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Properties and pozzolanic reaction degree of tuff in cement–based composite

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Abstract. In order to investigate the feasibility and advantage of tuff used as pozzolan in cement-based composite, the representative specimens of tuff were collected, and their chemical compositions, proportion of vitreous phase, mineral species, and rock structure were measured by chemical composition analysis, petrographic analysis, and XRD. Pozzolanic activity strength index of tuff was tested by the ratio of the compression strength of the tuff/cement mortar to that of a control cement mortar. Pozzolanic reaction degree, and the contents of CH and bond water in the tuff/cement paste were determined by selective hydrochloric acid dissolution, and DSC-TG, respectively. The tuffs were demonstrated to be qualified supplementary binding material in cement-based composite according to relevant standards. The tuffs possessed abundant SiO_2+Al_2O_3 on chemical composition and plentiful content of amorphous phase on rock texture. The pozzolanic reaction degrees of the tuffs in the tuff/cement pastes were gradually increased with prolongation of curing time. The consistency of CH consumption and pozzolanic reaction degree was revealed. Variation of the pozzolanic reaction degree was enhanced with the bond water content and relationship between them appeared to satisfy an approximating linear law. The fitting linear regression equation can be applied to mutual conversion between pozzolanic reaction degree and bond water content.

Keywords: cement; tuff; pozzolan; content

1. Introduction

Pozzolan now embraces a wide variety of materials possessed a reactive and amorphous siliceous component, which can combined with the hydrated lime derived from Portland cement hydration. Moreover, accelerated form of additional calcium-silicate-hydrate during second hydration reaction is generated. Pozzolan can be either natural in origin or artificial. The motivation for their application is technical and economical, as well as ecological. Pozzolan can be added as a separate ingredient to concrete or mortar in mixer, or it can also be blended with cement clinker to produce blended cement in which part of the Portland cement has been replaced by it. Thus, finding new and improved ways to produce a high strength or high performance concrete with new pozzolan are receiving more attention. Mehta and Monteiro (1993) stated many examples of natural pozzolans used in cement and concrete, such as volcanic glasses including

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Santorin Earth of Greece and Bacoli Pozzolan of Italy, as well as volcanic tuffs just like trass of Rhrinland and Bavaria in Germany. Most of the previous research has been concentrated on by-product pozzolanic materials with very little effort dedicated to the natural pozzolanic materials in China. However, there is more attention towards research on natural pozzolan just as natural zeolite (Feng *et al.* 1990) and metakaolin (Poon *et al.* 1999, 2001). The influence of perlite from Jiangxi Province, China on pozzolanic effect and pore structure of cement paste was investigated by Yu *et al.* (2003, 2010), it was concluded that perlite possessed preferably pozzolanic activity and played the role of subtracting pore volume and refining pore size so to improve mechanics strength and durability for cement-based composite. Despite of a few tuffs researched well on use of pozzolans in cement-based materials, the papers mentioned on pozzolanic reaction degree of tuff have been published relative scarcely. Turkmenoglu and Tankut (2002) researched use of tuffs from central Turkey as admixture in pozzolanic cements assessment of their petrographical properties. Liguori *et al.* (2003) evaluated zeolite-bearing tuffs as pozzolanic addition for blended cements. Uzal and Turanli (2003, 2012) studied the properties, hydration characteristics, and paste microstructure of blended cements containing 55% zeolitic tuff. Ahmet and Sukru (2007) probed availability of tuffs from northeast Turkey as natural pozzolan in cement on chemical compositions, mechanical relationships with pozzolanic activity. Uzal *et al.* (2007) reported the results of preliminary studies for structural applications on concrete mixtures containing high volumes of natural pozzolan, which was 50% by mass of total cementitious materials and included natural zeolite, volcanic tuff and perlite. Mertens *et al.* (2009) determined quantitatively the pozzolanic reaction between portlandite and tuffs by thermogravimetrical analyses from 3 to 180 days. Wong and Askury (2011) presented the result of using tuff in Lawin, Grik, Perak, Malaysia to generate Portland fly ash cement to be used in oil well cementing. Based on testing chemical and physical properties of volcanic tuff, and properties of concrete incorporating the pozzolanic material as a partial cement replacement, Khan and Alhozaimy (2011) confirmed potential utilization of volcanic tuff from Saudi Arabia in environmental friendly concrete..

There are a lot of volcanic origin rocks distributed in Jiangxi Province of China, erupted during the late Mesozoic, and among which tuffs occupy important volume.These tuffs are extrusive igneous silica rocks with abundance of SiO_2 and Al_2O_3 in chemical composition and glassy on texture, they are similar to other natural material, e.g., alumino-silicate glass and pozzolan to be able to use as mineral admixtures in concrete with particles ground to mostly under 45 μm (Mehta and Monteiro 1993).

The objective of the present study was by means of experimental work to investigate the availability of tuff used as a supplementary binding material in cement-based composite, similar to other pozzolanic materials fly ash, blast-furnace slag, condensed silica fume, rice husk ash, and zeolite. The representative specimens of tuff were extracted from main volcanic area in the northeast region of Jiangxi Province, China. Their properties such as chemical composition, amorphous phase content, mineral species, and rock structure were examined by chemical composition analysis, petrographic analysis and XRD. Pozzolanic activity strength index for the tuff was tested by the ratio of the compression strength of the tuff/cement mortar to that of a control cement mortar. Meanwhile, the pozzolanic reaction degree was quantitatively determined using a selective dissolution method. And the contents of CH and bond water in the tuff/cement paste were measured using DSC–TG. The hydration progress of tuff was then assessed from pozzolanic reaction degree and the contents of CH and bond water. Relationships between tuff properties and pozzolanic activity reaction were further discussed and revealed.

2. Experimental methods

2.1 Collection and grinding of tuffs

The tuffs were collected as specimens for research in our work from the two large surface quarries, respectively near the northeastern Qingxi Town (Specimen QA and QW) and the southern Ehu Town (Specimen E) in Yanshan County, Jiangxi Province, China. They were typical representatives of volcanic rocks distributed in the main volcanic areas in the northeast region of Jiangxi..These tuffs are currently mined and used as building stones in road, highway, railway, building construction and in other applications.

The tuff specimens were crushed and ground into powder by ball mill. At least 90% of the tuff powder had to pass through 45 μm wet sieve. The powder particle sizes of the tuff specimens and cement were measured using a Laser Particle Size Analyzer and diagrammed in Fig. 1.

2.2 Experimental program

2.2.1 Chemical composition analysis

The analysis of bulk chemical composition for tuff was performed by means of wet chemical analysis, in accordance with Chinese Standard GB/T14506.28–2010(Methods for Chemical Analysis of Silicate Rocks—Part 28: Determination of 16 Major and Minor Elements Content).

2.2.2 Petrographic analysis

In order to make the petrographic identification, thin sections of the tuff specimens were prepared and observed under the petrographic microscope. Acquisition observation based on tuff original-site, petrography features were inspected under polarizing microscope by using their thin sections. The main viewed programs include estimating proportion of vitreous matrix semi-quantitatively, the type of porphyritic bodies (crystal mineral, debris or breccia) and their proportion, rock structure, etc.

