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Alkali-activated fly ash-based geopolymers with zeolite or bentonite as additives

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A R T I C L E I N F O

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A B S T R A C T

Geopolymers were synthesized by using fly ash as the main starting material, zeolite or bentonite as supplementary materials, and NaOH and CaO together as activator. An orthogonal array testing protocol was used to analyze the influence of the mix proportion on the properties of the geopolymers. The results indicate that the concentration of NaOH solution and the CaO content play an important role on the strength of the materials. Especially, with zeolite as additive, the fly ash-based geopolymer shows the highest strength and the best sulfate resistance. Infrared spectroscopy, X-ray, and SEM–EDX demonstrate that supplementary zeolite may involve the process of geopolymerization to form a stable zeolitic structure and improve the properties of the geopolymer. Bentonite simply acts as a filler to make the geopolymer more compact, but shows no improvement on the compositions and the microstructures of the geopolymer.

1. Introduction

Geopolymers are amorphous to semi-crystalline equivalent of certain zeolitic materials with excellent properties, such as high strength, high fire and erosion resistances, and good capability of immobilizing nuclear waste materials [1–3]. Besides metakaolin, some waste materials such as fly ash can also be used for the synthesis of the geopolymers. In the view of environmental benefits, great interest is derived from the latter by producing new materials with resources recovered from residue. Generally, alkali metal (Na or K) silicate or hydroxide is often used as an activator for synthesis of the metakaolin-based or fly ash-based geopolymers [4–7]. However, if only alkali metal (Na or K) silicate or hydroxide is used for the fly ash-based geopolymerization, the early strength of the materials synthesized is low and their durability properties (e.g. sulfate resistance) are not significantly improved, since the chemical activity of fly ash is usually lower than that of metakaolin. So, it is necessary to explore new pathways for fly ash-based geopolymerization and improve the properties of the materials. Recent works [8–10] have shown that the addition of moderate amount of minerals to a geopolymer can have significant improvements on the geopolymer structure and properties. Temuujin et al. [8] suggested that the addition of calcium compounds CaO and $Ca(OH)_2$ improves mechanical properties of the fly ash-based geopolymers cured at ambient temperature. Yip et al. [9] investigated the effect of adding significant percentages of alkaline earth carbonate minerals to metakaolin based geopolymers and showed that addition of around 20% calcite or dolomite is seen to improve the compressive strength of the geopolymeric material. Rees et al. [10] revealed that seeding of hydroxide-activated geopolymer syntheses with high surface area Al_2O_3 nanoparticles causes significant changes both in the kinetics of the reaction and in the structures of the products formed.

Herein, we report the synthesis of geopolymers at ambient temperature by using fly ash as the main starting material, zeolite or bentonite as the supplementary material, and NaOH and CaO together as activators. An orthogonal array testing protocol was used to analyze the influence of the mix proportion on the strength of the geopolymers. The products obtained were characterized by means of Infrared (IR) spectroscopy and X-ray diffraction, and their microstructure and compositions carried out by means of SEM coupled with EDX. Finally, the sulfate resistance of the fly ash-based geopolymers was tested.

2. Starting materials

2.1. Fly ash

Class F fly ash was obtained from the Xinyu power plant located in Jiangxi, China. In order to improve the reactivity, the fly ash was ground to the fineness so that the residue percentage of the fly ash passing through a 0.08 mm sieve mesh is 0.2%. The chemical compositions of the fly ash are presented in Table 1.

2.2. Supplementary materials

Though fly ash is pozzolanic material, its reactivity is much lower than that of metakaolin. Therefore, its reaction rate is quite low

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Table 1
The chemical compositions of fly ash, zeolite and bentonite.

Material	Weight (%)										
	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	LOI	Total
Fly ash	57.60	26.38	4.15	–	–	2.25	0.38	2.18	–	4.89	97.83
Zeolite	70.92	11.71	0.92	–	0.33	2.10	2.06	3.09	–	9.96	101.09
Bentonite	68.10	15.44	0.34	0.33	3.79	0.77	2.58	0.93	0.12	7.43	99.83

at ambient temperature. To explore this property, the following supplementary materials were used in this study to accelerate the geopolymerization and to improve the properties of the fly ash-based geopolymers.

2.2.1. Zeolite

The structure of geopolymer is closely related to that of artificial zeolite [4,5] though geopolymer is amorphous to X-rays. Therefore, a small amount of zeolite was added in the synthesis system of geopolymer as a 'seed'. Natural zeolite used was obtained from Lishui in Zhejiang, China. The major minerals of the zeolite are clinoptilolite and mordenite, and the compositions are listed in Table 1. The fineness of the zeolite used is that of the residue percentage passing through a 0.08 mm sieve mesh, which is 27%.

