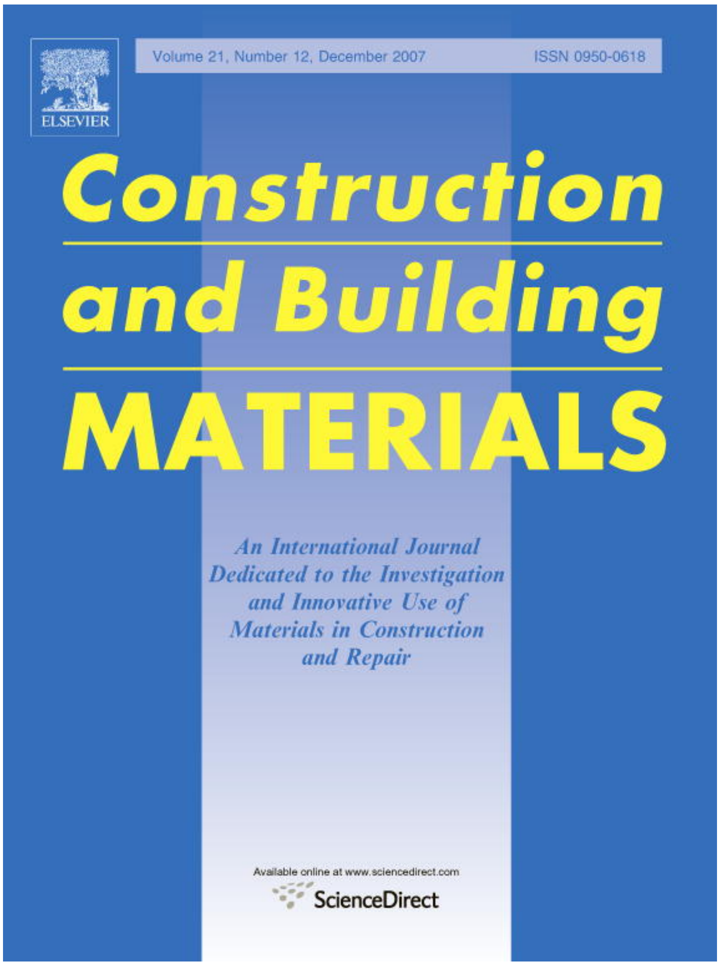
Volume 21, Number 12, December 2007
ISSN 0950-0618
ELSEVIER
Construction and Building MATERIALS
An International Journal Dedicated to the Investigation and Innovative Use of Materials in Construction and Repair
Available online at www.sciencedirect.com
ScienceDirect

Available online at www.sciencedirect.com
ScienceDirect
Construction and Building Materials 21 (2007) 2066–2071
Construction and Building MATERIALS
www.elsevier.com/locate/conbuildmat

Availability of tuffs from northeast of Turkey as natural pozzolan on cement, some chemical and mechanical relationships

Ahmet Çavdar, Şükrü Yetgin *

Department of Civil Engineering, Karadeniz Technical University, Gumushane 29000, Turkey

Received 2 June 2005; received in revised form 28 February 2006; accepted 31 May 2006
Available online 20 September 2006

Abstract

At Northeast of Turkey, it is possible to find plenty of volcanic origin rocks and rich natural pozzolan beds. In this study, the pozzolanic activities of six types of different tuff samples taken from Trabzon and Bayburt regions (Northeast of Turkey) were examined according to the related standard and it was determined that the compressive strengths were varying between 6.7–11.0 MPa. In addition, the chemical compositions of these samples, except one, were consistent with the related standard. On the other hand, the results obtained from these studies were that increase in the proportion of SiO_2 in the pozzolan increases the pozzolanic activity.

Keywords: Characterization methods; X-ray diffraction; Petrography; Compressive strength; Natural pozzolan

1. Introduction

Use of natural pozzolans, also known as "trass", in cements or concrete systems make important effects on several properties of cement mortar such as strength, setting times, volume expansion and durability depending on its substitution ratio and its fineness [1–6]. In addition, since these materials enter the cement production after kiln process they also provide important economical and ecological benefits [7–9].