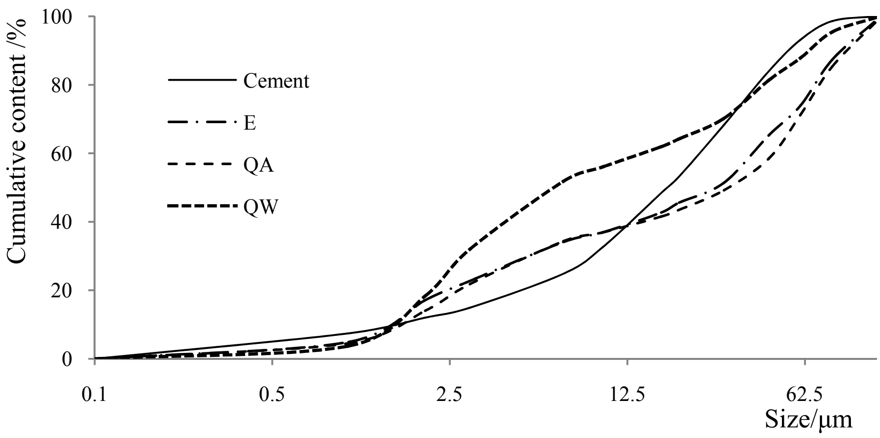

Fig. 1 Powder particle size distribution

2.2.3 Powder XRD

Tuff powder XRD was carried out using a Bruker (D–8) X-ray diffractometer (Cu/Kα =1.54 Å, Ni filter, 40 kV, 40 mA, 2º/min, 2θ=2°~90º),the results were then used to identify crystalline phase minerals and to calculate content of amorphous phase in tuff.

The crystalline mineral species in tuff could be identified by characteristics diffraction spectral pattern.

In petrology, the content of amorphous phase might be calculated from the percentage difference between the total content and the content of the crystalline phase in tuff (Ye and Jin 1984). Here, crystalline phase content of tuff was obtained from XRD data by application of MDI Jade 5.0 soft ware produced by Rigaku Company in Japan. The procedure was as follows. Firstly, the diffraction background curve was drawn, and the area above background curve was regarded as the integral area of crystal phase. The area below the diffraction peak cure was then considered to integral area of the total phase. Finally, the percentage of crystal phase integral area in the total phase integral area was defined as the content of crystalline phase in tuff, also called crystallinity.

It is known that XRD is a semi-quantitative technique to assess the crystalline phase content. As Fe-rich materials may result in much higher backgrounds in using Cu/Kα radiation during XRD experiment, the acidic tuffs own low content of Fe element with an average content of about 2%, and there occurs less difference of Fe content among these tuffs. Therefore, the above test result is reliable and considerable precision. So far, the test results provide a significant reference in the absence of better method for determining the content of crystalline phase, excepting for the quantitative determination of amorphous content by reference to internal or external standards.

2.2.4 Test on pozzolanic activity strength index and pozzolanic activity index

At the macro level, the impact of pozzolanic activity of various pozzolan on cement-based composite will be reflected through mechanical conduct. The pozzolanic activity strength index (Abbreviation: PASI) is mostly and easily used to evaluate pozzolanic activity of pozzolan in cement-based composite. The PASI is defined as the ratio of the compression strength of the pozzolan/cement mortar with pozzolan replacing cement to that of the cement mortar without pozzolan under the same standard curing environment and curing time. In particular, just as outlined in Chinese industry standards JG/T 315-2011(Natural Pozzolanic Materials Used for Cement Mortar and Concrete), the pozzolanic activity index for pozzolan is defined as the ratio of the compression strength of a pozzolan/cement mortar with 30% pozzolan to that of cement mortar. According to this standard, a set of testing mortars (including three samples) were prepared by mixing cement, ISO standard sand, and tuff powder, shown in Table 1. After molding, the mortar samples were immediately covered to prevent evaporation and cured in a moist environment at 20±2℃ for 24 h. The mortar samples were then removed from the moulds and cured in thermostatic water bath (at 20±2℃) for their 28 or 90 days before strength testing.

Table 1 Proportions of the ingredients of 3 mortar samples

Material	Cement	Tuff powder	ISO Standard sand	Water
Weight /gram	315	135	1350	225

For the experiment, mortars were made with ISO standard sand and control Portland cement, which was produced by China United Cement Group Co., LTD. and Lucheng Cement Co., LTD. in Shandong Province. The control Portland cement was P.Ⅰ 42.5grade, which is a type Ⅰ Portland cement with a compressive strength more than 42.5 MPa at the 28th day of curing under standard conditions (According to ISO 679).

2.2.5 Preparation of paste for determining pozzolanic reaction degree

The tuff/cement pastes were prepared at a ratio of water to cementitious materials (W/CM) of 0.3. Tuff powder was used as a direct replacement for cement on a weight basis at percentages of 0, 10, 20, 30, or 40%. The prepared tuff/cement pastes were cured in a moist environment (at 20±2℃) for one day, then at a constant temperature of 20±2℃and relative humidity ≥90% for 3, 7, 14, 28, 60, or 90 days until termination of pozzolanic reaction. The tuff/cement pastes were immediately soaked in anhydrous alcohol to cease the further hydration, following which pozzolanic reaction degree and content of bond water and CH were determined.

2.2.6 Determination of pozzolanic reaction degree by hydrochloric acid dissolution

The pozzolanic reaction degree (Abbreviation: PRD) of tuff in the pastes was quantitatively determined using a selective dissolution method developed by Ohsawa *et al.* (1985) and Li *et al.* (1985). The principle of the procedure is based on the assumption that the majority of the unreacted pozzolan is acid insoluble. In a blended cement paste, the pozzolan reacts with calcium hydroxide to form acid soluble hydration products. Thus, it is possible to dissolve the hydration products of cement and pozzolans, and the unreacted cement, leaving the unreacted pozzolan as insoluble residue (Li *et al*. 1985). The pozzolanic reaction degree for pozzolan is defined as the proportion of reacted pozzolan as a percentage of the initial amount of pozzolan in the pozzolan/cement paste.

The prepared samples were placed in a vacuum desiccator overnight to remove the anhydrous alcohol and then dried at 60℃ in an oven. To determine the degree of hydration, the dried samples were ground into powder and passed through 80 μm sieve before the chemical analysis was performed.