2.2.2. Bentonite

Bentonite can form significantly fine aluminasilicate particles with a stratified structure. Some of the fine particles may dissolve and have the potential of polymerization when they contact with the high pH alkaline solution. The bentonite used was obtained from Guangfeng in Jiangxi, China. The fineness of bentonite with residue passing through a 0.08 mm sieve mesh is 0.3%. The chemical compositions of bentonite are shown in Table 1.

2.3. Alkaline activator

NaOH is usually used as an alkaline activator. However, previous studies [7,11] showed that higher CaO content of fly ash may be beneficial to geopolymerization because the apparent Ca dissolution is likely to be indicative of the overall dissolution of the phase within fly ash. As an exploration, in this work NaOH and CaO were used together as alkali-activator.

2.4. Sand

The China ISO standard sand was used and its quality conformed to the requirement of GB/T17671–1999.

3. Experimental procedures

3.1. Orthogonal array testing

Orthogonal array testing is an effective approach to arrange and analyze multifactor experiments, which has the advantage of selecting the optimal test scheme and searching for the optimal test condition. Two systems of orthogonal array testing about zeolite or bentonite as supplementary material with three factors at three levels were designed in this study, which includes nine groups of tests containing each of the supplementary materials. The scheme is presented in Table 2.

The test was conducted following the method of strength-test for cement. The mass of the starting materials (fly ash, zeolite or bentonite, and CaO) was 500 g. Fly ash, CaO, and zeolite or bentonite were mixed to homogeneity in a mixer in accordance with the proportions in Table 2. After that, 1350 g of standard sand was added and mixed to homogeneity. The alkaline solution of NaOH (prepared as in Table 2) was added at the solution-to-binder ratio of 0.4. The mixture was mixed to homogeneous paste and cast to the size of 40 mm × 40 mm × 160 mm. The specimens were cured at 20 °C with a relative humidity above 90%.

The tests of flexural strength and compressive strength were performed at the ages of 7 days, 28 days, and 60 days. All experiments were repeated three times, and the errors of the flexural and compressive strength were less than 0.3 MPa and 0.7 MPa, respectively.

3.2. Infrared spectroscopy, X-ray diffraction and SEM analyses

There was no sand in the samples prepared for these analyses, and the compositions of the matrices are shown in Table 3; the matrices ZEO and BEN are the ones with zeolite and bentonite as supplementary materials, respectively, and the matrix FA is the one without any supplementary material. The samples were cast in the size of 10 mm × 10 mm × 40 mm, and cured at 20 °C with a relative humidity above 90% for 60 days. Infrared spectra were recorded on a SPECTRUM ONE spectrometer using the KBr pellet technique (3 mg powder sample mixed with 100 mg KBr). The X-ray powder diffractometer data were obtained using Bede D1 system diffractometer with Cu Kα radiation. SEM secondary electron images and the EDX data of the geopolymers were obtained using JXA-8100 electron probe microanalyzer. Fresh fractures were coated with carbon.

3.3. Sulfate resistance test

The compositions of matrices for three kinds of geopolymer are listed in Table 3, where the matrices for ZEO, BEN, and FA are the same as those presented in Section 3.2. The samples were cast in the size of 10 mm × 10 mm × 40 mm and cured at 20 °C with a relative humidity above 90% for 28 days. After that, they were immersed in the solution of 10% magnesium sulfate for 60 days. The rate of weight loss was determined and the degradation of the samples surveyed.

