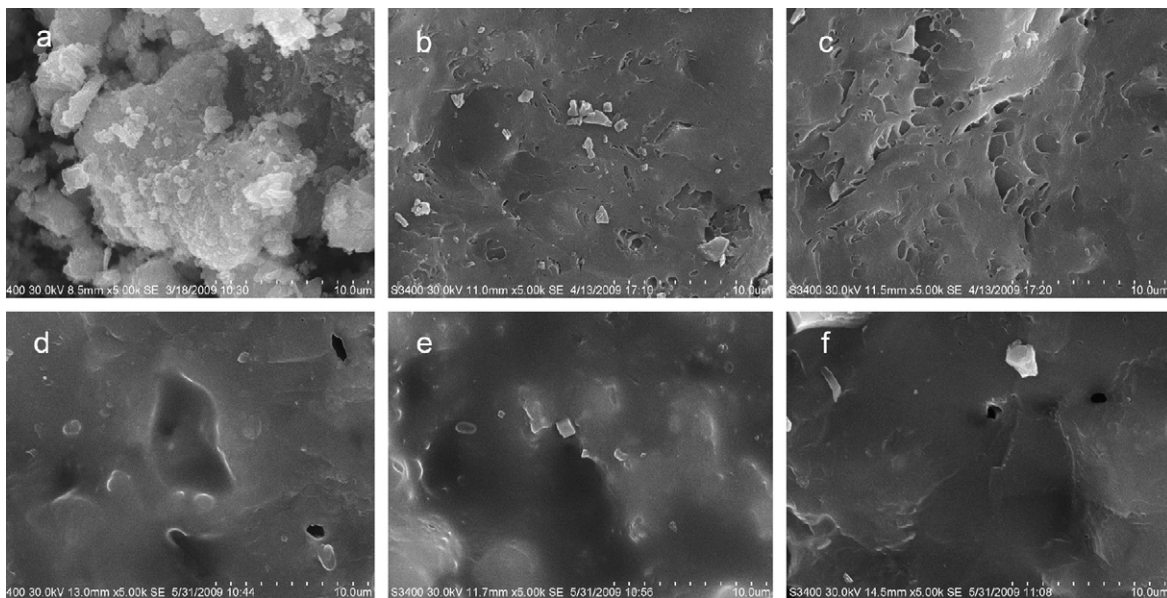


Fig. 7. Scanning electron microscope image of (a) CFBC bottom ashes; (b) selected geopolimer GB2; (c) GB2 after exposure to 800 °C and cooling in air; (d) GB2 after exposure to 1050 °C and cooling in air; (e) GB2 after exposure to 1050 °C and cooling in water, showing the presence of some new crystals; (f) GB2 after exposure to 1050 °C and cooling in the furnace.