The details of the procedure for determining the pozzolanic reaction degree of tuff using hydrochloric acid dissolution are as following. First, the mass fractions for insoluble parts of cement and tuff powder in hydrochloric acid dissolution are measured separately. Second, the sample of tuff/cement paste is divided into two parts. One part is gradually burned up to 950 ℃for 1h in an electric furnace. The other part is used in hydrochloric acid dissolution method for determining the mass fraction of the residual tuff that does not participate in a pozzolanic reaction in the tuff/cement paste sample. The ground powder of tuff/cement paste sample is placed in hydrochloric acid solution prepared with hydrochloric acid and deionized water in weight proportion of 1:2 at 40℃. The residue insoluble in hydrochloric acid is weighed after filtered out and dried to constant weight under the 105℃. Thus, the mass percentage of the partial tuff that does not participate in a pozzolanic reaction in the tuff/cement paste can be calculated using the following formula (1) given below. Finally, using differential calculation, the mass fraction of the partial tuff that does participated in a pozzolanic reaction in the tuff/cement paste (i.e., PRD) could be achieved. The PRD (%) is given by

$$PRD = \left(1 - \frac{\frac{W_H}{1 - W_N} - W_{C,O}W_{C,H}}{W_{T,O}W_{T,H}} \right) \times 100 \tag{1}$$

Where

$$W_N = \frac{W_L - L_C}{1 - L_C} \tag{2}$$

$$W_L = \frac{m_0 - m_{950}}{m_0} \tag{3}$$

$$L_c = (1 - W_{T,O})L_P + W_{T,O}L_T \tag{4}$$

Here, $W_{C,O}$—the mass fraction of cement in the tuff/cement paste (%); $W_{T,O}$—the mass fraction of tuff in the tuff/cement paste (%); W_H—the mass fraction of insoluble material in hydrochloric acid in the tuff/cement paste (%); $W_{C,H}$—the mass fraction of insoluble material in the acid in the pure cement (%);$W_{T,H}$—the mass fraction of insoluble material in the acid in the pure tuff powder (%); W_N—the mass fraction of non-evaporable water in the tuff/cement paste (%); W_L—the ignition loss of the tuff/cement paste (%); m_0—the mass of the tuff/cement paste before burning (g); m_{950}—the mass of the tuff/cement paste after calcination at 950℃ (g); L_P—the ignition loss of the pure cement (%); L_T—the ignition loss of the tuff powder (%); L_C—the ignition loss of the mixture of cement and tuff powder before pozzolanic reaction (%).

2.2.7 Determining contents of bond water and CH

The contents of bond water and CH in the tuff/cement paste were quantitatively measured using a differential scanning calorimeter (DSC-TG). The thermo-gravimetric analyzer SDT Q600 and the Universal Analysis 2000 program produced by TA Instruments Company in the United States were used for the work.

Dehydration of hydrated calcium silicate gel and ettringite in the tuff/cement paste occurs mainly in the 50–400℃, marked as Ta. The decomposition temperature of CH in the paste is about 400–550℃, denoted by Tb. The CH content is calculated from the weight loss between 400℃ and 550℃, and is expressed both as a percentage by weight of ignited sample and a percentage by weight of the cement in the sample. Decomposition of carbide parts in the cement paste and water decomposition of calcium silicate gel and late ettringite occur at 550–770℃, marked as Tc, in which the proportion of the two reactions is currently not accurately known, but on the basis of past experience, the two-thirds in the Tc from decomposition of carbide carbonated part of hydration products, and the rest from water decomposition of calcium silicate gel and late ettringite. Therefore, the contents of bond water and CH in cement hydration products can be calculated according to the following formula (Li 2003).

$$\textit{Content of bond water} = T_a + T_b + \frac{T_c}{3} + \frac{2}{3} \times \frac{Tc}{44} \times 18 \tag{5}$$

$$Content\ of\ CH = \left(\frac{T_b}{18} + \frac{2}{3} \times \frac{T_c}{44}\right) \times 74 \qquad (6)$$

3. Results and discussion

3.1 Chemical composition

The results in chemical composition analysis of the tuffs are listed in Table 2. They displayed that the tuffs were close to granite composition and contained high quantities of SiO_2+Al_2O_3, with an especially great amount of SiO_2.The chemical composition of natural pozzolan is limited to the minimum sum of SiO_2+Al_2O_3+Fe_2O_3 ≥70% in ASTM C 618 and the Turkey Standards (TS 25). The tuff specimens in our study have the sum of SiO_2+Al_2O_3 >86% and fulfill the primary chemical requirement. A relatively high content of SiO_2+Al_2O_3 could also indicate the acidic nature of the pozzolanic material.

The concept had been declared that the most important composition of pozzolan is SiO_2 and it can provide contributions to pozzolanic activity in non-crystalline form (Ahmet and Sukru 2007, Alp *et al*. 2009). The chemical composition of natural pozzolan is stated as 50–67% SiO_2 in the German standards (DIN 51043). Because the tuffs investigated contained a far greater proportion of SiO_2 than required by this standard, which implies that they may provide more potential for SiO_2activity to actuate the pozzolanic activity during second hydration reaction. Compared with other tuffs used as pozzlans in Turkey (Ahmet and Sukru 2007, Alp *et al*. 2009), Saudi Arabia (Khan and Alhozaimy 2011), and Malaysia (Wong and Askury 2011), the tuffs have higher quantity either the sum of SiO_2+Al_2O_3 or the SiO_2 content, but less Fe_2O_3.

Rodriguez-Camacho and Uribe-Afif (2002) examined the performance of nine natural pozzolan in Mexican. They found that the pozzolan with 11.6-14.7% alumina was highly resistant to sulphate attack. In this regard, the tuffs used in this study could be expected to produce a moderate resistance to sulphate attack when used as an admixture in the cement-based composite, but further tests should be performed to verify this assumption.

3.2 Petrographic features

Petrography characteristics of the tuffs were inspected under polarizing microscope using the thin sections. Natural pozzolans generally contain pyroclastic rocks. The tuffs have evident porphyritic texture with 70—80% matrix of volcanic ash in a vitreous state according to visual microscopic inspection. The porphyritic bodies comprise fragments of crystal, rock, and glass accompanied in their margins partly melted. The majority of the crystals are classified as quartz and feldspar minerals.

3.3 Powder XRD result

XRD patterns of the tuff powder are described in Fig. 2. The results of identification of crystalline phase minerals and calculation of amorphous phase content are showed in Table 3.

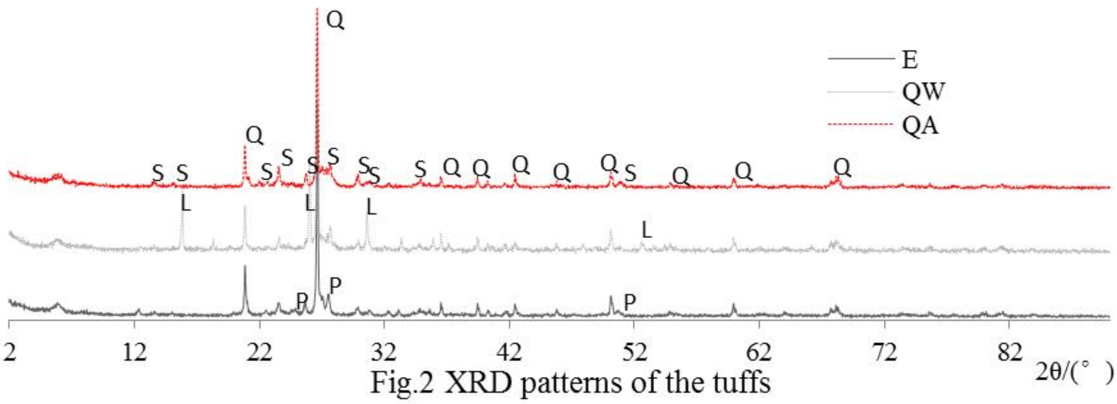

Fig.2 XRD patterns of the tuffs

Q--quartz, S--sanidine, L--leucite, P--potassiun aluminum silicate

Table 2 Major chemical composition of tuffs and cement, in mass percent

No.	Specimen	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3	Loss on ignition
1	Tuff E	74.99	12.87	7.23	0.21	0.082	0.11	1.37	1.74
2	Tuff QW	74.13	12.05	3.84	3.75	0.65	0.38	2.25	3.30
3	Tuff QA	75.27	12.40	6.12	1.91	0.23	0.27	1.82	1.18
4	Cement	25.26	6.38	--	0.56	54.67	2.68	--	2.59

Table 3 Powder XRD results

No.	Specimen	Mineral	Amorphous phase content/%	Pozzolanic active component/%
1	Tuff E	Quartz, sanidine, potassiun aluminum silicate, silicon oxide	57	50
2	Tuff QW	Quartz, leucite, sanidine	59	51
3	Tuff QA	Quartz, sanidine	60	53

The amorphous phase content determined by XRD was a little less but more precise than the matrix content estimated by petrographic analysis under polarizing microscope, since there were a great deal of micro-crystals hidden in matrix of volcanic ash so that matrix content was apparently evaluated on the higher level.