4. Results and discussion

4.1. The orthogonal array testing

Tables 4 and 5 present the strength results for two kinds of the fly ash-based geopolymer with zeolite and bentonite as the supplementary material, respectively. The calculation results of the orthogonal array testing data for the compressive strength at 7 days, flexural strength and compressive strength at 28 days, and the compressive strength at 60 days in Table 4 are listed in Table 6, where k_{ij} is the sum of strength of each level, $\overline{k}_{ij} = k_{ij}/3$, and by comparing to $\overline{k}_{ij}$, the optimal level of variables can be confirmed. $R_j = \max\{\overline{K}_{1j}, \overline{K}_{2j}, \ldots, \overline{K}_{3j}\} - \min\{\overline{K}_{1j}, \overline{K}_{2j}, \ldots, \overline{K}_{3j}\}$, which scales the effect of variables on the results. Higher R_j-value of a variable means that the variable has stronger impact on the result. As shown in Table 6, except compressive strength at 7 days, the orders of the factors influencing the strength of the fly ash-based geopolymers containing zeolite are *C* (the concentration of NaOH solution) > *B* (the CaO content) > *A* (the zeolite content). Similarly, by the calculating of the data in Table 5, it is known that the R_j-values about the factor *A*, *B*, and *C* are 1.59, 2.23, and 9.16 for the compressive strength at 7 days, 0.73, 3.20, and 1.63 for the flexural strength at 28 days, 2.06, 9.30, and 10.13 for the compressive strength at 28 days, and 0.92, 12.21, and 11.63 for the compressive strength at 60 days, respectively, which demonstrates that, when bentonite as supplementary material, the strongest impact on the result is *C* (the concentration of NaOH solution) or *B* (the CaO content). Overall, the best composition of the matrix is that the zeolite or bentonite content is 10% or 15%, CaO content is 15%, and the concentration of NaOH solution is 0.15 g/ml.

4.2. Infrared spectroscopy analysis

Fig. 1 shows the IR spectrum of the fly ash. In Fig. 1 the bands at 1083.79 cm^{-1} and 798 cm^{-1} are attributed to the α-quartz, and the band at 561 cm^{-1} is ascribed to mullite by referring to the previous study [11]. Figs. 2 and 3 show the IR spectra of zeolite and bentonite, respectively.

Figs. 4–6 show the spectra of the fly ash-based geopolymers containing zeolite, bentonite, and no supplementary material, respectively. By comparing Fig. 4 with Figs. 1 and 2, Fig. 5 with Figs. 1 and 3, and Fig. 6 with Fig. 1, it is found that after geopolymerization the strong band at 1083.79 cm^{-1} for the fly ash broadens and shifts to lower frequency by more than 30 cm^{-1} for the fly ash-based geopolymer. These results indicate that the process of geopolymerization increases the amorphous aluminosilicates significantly [11]. Among the three kinds of fly ash-based geopolymers, the one with zeolite as supplementary material has the broadest and lowest band located in 600–1300 cm^{-1}, while the one with bentonite as supplementary material has the most similar bands at 1031.98 cm^{-1} to that of the fly ash except it shift to lower frequency by 50 cm^{-1}. Further analysis found that the band at 1055 cm^{-1} in the IR spectrum of zeolite (Fig. 2) does not exist in the IR spectrum of the geopolymer containing zeolite (Fig. 4). This is an indication that the zeolite, at least some of the zeolite, in the matrix involved the process of geopolymerization. Therefore, zeolite as a supplementary material may enhance structural reorganization and produce more amorphous aluminosilicates.

In addition, according to [12] in Figs. 4–6 the appearance of the new bands at 1428 cm^{-1} for the matrix containing bentonite and the matrix containing no supplementary material, or the band at 1435 cm^{-1} for the matrix containing zeolite, could be attributed to CO_3^{2-}. As indicated in Section 2.3, CaO was used as one of the alkali-activators. Thus, it is possible that before CaO took part in the geopolymerization reaction some of the CaO reacted with CO_2 and H_2O in a moist atmosphere to produce $CaCO_3$, which would explain the bands of CO_3^{2-} in the IR spectra of these fly ash-based geopolymers.

According to above-mentioned IR analysis, it is clear that the spectra of the fly ash-based geopolymers are very different from that of the main starting material (i.e., the fly ash) owing to the fact

Table 2
Orthogonal array testing of matrix composition.

No.	*A* zeolite/bentonite (%, m/m)	*B* calcium oxide (%, m/m)	*C* NaOH solution (g/ml)	*D* fly ash (%, m/m)
1	0	5	0.05	95
2	0	10	0.10	90
3	0	15	0.15	85
4	10	5	0.10	85
5	10	10	0.15	80
6	10	15	0.05	75
7	15	5	0.15	85
8	15	10	0.05	75
9	15	15	0.10	70

Table 3
Compositions of matrices for infrared, X-ray, SEM and sulfate resistance.

Matrix	Weight			Volume
	Mineral (g)	CaO (g)	Fly ash (g)	10 (g/ml) NaOH solution (ml)
ZEO	Zeolite 5	10	35	15
BEN	Bentonite 7.5	10	32.5	15
FA	–	15	35	15

Table 4
Results of orthogonal array testing with zeolite as supplementary material.