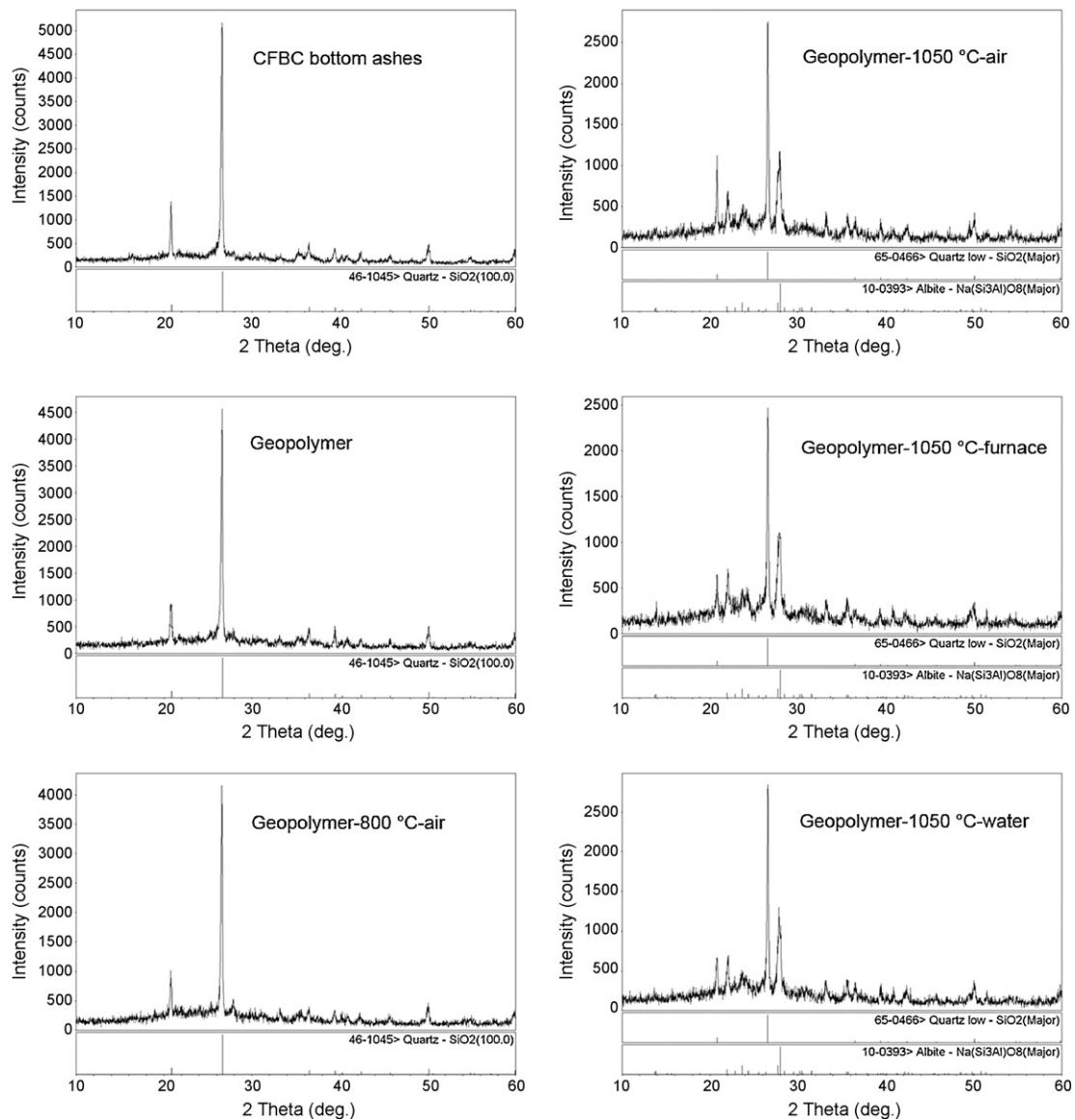


Fig. 8. X-ray diffraction data of CFBC bottom ashes and selected geopolymer before and after thermal exposures.

simple and similar, with the major crystalline phase being exclusively quartz (SiO_2), indicating that geopolymerization of CBAs does not lead to any substantial formation of new crystalline phases. It is also seen in Fig. 8 that the crystalline phase in the geopolymer matrix before and after thermal exposure to 800°C are almost the same. However, after exposure to a higher temperature of 1050°C , while the quartz phase in the geopolymer matrix remains almost unchanged, there are traces of the formation of new crystalline albite ($\text{NaAlSi}_3\text{O}_8$), which is supported by Fig. 7e in Section 3.5 and in agreement with the observation reported by Bakharev [25].