The tuffs were mainly composed of glassy groundmass, quartz, sanidine, sodium feldspar, and leucite in a decreasing order of abundance. From the view of crystal mineral genesis, the tuffs contained some silicon aluminum minerals generated under high temperature condition, such as quartz, sanidine (disorder), sodium feldspar (disorder), leucite and so on. On the other hand, the tuffs were comprised of amorphous phase no less than 57%. These are marked that tuffs were generated when silicon aluminum magma at high temperature erupted and was rapidly cooled, which is why such tuffs are not only rich in silicon aluminium on the chemical composition, but also an unstable structural state with high vitreous content. This could further explain why the tuffs have a great potential for pozzolanic activity.

3.4 Pozzolanic activity component

Factors affected the activity of pozzolan are content of (SiO_2 + Al_2O_3 + Fe_2O_3), the amorphous degree of their structure, and fineness of powder particles. Generally it was known that pozzolanic activity of pozzolans depends principally on the content of active SiO_2 and active Al_2O_3 below certain particle sizes. Thus, in order to express the total of active SiO_2 and active Al_2O_3, a pozzolanic activity component (%)(Abbreviation: PAC) for pozzolans can be defined as the sum of active SiO_2 and active Al_2O_3, and then calculated as the product of chemical composition (SiO_2 + Al_2O_3) content (%) and amorphous phase content (%)of the pozzolan as follows:

$$PAC = Chemical\ composition\ (SiO_2+Al_2O_3)\ content \times Amorphous\ phase\ content \quad (7)$$

If known at chemical composition (SiO_2+Al_2O_3) content from chemical composition analysis and amorphous phase content from XRD, as the above, PAC for pozzolan could be calculated using the Eq. (7). PAC declares quantitatively proportion of pozzolanic activity composition to be able to react during the second hydration reaction, and provides a characteristic index of potential pozzolanic activity, which expresses the intrinsic capacity of a pozzolan to react with CH without consideration of particle size. The PACs for the above tuffs are presented in the last column of Table 3. The result indicated that these tuffs possessed pozzolanic activity components no less than half of the total rock composition. Therefore, from the perspective of intrinsic property, the tuffs have sufficient potentiality for pozzolanic activity, and can be used as supplementary cementing material in cement-based composite so long as they are ground into powder with adequate fineness.

3.5 Pozzolanic activity strength index and pozzolanic activity index

Pozzolanic activity index is approved as a direct parameter for assessing pozzolanic activity of pozzolan. The tested achievements of pozzolanic activity index are enumerated in Table 4. The pozzolanic activity indices are so large enough to meet to demand of the Chinese industry standard JG/T 315–2011 (Natural Pozzolanic Materials Used for Cement Mortar and Concrete). Therefore, the three tuffs are mechanically suitable for use as pozzolans in cement-based composite.

It is generally appreciated that pozzolan should own pozzolanic activity index ≥75% so to satisfy demand of supplementary binding material on superior quality in cement-based composite, which is consistent with the Chinese Standard GB/T 18736–2002 (Mineral Admixtures for High Strength and High Performance Concrete) and ASTM C618-00 (Standard Specification for Coal Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete) in the United States. Here, Tuff E possessed pozzolanic activity index of no less than 75% and surpassed to the critical value for high grade pozzolan in 28 days curing period. Meanwhile, other tuff QA and QW had pozzolanic activity indices approximating the critical value for good pozzolan. Hence, the three tuffs could be confirmed as better pozzolans in cement-based composite.

Mechanical performance of blended cements in concrete and mortar is closely controlled by the level of pozzolan replacement. As just seen from Table 4, a consistent reduction in the compressive or flexural strength and rate of strength development for mortars was noted as the amount of raw pozzolan material in the blended cement increased. It is observed that the optimal ratio of tuff powder to control cement was 10% for compressive or flexural strength of mortar at anytime, for which the mortar strengths were the highest and some of them surpassed to control cement mortar. While the ground tuffs replaced up to 50% of control Portland cement, the tuff blended cements produced had the desired physical characteristics, with 28–day compressive strengths higher than 32.5 MPa. According to Chinese cement standard, pozzolan Portland cement need the minimum value of 28–day compressive strength above 32.5 MPa. The findings suggest that the tuffs can be used in the production of pozzolan cements blended with 50% tuff.

Similar to this, variation of PASI with mixing content of Tuff QA powder is plotted in Fig. 3. The PASI values for Tuff QA were decreased with increasing percentage of tuff powder within the mentioned range, and the relation between these indices and the mix percentage were very close to linear law. But these fitting linear regression equations had different correlation coefficients at various cured stage, which was in turn 0.92 at 28 days and 0.99 at 90 days. The development trend of PASI with mixing pozzolan content exhibited more stable in the late curing stage. So did Tuff E and QW.

Table 4 Mortar strength and pozzolanic active strength indices

No.	Specimen	Tuff content/%	Compressive strength/MPa		Flexural strength/MPa		PASI /%	
			28d	90d	28d	90d	28d	90d
0	Cement	0	47.5	53.3	7.3	8.6		
1	Tuff E	10	55.4	53.6	8.3	8.4	117	101
		20	48.7	48.9	7.8	7.9	103	92
		30	38.2	44.8	6.9	7.0	80	84
		40	35.6	39.3	6.3	6.6	75	74
		50	34.0	36.7	6.1	6.3	72	69
2	Tuff QW	10	54.1	52.7	8.4	8.6	114	99
		20	47.8	48.2	7.9	8.0	101	90
		30	35.2	43.3	7.1	7.5	74	81
		40	34.6	38.5	6.7	7.2	73	72
		50	32.9	34.6	6.0	6.1	69	65
3	Tuff QA	10	53.3	50.5	8.2	8.3	112	95
		20	46.9	46.4	7.8	7.6	99	87
		30	35.1	39.7	6.8	6.6	74	74
		40	37.2	37.8	6.4	7.0	78	71
		50	32.6	33.1	5.9	5.8	69	62
4	Chinese standard JG/T 315-2011	30					≥65	