No.	Compressive strength (MPa)			Flexural strength (MPa)		
	7d	28d	60d	7d	28d	60d
1	7.74	9.38	10.94	3.48	3.87	4.27
2	11.56	18.75	23.13	4.63	6.82	8.60
3	11.38	26.60	36.89	5.00	8.51	10.08
4	8.23	13.65	15.47	3.20	4.62	4.90
5	9.44	25.56	28.68	3.89	9.00	9.74
6	8.33	21.05	23.55	3.90	6.55	8.24
7	8.18	22.52	28.39	2.85	5.95	6.83
8	6.48	15.70	20.07	2.85	5.07	6.34
9	9.94	22.83	28.61	3.84	6.60	7.26

Table 5
Results of orthogonal array testing with bentonite as supplementary material.

No.	Compressive strength (MPa)			Flexural strength (MPa)		
	7d	28d	60d	7d	28d	60d
1	4.32	8.10	9.80	2.43	3.82	3.94
2	8.20	16.06	21.09	3.93	6.32	7.64
3	13.25	27.34	32.80	5.00	8.78	9.00
4	7.77	12.14	13.13	3.03	4.28	4.30
5	17.30	26.41	30.36	5.90	7.33	8.27
6	5.46	19.14	23.13	2.42	6.33	7.16
7	12.00	18.44	21.80	3.25	4.33	5.29
8	5.29	14.54	17.15	2.27	5.38	5.57
9	10.40	20.08	25.43	4.40	7.04	7.46

Table 6
Analysis and calculation using the results with zeolite as supplementary material.

	7d Compressive strength (MPa)			28d Flexural strength (MPa)			28d Compressive strength (MPa)			60d Compressive strength (MPa)		
	A	B	C	A	B	C	A	B	C	A	B	C
k_{1j}	30.68	24.15	22.55	19.20	14.44	15.49	54.73	45.55	46.13	70.96	54.80	54.56
k_{2j}	26.00	27.48	29.73	20.17	20.89	18.04	60.26	60.01	55.23	67.70	71.88	67.21
k_{3j}	24.60	29.65	29.00	17.62	21.66	23.46	61.05	70.48	74.68	77.07	89.05	93.96
$\bar{k}_{1j}$	**10.23**	8.05	7.52	**6.40**	4.81	5.16	18.24	15.18	15.38	23.65	18.27	18.19
$\bar{k}_{2j}$	8.67	9.16	**9.91**	**6.72**	6.96	6.01	20.09	20.00	18.41	22.57	23.96	22.40
$\bar{k}_{3j}$	8.20	**9.88**	9.67	5.87	**7.22**	**7.82**	**20.35**	**23.49**	**24.89**	**25.69**	**29.68**	**31.32**
R_j	2.03	1.83	2.39	0.85	2.41	2.66	2.11	8.31	9.51	2.04	11.41	13.13

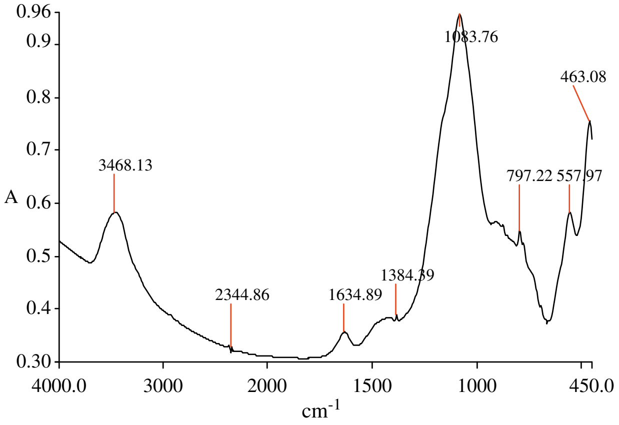

Fig. 1. IR spectrum of fly ash.

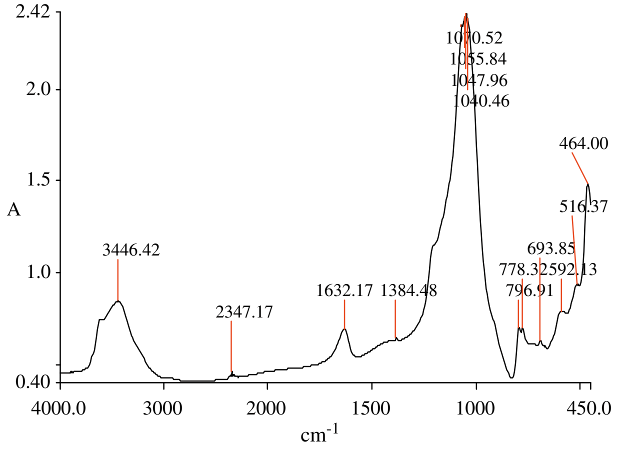

Fig. 2. IR spectrum of zeolite.