3.7. Infrared spectroscopy

FTIR spectra of the raw CBAs and the selected geopolymer before and after exposure to 800 and 1050°C are summarized in Fig. 9. The differences between absorption frequencies for the raw CBAs and the selected geopolymers before and after thermal exposures are indications of transformations that took place during geopolymerization and heating processes. The main features of all IR spectra are the prominent peaks between 1030 and 1090 cm^{-1} , the medium peaks around 795 cm^{-1} , and the strong peaks at about

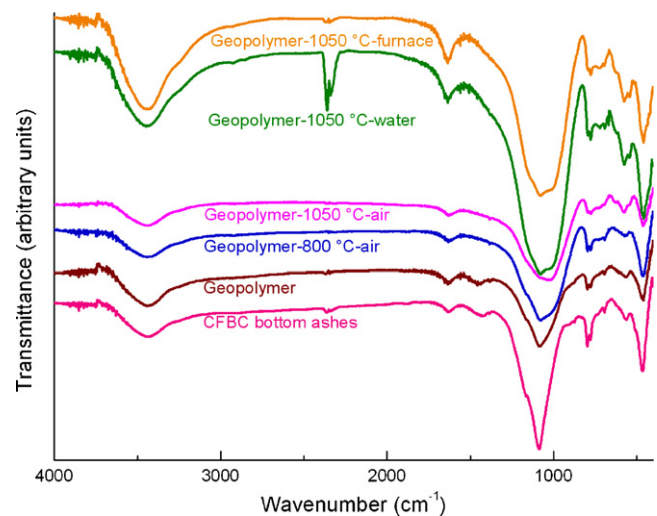


Fig. 9. Infrared spectra of CFBC bottom ashes and selected geopolymer before and after thermal exposures.

470 cm⁻¹, which are attributed to the Si–O–Si and Si–O–Al asymmetric stretching, Si–O–Si symmetric stretching, and Si–O and Al–O in-plane flexural vibration modes, respectively [14,26]. The broad bands at approximately 3450 cm⁻¹ and 1650–1600 cm⁻¹ are for O–H stretching and O–H bending, respectively [14]. For the specimen heated at 1050 °C and quenched in water, the sharp peak at about 2360 cm⁻¹ for stretching vibration of –OH under strong hydrogen bonding [26] is the evidence for the presence of adsorbed water. Compared with the raw CBAs, the selected geopolymer undergoes a very small shift of its Si–O–Si position to lower frequency as a consequence of polycondensation with alternating Si–O and Al–O bonds [14,27]. In general, only minute differences are shown within 450–1200 cm⁻¹ between the IR traces of the raw CBAs and the selected geopolymer before and after the thermal exposures, suggesting that most vibrant forms of the molecular chains existing in the CBAs retained in the raw and thermally treated geopolymer products [28].

4. Conclusion

This work has proven that, with a unique favorable thermal history as well as reasonable reactive silica and alumina contents, waste CBAs could serve as an alternative aluminosilicate source material for geopolymer production.

Mechanical properties of the CBAs geopolymers depend strongly upon the chemical compositions of the initial reacting systems. In this study, geopolymer of the optimal mix design gave the highest compressive strength of 52.9 MPa.

Both the SEM photomicrographs and the FTIR spectra have indicated the conversion of CBAs to geopolymers. SEM evidences indicate that the microstructure of geopolymer remained almost the same after exposure to 800 °C. However, after exposed to 1050 °C, there were traces of the formation of new crystalline albite (NaAlSi₃O₈) in the geopolymer matrix, which is further confirmed by the XRD patterns. As indicated by TG-DTA analysis, the optimal geopolymer retained about 9% free and hydration water.

The optimal geopolymer exhibits superior thermal stability to conventional OPC and most organic polymers in terms of compressive strength gain after thermal exposures. After heating at 800 or 1050 °C for 2 h in combination with cooling in air, in the furnace, and in cool water, respectively, the compressive strength of the optimal geopolymer generally evolved to certain extents up to 65 MPa, which may be due to the viscous sintering as well as completion of the geopolymerization reactions. The results of this study also suggest that the CBAs geopolymers may hold a potential to replace OPC and organic polymers in a variety of applications, especially where excellent thermal stability is highly required.

Acknowledgments

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