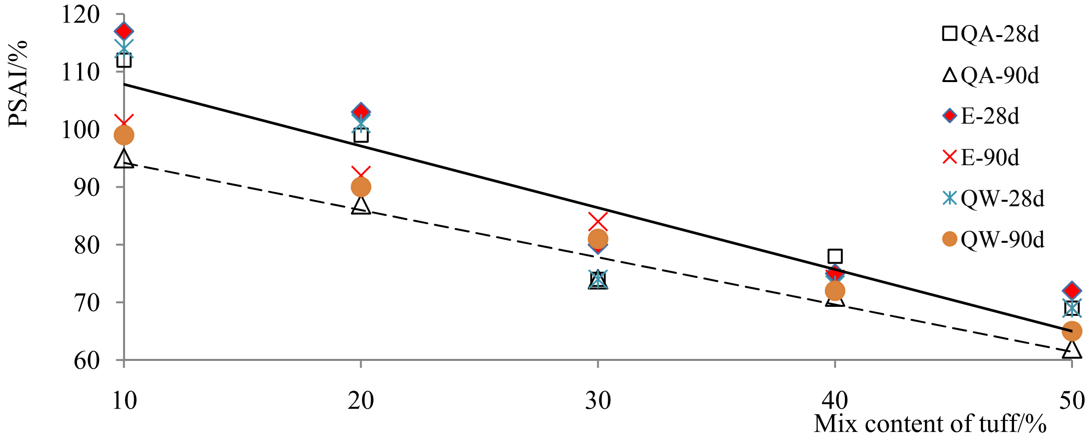

Fig. 3 Variation of PSAI with mixing content of tuff

3.6 The relationship between pozzolanic activity and chemical composition

When the relationship between pozzolanic activity and SiO_2, Al_2O_3, and the other components is concerned, the probability of having an idea about the strength of the pozzolan by looking at its chemical composition can be possible. Highly correlated (88%) relation between the SiO_2 rate and the 7 days compressive strength of tuff/lime mortar was established by Ahmet and Sukru (2007), and as seen from the follow Eq. (8).

$$\textit{Compressive strength} = 0.309\ (\%SiO_2)\quad - 11.24 \tag{8}$$

On the basis of calculation according to the data in Table 2 and Eq. (8), the 7 days compressive strengths of mortars with lime and tuffs in our work were estimated within 11.67—12.02 MPa, and larger than that of mortars prepared with lime and tuffs from northeast region of Turkey (Ahmet and Sukru 2007).

It was ensured that pozzolanic activity increases with the increase in SiO_2 rate. The results by Ahmet and Sukru (2007) showed that the most important component increasing the pozzolanic activity of a pozzolan is SiO_2, but Al_2O_3, Fe_2O_3, MgO and K_2O decrease the pozzolanic activity. It is possible to say that there are two reasons of increasing strength of pozzolan, and so cements, by increasing SiO_2 ratio. Firstly, the minerals that contain SiO_2 can be ground finely and so it can fill micro pores. The second is that the capable of binding $Ca(OH)_2$ of SiO_2 is higher than the others' (Al_2O_3, Fe_2O_3). According to latter, this reaction contributes to form of calcium-silicate-hydrate in shorter time. Therefore, it is possible to say that the tuff used as pozzolan should be high proportion of SiO_2.

3.7 Pozzolanic reaction degree

The pozzolanic reaction degrees of tuffs at different ages and mixing contents are presented in Table 5 and compared with the result of previous research (Poon *et al*. 1999).

Although there was a small difference on trend pattern of pozzolanic reaction degree among three tuff specimens during the early stage (3days, 7days and 14 days), the pozzolanic reaction degree of Tuff QA was still higher than that of Tuff E and QW after 28 days, with individual exception. From the viewpoints of the chemical reaction properties reflected by pozzolanic reaction degree and the potential pozzolanic activity expressed by pozzolanic activity component, Tuff QA possessed better pozzolanic activity and was preferable pozzolan in cement-based composite.

Tuff QA is an example to discuss a varying pattern for the pozzolanic reaction degrees of tuff. At the age of 3 days, the reaction degree of the tuff was recorded to scatter between 9–15% for various mixing contents, seen in Table 5. At the age of 14 days, the reaction degree of the tuff was approximately 25–29%. Then, at 90 days, more than 29% of the tuff had been reacted at least, so much as 51% of the tuff had been participated in pozzolanic hydration with a 10% tuff replacement in the tuff/cement paste. The pozzolanic reaction degree of the tuff in the paste gradually increased with prolongation of curing time, seen in Fig.4. Growth rate of the pozzolanic reaction degree during early hydration period was obviously larger than that after 14 days. Then the pozzolanic reaction degree was grown slowly, but had been in progress for a long-term. It is important to note that, although the rate of tuff reaction becomes slower after prolonged curing, there was still a considerable increase in the pozzolanic reaction degree of tuff from 14 to 90 days. For example, for a tuff/cement paste with 20% Tuff QA, the pozzolanic reaction degree was 29.6% at 14 days upto51.1% at 90 days. The reaction of tuff was still not completed at the ages of 90 days, and about half of the tuff are still unreacted.

Table 5 Pozzolanic reaction degree of tuff in the tuff/cement paste

No.	Specimen	Mix content/%	3days	7 days	14 days	28 days	60 days	90 days
1	Tuff E	10	8.98	17.14	26.91	33.18	32.98	33.15
2		20	19.29	21.07	26.31	26.53	28.97	32.42
3		30	15.90	20.87	25.92	24.19	25.13	30.60
4		40	18.13	24.47	26.63	28.51	25.91	28.49
5	Tuff QA	10	15.01	23.25	29.55	44.10	49.14	51.07
6		20	11.77	23.84	26.84	31.16	33.80	36.76
7		30	8.83	25.08	29.37	30.37	30.94	33.36
8		40	12.12	23.58	25.12	24.75	27.11	29.29
9	Tuff QW	10	13.36	20.47	27.19	38.64	43.54	45.20
10		20	10.59	24.93	26.57	29.85	31.03	34.96
11		30	9.33	23.56	27.42	28.37	28.75	31.17
12		40	12.82	22.80	25.73	26.41	26.74	28.53
13	Zeolite (Poon *et al.* 1999)	15	5.17	9.08		28.94		36.32
14		25	4.93	8.92		28.45		36.14