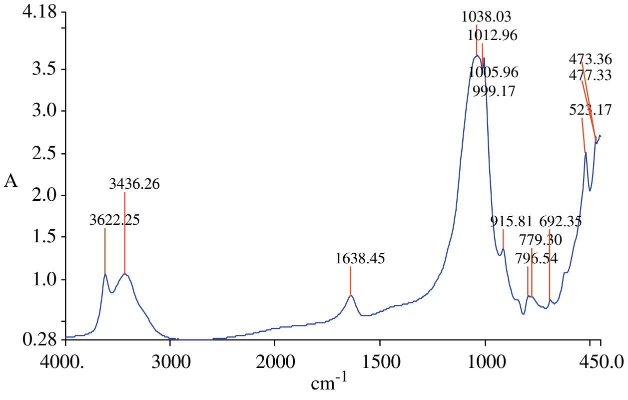

Fig. 3. IR spectrum of bentonite.

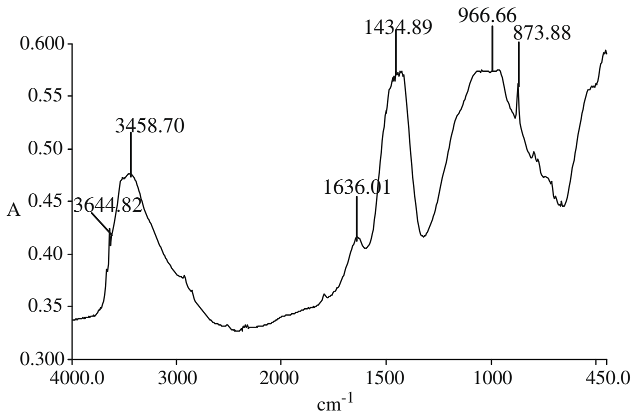

Fig. 4. IR spectrum of the matrix containing zeolite.

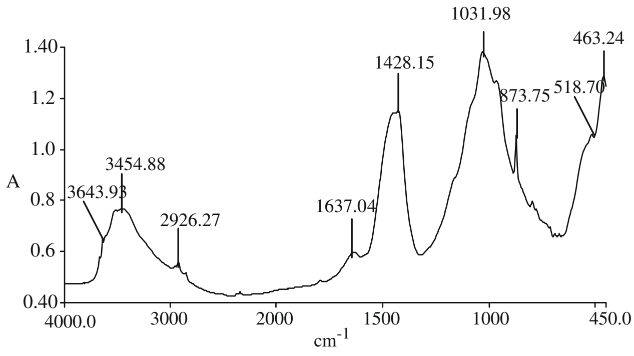

Fig. 5. IR spectrum of the matrix containing bentonite.

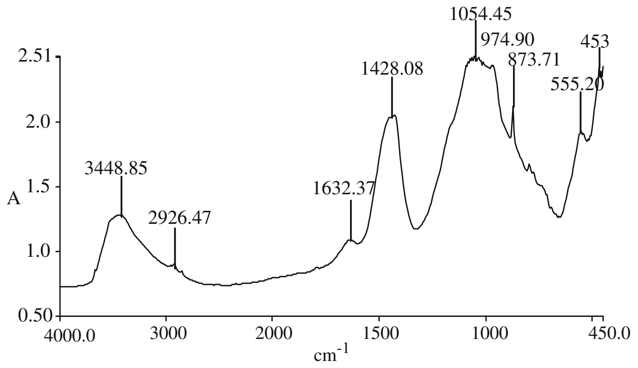

Fig. 6. IR spectrum of the matrix containing no any supplementary material.

that a number of amorphous aluminosilicates produced in the geopolymerization. With regard to the three kinds of fly ash-based geopolymer, the geopolymers containing zeolite and containing no supplementary material have more amorphous aluminosilicates, which may result in different properties of the three geopolymers.

4.3. X-ray diffraction

For comparison between the geopolymers and the fly ash, the X-ray spectra are shown in Fig. 7, which shows that except the peaks of $CaCO_3$ (C), the X-ray spectra of the geopolymers are similar to those of the fly ash, indicating that the geopolymerization reaction did not cause the formation of significant amount of new crystalline phases. A small decrease in intensity of the quartz (Q) peaks and the mullite (M) peaks was observed for the matrix containing zeolite, bentonite and no any supplementary material (Fig. 7). The above analysis has shown that the IR spectra of the fly ash-based geopolymers are very different from that of the fly ash. This suggests that no new crystalline but new amorphous products were formed in the geopolymerization reaction.