Natural pozzolans generally contain pyroclastic rocks. These rocks generally contain carbonate, clay and zeolite group minerals as filling/binding materials. Zeolitization is the transformation of the glassy structure in natural pozzolan to zeolite-group minerals with external effects. Zeolites can loose their water contents with the effect of heat. In other words, with the help of their channel shaped and largely spaced ($d = 11.4$ Å) framed mineral structures they can easily take and release water ions [10]. These ions do not take part in the cage structure. One more important aspect is that zeolites can release alkali atoms and take in calcium and magnesium ions [11]. Therefore, when pyroclastics rich in zeolite minerals are mixed with slaked lime and water, they can form stable silicate minerals [12]. Besides zeolite, natural pozzolans can also include combinations of various silicate minerals such as quartz, feldspar, mica, hornblende, pyroxene, cristobalite, clay minerals, amorphous pumice, and glass shards. In general, a good pozzolan has low quantities of clay minerals, low quantities of alkali feldspar, high quantities of zeolite minerals, and volcanic glass. In addition, it should exhibit high porosity and specific surface area [13]. Turkey is rich in natural pozzolans. Almost 155,000 km^2 of the country is covered by Tertiary- and Quaternary-age volcanic rocks, among which tuffs occupy important volumes. Although there are many geological investigations on these volcanics and their potential as natural pozzolans is not well established [14]. Former studies show that there are zeolites as the most common secondary mineral in the volcanic rocks of the

* Corresponding author. Tel.: +90 456 233 74 25; fax: +90 456 233 74 27.
E-mail address: yetgins@hotmail.com (Ş. Yetgin).

0950-0618/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.conbuildmat.2006.05.034

Trabzon region, especially those containing feldspars. Besides these, widely found clay has completed its weathering period [15].

Pozzolanic activity can be defined as the reactivity capacity with $Ca(OH)_2$ and hardening capacity in humid medium [16]. Although some other properties have effects on the pozzolanic activity, the references states that the pozzolan's strength is especially affected by the chemical composition, fineness and the amount of its glassy phase [17]. In the German standards (DIN 51043) the chemical composition of natural pozzolans is stated as 50–67% SiO_2, 14–20% Al_2O_3, 2–5% Fe_2O_3, less than 10% $CaO+MgO$ and 3–8% Na_2O+K_2O [18]. The restrictions in the Turkish standard (TS 25 [19]) are given as a sum of the main ingredients similar to ASTM C311 [20].

The objective of this study is determining the availability of the tuffs taken from unused new fields of the Northeast of Turkey (Trabzon and Bayburt district) as natural pozzolan on cement and making the connections between pozzolanic activities of the materials and their petrographic-chemical compositions. In addition, the correctness of restrictions in the standard, TS 25 [19], will be discussed in a way.

2. Materials and experimental methods

Locations of samples were carried out, by examining geological maps of Trabzon and Bayburt (cities in Northeast of Turkey), and 42 samples were chosen for studies. Mineralogical and petrographical properties of the natural pozzolan samples were identified under the polarizing microscope by using their thin sections (Fig. 1) and X-ray powder diffraction (XRD) analysis of the powdered bulk samples were carried out (Fig. 2). Major element analysis of the samples comprising SiO_2, $A1_2O_3$, Fe_2O_3, MgO, CaO, Na_2O and K_2O were carried out by means of wet chemical analysis. The pozzolanic activities, the behavior of pozzolan in mortar, of these six samples were determined according to TS 25 [19]. According to this standard, at least three mortar specimens were prepared by mixing slaked lime, standard sand, and natural pozzolan (tuff) having the weights shown in Table 1. Immediately after molding, the mortar specimens were covered to prevent evaporation and cured in a moist environment (at 21±1 °C) for 24 h. The specimens were tested for their 7th day flexural and compressive strength according to EN 196–1 by the "Rilem–Cembureau Method" [21].