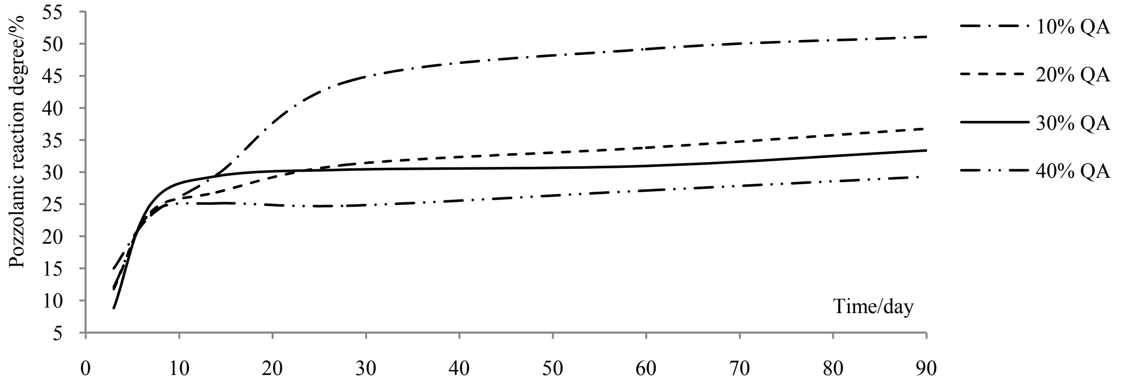

Fig. 4 The trend of pozzolanic reaction degrees of Tuff QA

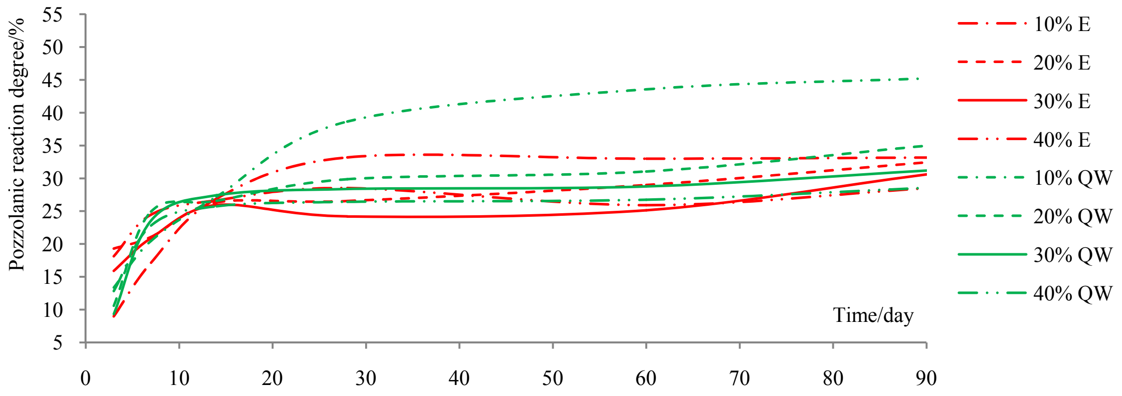

Fig. 5 The trend of pozzolanic reaction degrees of the tuffs

From Figs. 4 and 5, it can also be noted that the pozzolanic reaction degree of the tuff in a tuff/cement paste with a higher percentage of replacement is lower than in that with a lower percentage of replacement. This is similar to the results in study of the hydration of the zeolite/cement pastes (Poon *et al.* 1999), fly ash/cement pastes (Lam *et al.* 2000), and metakaolin/cement pastes and silica fume/ cement pastes (Poon *et al*. 2001). The higher rate of pozzolanic reaction in cement pastes with a lower replacement level can be attributed to the higher concentration of CH available for the pozzolan to react with.

A comparison of the reaction degrees of tuffs with zeolite measured by a selective dissolution procedure using picric acid-methanol solution and water (Poon *et al.* 1999) is given in Table 5. It can be seen that the reactivity of tuff is distinctly higher than that of zeolite during the early stage (3days and 7days), but close to or lower than that of zeolite after 28 days. That is indicated that the tuff in cement-based composite has more advantages than zeolite on rapid hardening in early stage and accelerating construction in site.

3.8 The bond water content and CH content

The bond water content and CH contents of the pastes at different ages and various blended proportions for the tuffs are shown in Fig. 6-11.