4.4. SEM analysis

Fig. 8 shows the secondary electron image of the matrix containing zeolite, which demonstrates that although some un-reacted fly ash particles still exist in the sample after it was cured at ambient temperature for 60 days, there are a number of network products on top of the fly ash particles. A great many of the network products, with nearly no interfacial area between them, randomly scatter on top of the fly ash and mineral particles, which leaves the material with quite compact microstructure. Combined with the result of IR analysis that a number of amorphous aluminasilicates formed in the geopolymerization reaction, it can be suggested that the network products are the amorphous aluminasilicates. SEM–EDS analysis of the geopolymer is presented in Table 7. The elemental compositions on the area *B* of the matrix containing zeolite are Si, Ca, and Al, and the ratio of silicon-to-aluminum is 3/1 (Table 7).

Fig. 9 presents the secondary electron image of the matrix containing bentonite, demonstrating some discontinuous network products between the fly ash particles. Due to the filling function of the fine bentonite particles, the sample shows very low porosity. The elemental compositions on the area *A* of the matrix containing bentonite are Si, Al, and Ca. The Si/Al ratio of the product is 1.43/1 (Table 7), which is much lower than that of area *B* on the matrix containing zeolite (Fig. 8).

Fig. 10 presents secondary electron images of the matrix containing no supplementary material, from which it is known that around the fly ash particles there are significant network products between fly ash particles. However, because of absence of a supplementary material, its porosity is larger than that of the matrix containing either zeolite or bentonite. The elemental compositions on the area *C* of the matrix containing no any supplementary material are Si, Al, and Ca, and the Si/Al ratio of the product is 1.47/1 (Table 7), which is similar to that of the area *A* for the matrix containing bentonite.

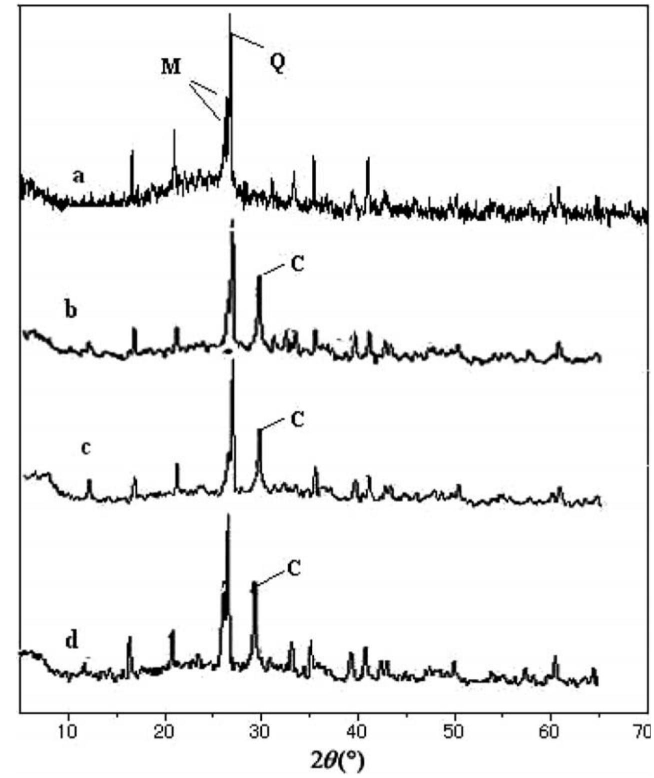

Fig. 7. XRD spectra collected using Cu Kα radiation (a) fly ash; (b) the matrix containing zeolite; (c) the matrix containing bentonite; (d) the matrix containing no any supplementary material. Q, α-quartz. M, mullite. C, calcium carbonate.