3. Results

3.1. Mineralogical and petrographical evaluations

The results of the carried out thin section and XRD investigations, as summarized in Table 2, the samples, except one (P; basanite), were characterized as dacidic and andesitic tuffs. These samples generally contain minerals having high ratio of SiO_2 such as quartz, plagioclase, amphibole, chlorite, illite, sanidine, clinoplolite and pyroxene. Besides, there are also zeolitization in secondary intergaps of the samples.

SiO_2 component can exist in both crystalline and non-crystalline form minerals. That the non-crystalline minerals like zeolites have high pozzolanic activity is well known. However, besides this, crystalline and mix-crystalline minerals also contribute pozzolanic activity. The high pozzolanic activity results in this study also prove this.

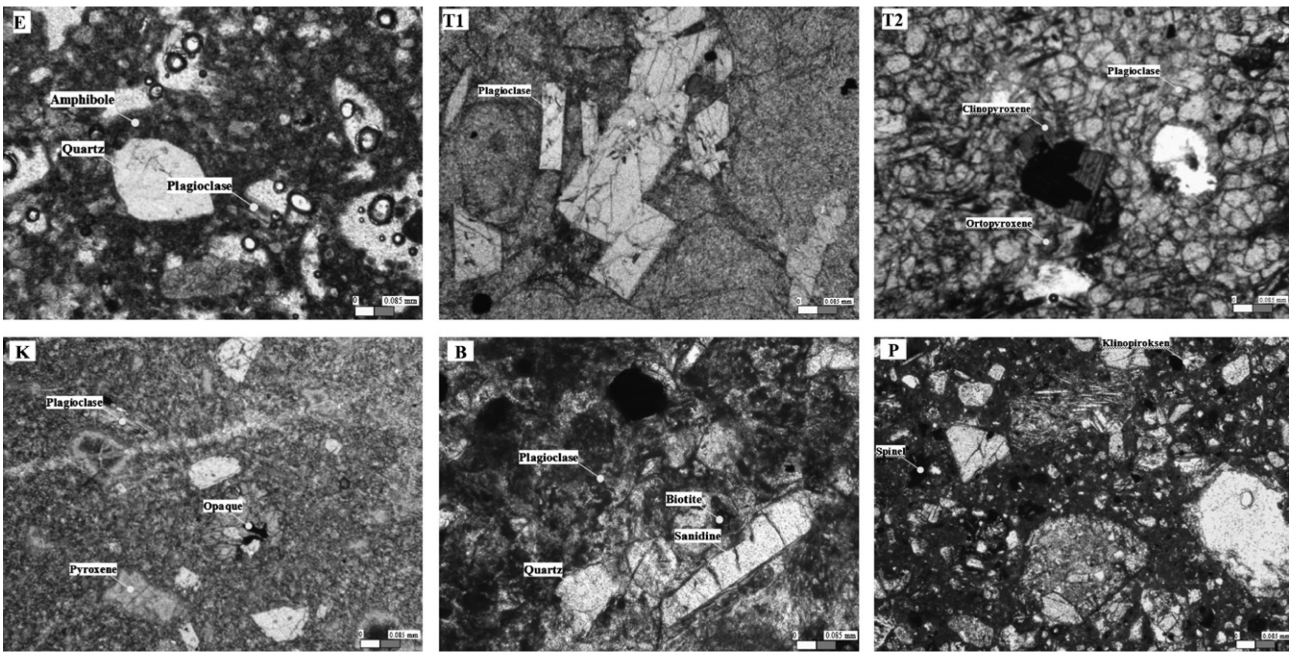

Fig. 1. Thin sections of the pozzolan.