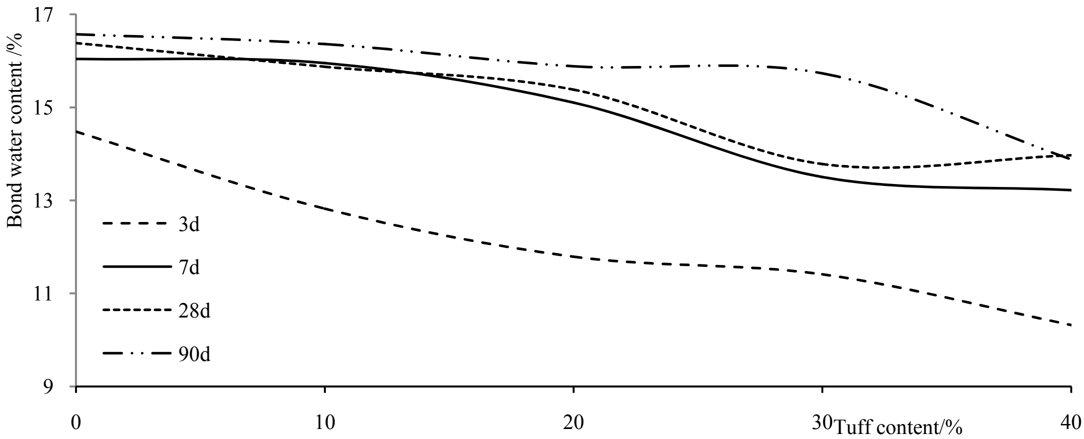

Fig. 6 Relation between the bond water content and Tuff QA content

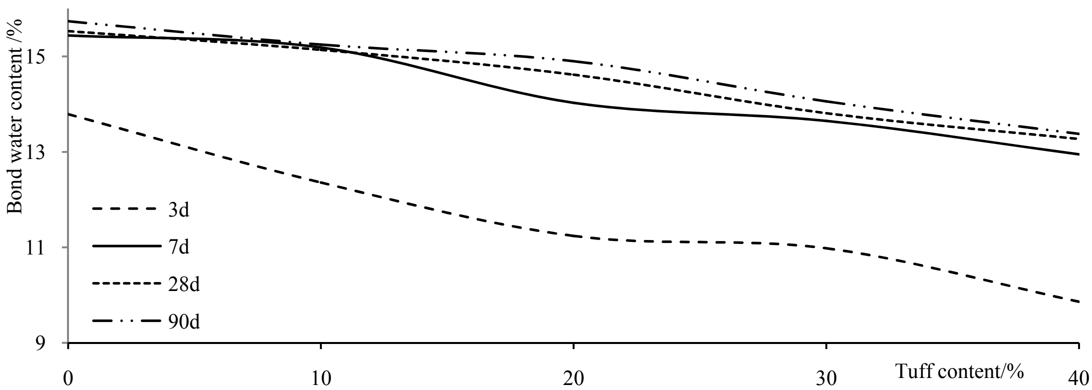

Fig. 7 Relation between the bond water content and Tuff E content

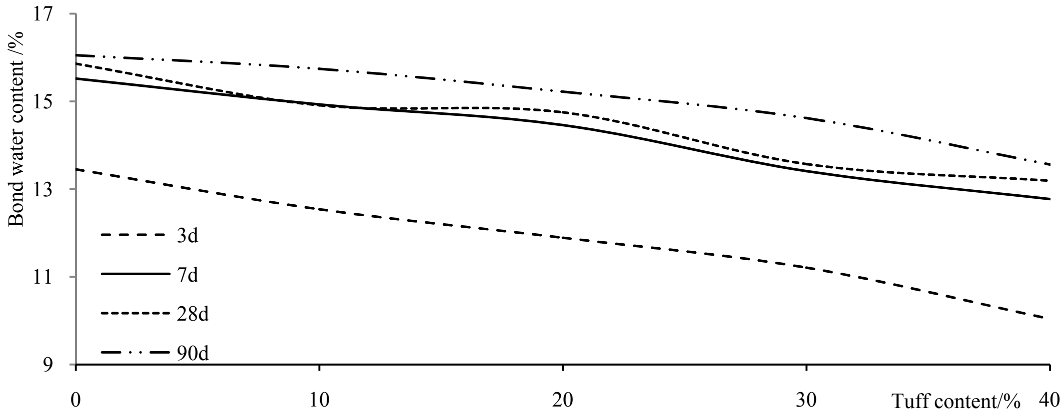

Fig. 8 Relation between the bond water content and Tuff QW content

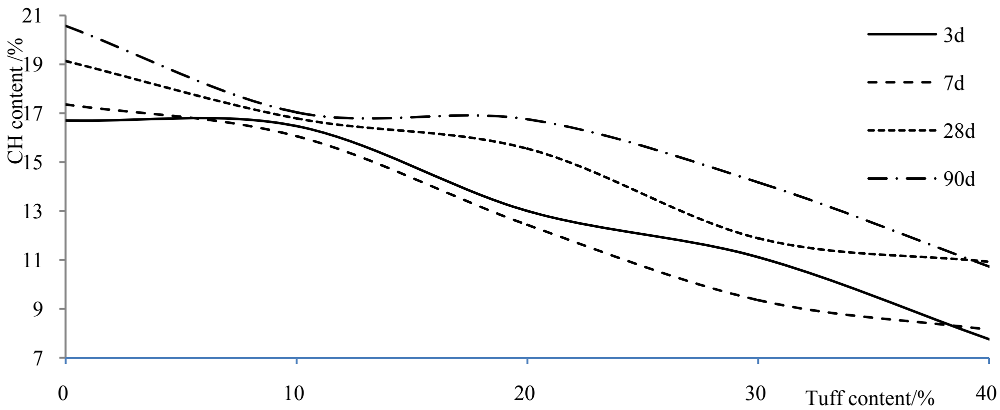

Fig. 9 Relation between CH content and Tuff QA content

It can be seen that all tuff/cement pastes had lower the bond water contents and CH contents than the control paste (0% tuff content). CH content of tuff/cement pastes was lower than that of the control paste at all test ages due to lower amount of CH production as well as its consumption by pozzolanic activity of tuff. Both of the bond water content and CH content decreased with increasing tuff content in the pastes. Furthermore, the amounts of CH consumed by the reaction of tuff in the pastes with different replacement level can be roughly estimated by subtracting the CH contents of the tuff/cement pastes from that of the control cement paste. The estimated results are plotted in the following Figs. 12 and 13. Thus, the reduction of CH is enhanced with increasing content of the tuff in the paste. The higher the tuff replacement level, the greater the reduction in CH content is. This reduction could be attributed to a great extent of the replacement level (lower cement content).

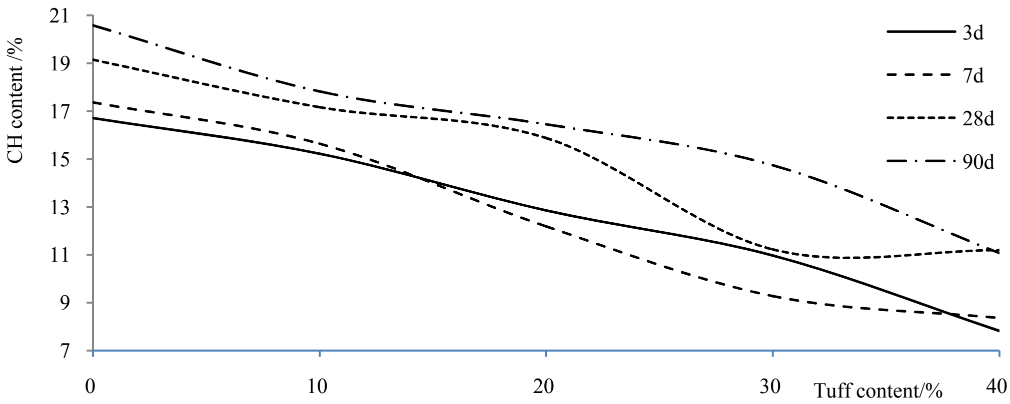

Fig. 10 Relation between CH content and Tuff E content

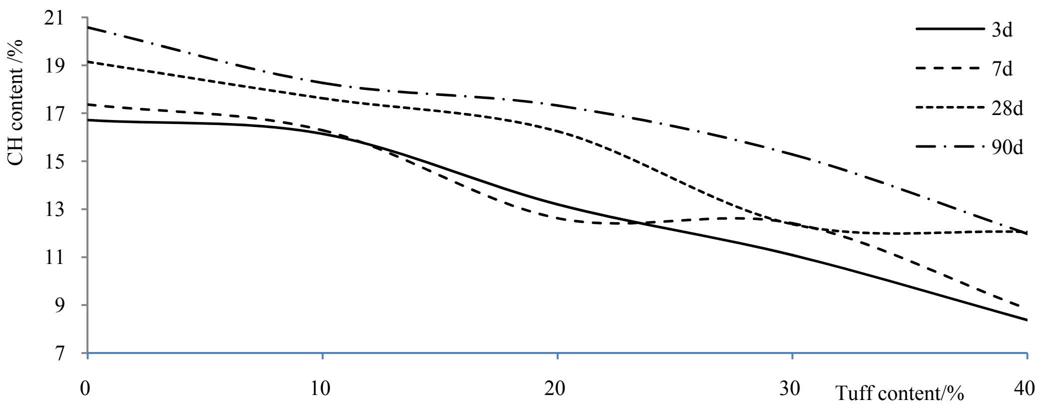

Fig. 11 Relation between CH content and Tuff QW content

It is known that the CH content of a Portland cement paste indicates the hydration degree of the cement, while the CH consumption in a blended cement paste is related to the pozzolanic reaction degree (Lam *et al*. 2000, Poon *et al*. 2001). Compared Fig. 12 with Fig. 4, there are some striking similarities. At age of 28 days, growth rate of the pozzolanic reaction degree for 10% tuff in the blended cement paste was obviously turned to reduce, while the CH reduction in the blended cement paste attained to the maximum. However, since high volume of tuff at a 40% replacement level was blended in the cement paste, both of the altering growth rate of the pozzolanic reaction degree and the maximum of CH depletion occurred forward at 7 days. This phenomenon is somewhat similar to those observed at 14 days for the 20% and 30% tuff replacement in the blended cement paste, respectively. Sufficient CH from hydration of cement existed under the lower dosage of tuff in the paste, then accelerated more pozzolanic reaction of tuff in the system and maintained higher growth rate of the pozzolanic reaction degree for longer time. A positive CH reduction indicates that pozzolanic reaction from tuff occured and consumed more CH than was produced by the hydration between cement and water. From Fig. 4 to Fig. 13, it is evident that the incorporation of a high volume of tuff in a cement paste may accelerate second hydration and deplete more CH at early ages. But the reduction in CH content becomes positive and keeps on increasing with age. These above revealed fully the consistency of pozzolanic reaction degree and CH depletion, which could be indicators to reflect process of pozzolanic reaction for the tuff. The similar results could be found in study of the hydration of the fly ash/cement pastes by Zhang *et al*. (2000).