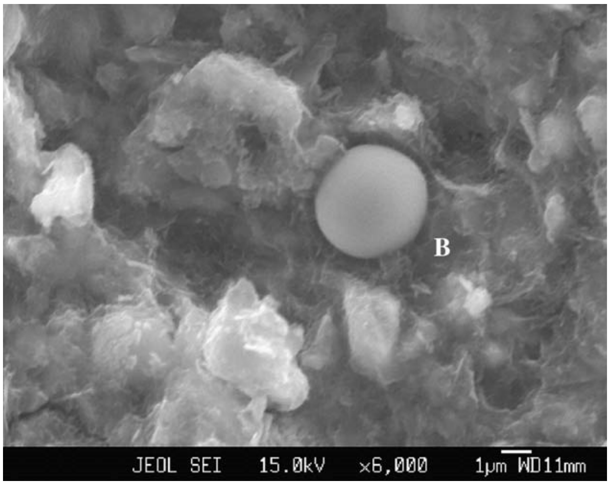

Fig. 8. SEM image of the matrix containing zeolite.

Table 7
EM–EDX analysis of the three fly ash-based geopolymers.

Element	Elemental composition (%)		
	ZEO	BEN	FA
K	1.65	0.93	2.05
Na	1.72	2.56	1.31
Mg	1.31	0.81	1.05
Al	9.16	15.40	17.53
Si	27.80	22.08	25.73
Ca	9.61	11.73	2.38
Fe	1.85	1.05	1.22

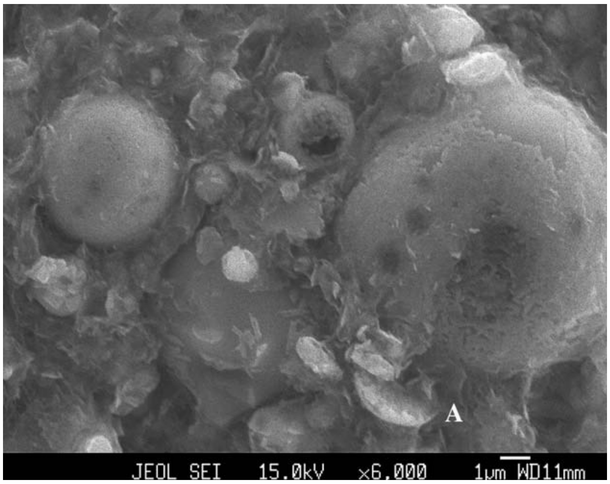

Fig. 9. SEM image of the matrix containing bentonite.

4.5. Sulfate resistance

The rates of weight loss of the three groups of samples for sulfate resistance test are listed in Table 8, which shows that after immersed in the same magnesium sulfate solution for 60 days, the geopolymer containing no supplementary and the geopolymer containing zeolite demonstrated lowest rates of weight loss, but the geopolymer containing bentonite fell apart and had highest rate of weight loss.

The photos of the samples immersed in the magnesium sulfate solution for 60 days are shown in Fig. 11. In Fig. 11, the geopolymer

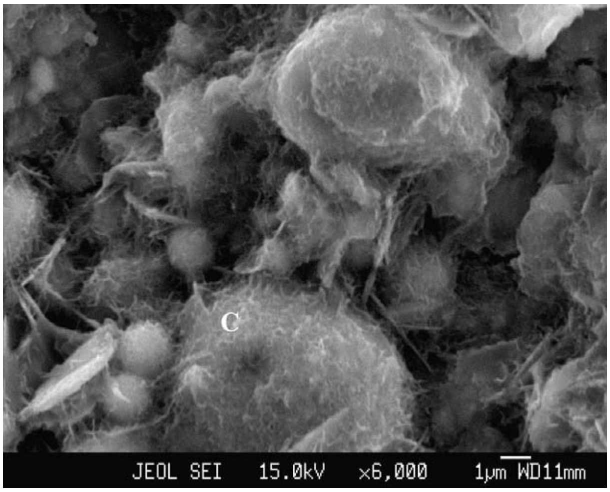

Fig. 10. SEM image of the matrix containing no supplementary material.

containing bentonite fell apart, indicating that it has the poorest resistance to sulfate attack as compared to the geopolymer containing zeolite and the geopolymer containing no supplementary material. Although the rate of weight loss of the geopolymer containing no supplementary material was lowest, some penetrating cracks were observed in it. Of all the three fly ash-based geopolymers, only the geopolymer containing zeolite was intact, the surface was smooth and without any crack, and its weight loss was quite low. Therefore, the geopolymer containing zeolite has the best resistance to sulfate attack.