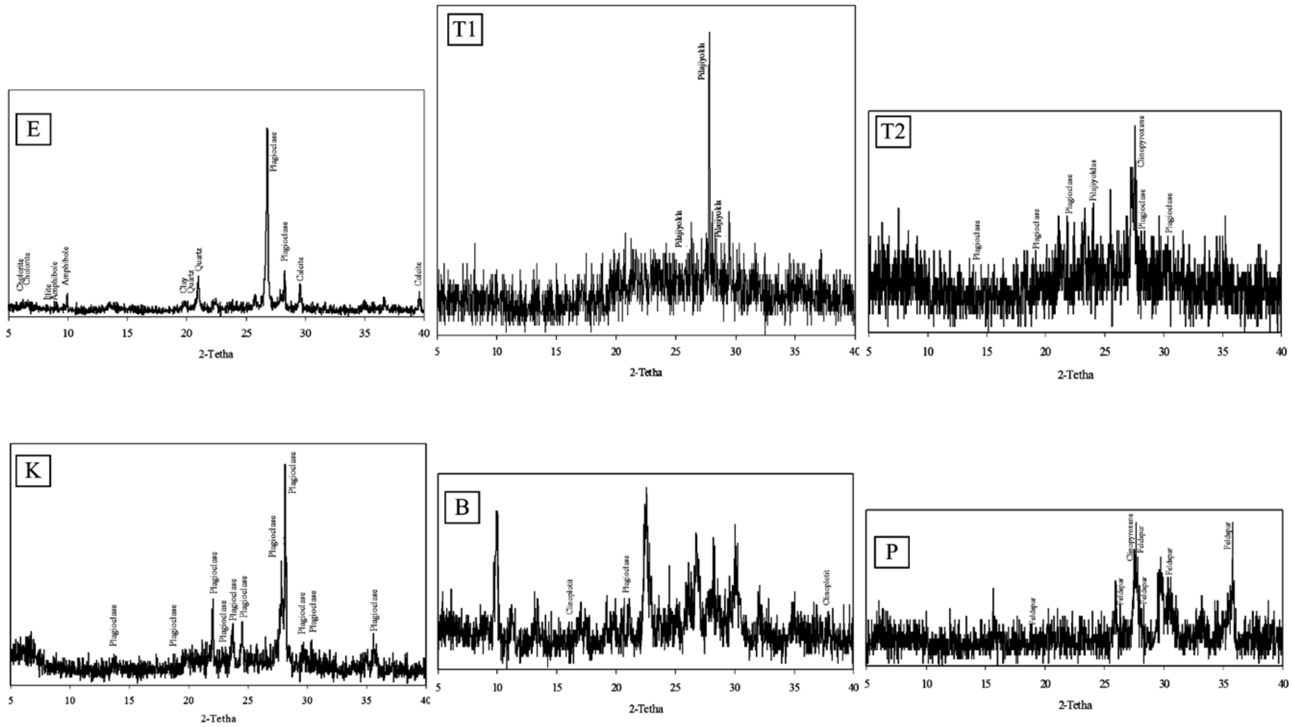

Fig. 2. XRD of pozzolans.

Table 1
Proportions of the ingredients of mortar specimens according to TS 25 standard

Material	Weight (in gram)
Slaked lime $Ca(OH)_2$	150
Pozzolan	$2\times150\times N = T$
Standard sand	1350
Water	$0.5\times(150 + T)$

N = factor obtained by dividing density of tuff by the density of lime.

Table 2
Petrographic properties of the pozzolans

Sample	Characteristic	Mineral content
E	Dacidic tuff	Quartz, plagioclase, amphibole, chlorite, illite, calcite
T1	Andesitic tuff	Plagioclase
T2	Andesitic tuff	Plagioclase, Orthopyroxene, clinopyroxene
K	Andesitic tuff	Plagioclase, pyroxene, opaque
B	Dacidic tuff	Quartz, plagioclase, sanidine, biotite, clinoptilolite
P	Basanite	Clinopyroxene, spinel, leucite

3.2. Chemistry of samples

According to the results of the performed chemical analyses, it was determined that the samples have high ratio of SiO_2. The sources of this component were given above. According to related standard [19], some chemical properties are required from the materials that are to be used as pozzolan. The results of the chemical analysis of the pozzolan samples (Table 3) and their consistency with this standard (Table 4) are shown briefly. Besides, the physical properties of the samples were given in Table 5.