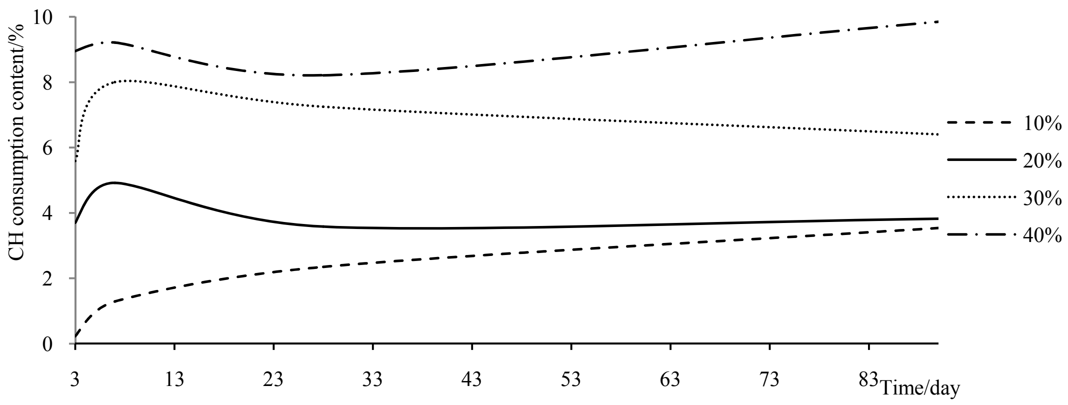

Fig. 12 Relation between CH consumption content and hydration time for Tuff QA

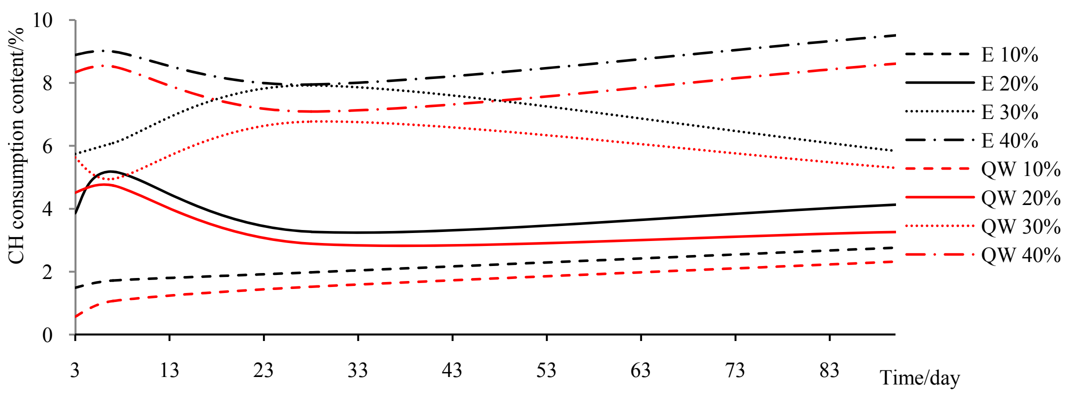

Fig. 13 Relation between CH consumption content and hydration time for the tuffs

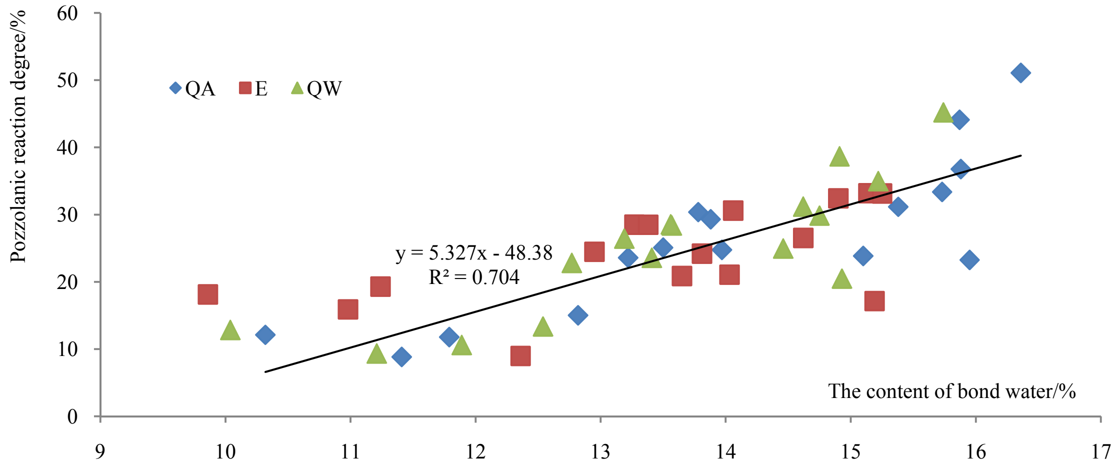

Fig. 14 Variation of pozzolanic reaction degree with the bond water content

Nevertheless, the conclusion above was different from the results pointed by Uzal and Turanli (2012),who drawn a conclusion that CH formed from hydration of PC phase in the clinoptilolite tuff/cement pastes was almost completely consumed at the end of 28 days of hydration. Accordingly blended cements containing large amounts of clinoptilolite tuff were found to be more reactive in terms of pozzolanicity, when compared to similar blended systems with non-zeolitic natural pozzolans.

The parallel discussion is conducted for the relationship between the bond water content in the tuff/cement paste and the pozzolanic reaction degree of tuff. Based on data from Table 5 and Figs. 6-8, variation of the pozzolanic reaction degree for the tuffs in the paste at different times with the bond water content in the homologous paste were plotted in Fig. 14. Variation of the pozzolanic reaction degree was increased with the bond water content within the discussed range, and relation between them appeared well linear law. Their fitting linear regression equations possessed correlation coefficient 0.84, 0.61, and 0.84 for Tuff QA, E, and QW, respectively. The relative equation can be used in mutual conversion between the two parameters, meanwhile which was ensured accuracy due to favorable correlation coefficient. These are evidence that both of the methods for applications of CH depletion content and bond water content in the paste are feasibility to estimate pozzolanic reaction for tuff.

4 . Conclusions

The consequence of the analysis and discussion are summarized as follows.

- The three tuffs were demonstrated to be qualified supplementary binding material in cement-based composite according to relevant standards. The tuffs possessed abundant SiO_2+Al_2O_3 on chemical composition and plentiful amorphous phase content on rock texture.
- It was also evident that the tuffs have great potential of pozzolanic activity with the parameters of pozzolanic activity component, pozzolanic activity index, and pozzolanic reaction

degree.

• The pozzolanic reaction degrees of the tuffs in the cement paste were gradually increased with prolongation of curing time. After 14 days, the pozzolanic reaction degree was grown slowly down, but had been in progress for a longterm.

• The analysis results revealed the consistency of CH consumption and pozzolanic reaction degree, which could be used as indicators to reflect process of pozzolanic reaction for the tuff. Variation of the pozzolanic reaction degree was improved with the bond water content. The fitting linear regression equation can be applied to mutual conversion between pozzolanic reaction degree and bond water content.

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