4.6. Comprehensive analysis

The analysis of orthogonal array testing in this study has shown that though the concentration of NaOH solution plays the most important role on the strength of the material, the function of calcium oxide is also significant. Lee and van Deventer [11] verified that the polysilicate can absorb the dissolved Ca and Al, and stabilize Ca and Al in it in highly alkalized conditions. The Ca and Al-containing polysilicates coagulate and polymerize to produce the final gel of amorphous silicate with network substitution of Al and network modifiers of Ca and M (Na or K). Temuujin et al. [8] indicated that calcium compound addition is likely to result in precipitation of calcium silicate hydrate or calcium silicate aluminate hydrate phases and at the same time improve the dissolution of the fly ash in the alkaline medium and subsequently the geopolymerization reaction. Therefore, it is reasonable to use NaOH and CaO together as alkaline activators.

Although orthogonal array testing shows that the supplementary materials did not play the most important role on the strength of the materials, the microstructures of the geopolymers with different supplementary materials were very different. The analyses of infrared spectroscopy, SEM–EDX and X-ray show that the fly ash-based geopolymer containing zeolite has most amorphous aluminosilicates, the geopolymer containing bentonite are more compact, and that among the three fly ash-based geopolymers the one containing supplementary zeolite has the highest Si/Al rate, while the one containing supplementary bentonite has the similar Si/Al rate to that of the one containing no any supplementary material. Furthermore, the test results in this work verified that the geopolymer containing zeolite has the highest strength and the best sulfate resistance. Because the strength and attack-resistance of materials have close relation to their compositions, macrostructures, and microstructures, it can be induced that zeolite used as a supplementary material may involve the process of geopolymerization to form a stable zeolitic structure and improve the properties of the fly ash-based geopolymer. Bentonite simply acts as a filler to make up the geopolymer more compact, but shows no improvement in the compositions and the microstructures of the material.

Table 8
Weight losses of the geopolymers before and after immersion in sulfate solution.

Matrix	Weight		Mass loss (%)
	Before immersion (g)	After immersion (g)	
ZEO	7.9	7.5	5.1
BEN	8.9	Fell apart	Highest
FA	7.4	7.3	1.4

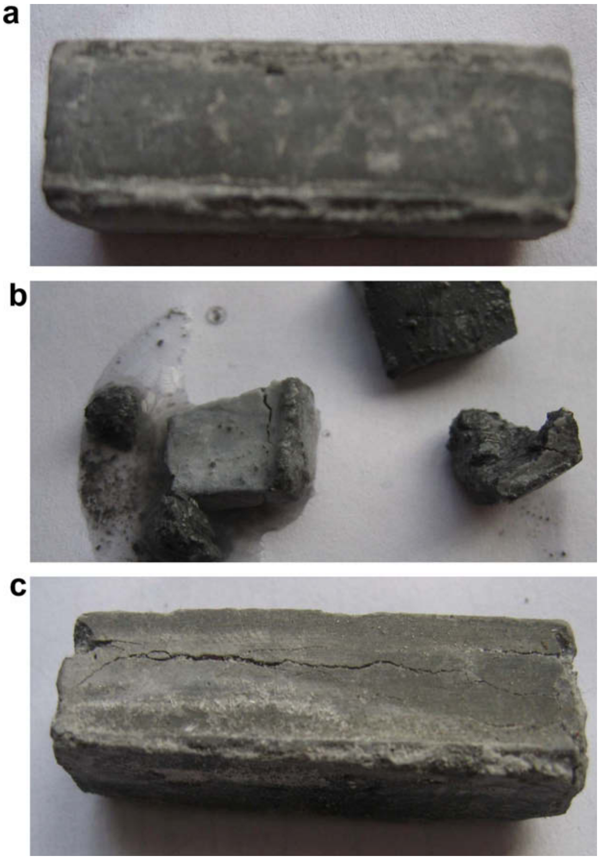

Fig. 11. Geopolymer samples after immersed in solution of 10% magnesium sulfate for 60 days (a) geopolymer containing zeolite; (b) geopolymer containing bentonite; (c) geopolymer containing no any supplementary material.

5. Conclusion

This work has demonstrated that the concentration of NaOH solution plays the most important role on the strength of the fly ash-based geopolymers, whereas the function of calcium oxide is also significant. It is reasonable to use both NaOH and CaO as alkaline activators for accelerating the synthesis of the fly ash-based geopolymers.

Through the comprehensive analyses with infrared spectroscopy, X-ray, and SEM–EDX, it was shown that when zeolite is used as supplementary material the fly ash-based geopolymer has the highest strength and the best sulfate resistance. Zeolite used as a supplementary material may involve the process of geopolymerization to form a stable zeolitic structure and improve the properties of the fly ash-based geopolymer. Bentonite simply acts as a filler to make up the geopolymer more compact, but shows no improvement in the compositions and the microstructures of the material.

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