As seen in Table 4, the samples with the exception of the P sample are within the limits of TS 25 standard. Because the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ is 66.43% <70% (by mass) for sample P. This sample is not appropriate for using as pozzolan in cement in the view of chemical properties. Besides, it was seen that MgO ratio was only a little below the limit. Although sample P did not fulfill the required properties, it was also subjected to the pozzolanic activity tests and according to these results, it was appropriate to standard exceedingly (Table 6).

3.3. Pozzolanic activities and their relationships with chemical compositions

Pozzolanic activity experiment results (Table 6) of prepared pozzolan samples are above the minimum strength values determined by the standards. According to the results, all six samples are mechanically suitable for usage in the cement as pozzolan. Additionally, although sample P does not fulfill the chemical requirements due to the scarcity of Si, Al, Fe oxide rates, it is suitable as high as the mechanical properties expressed in the TS 25 standard [19].

When the relationship between SiO_2, Al_2O_3, Fe_2O_3, CaO and the other components, which are the main ingredients of pozzolan, and pozzolanic activity is concerned, the probability of having an idea about the strength of the pozzolan by looking at its chemical composition can be possible.

Table 3
Chemical properties of the pozzolans

Sample	Insoluble residue	Chemical analysis ($\%_{mass}$)									
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI	Na_2O	K_2O	Total
E	77.24	70.89	9.08	2.96	5.40	0.62	–	7.23	1.11	1.92	99.21
T1	83.65	67.96	13.73	2.57	3.24	1.12	0.51	6.37	2.54	1.40	99.44
T2	85.75	67.93	4.43	1.26	2.28	0.61	0.48	4.61	4.48	2.92	88.39
K	79.90	61.01	15.10	5.35	5.16	1.74	0.71	3.88	3.76	2.88	99.59
B	55.33	60.14	13.17	4.35	4.83	2.34	0.17	10.71	0.71	3.08	99.50
P	54.63	43.10	13.77	9.56	13.52	4.80	–	6.00	2.29	2.02	95.06

Table 4
The comparison of the pozzolans with TS 25 in point of chemical composition

	TS 25	E	T1	T2	K	B	P
$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	Min. %70	82.93	84.26	73.62	81.46	77.76	66.43
MgO (%)	Max. %5	0.62	1.12	0.61	1.74	2.34	4.80
SO_3 (%)	Max. %3	–	0.51	0.48	0.71	0.17	–

Table 5
The physical properties of pozzolan samples prepared for experiment

Sample	Remain 200 μm sieve (%)	Remain 90 μm sieve (%)	Specific surface cm^2/g	Specific mass g/cm^3	Unit mass g/cm^3	Grinding time (minute)
B	0.1	4.6	6226	2.25	658	35
K	0.1	3.3	5286	2.40	747	30
T1	0.1	3.0	4153	2.29	739	30
T2	0.1	3.0	4869	2.40	765	25
E	0.6	4.4	5908	2.49	–	45
P	0.3	2.7	5887	2.71	–	40

Table 6
The mechanical properties of pozzolan samples and comparison with TS 25 standard

Sample	7th day flexural strength (MPa)	Min. according to TS 25 (MPa)	7th day compressive strength (MPa)	Min. according to TS 25 (MPa)
B	3.02	1.00	8.30	4.00
K	1.90		6.70	
T1	3.96		10.10	
T2	3.14		9.10	
E	4.45		11.00	
P	2.86		9.00	

According to TS 25 standard, SiO_2, Al_2O_3, Fe_2O_3 sum should be at least 70% (by mass) [19]. This shows that, in addition to durability contribution, these components are the main effects at actuating the pozzolanic activity. The validness of the present claim is discussed with the help of graphics and relations by taking into consideration the effects of each element separately and totally. In addition, these investigations are performed for also MgO and K_2O.

In the graphics (Fig. 3), the discontinuous lines represent the linear relation of the six samples, whereas the continuous lines represent the relations obtained by not considering the one sample–indicated with hollow symbol–, which does not have close values with the others. Namely, the relations in the graphics are deduced from the closest five samples.

As a result of the comparisons made, highly correlated (88%) relation between the SiO_2 rate and compressive strength was established, and as seen from the graph (Fig. 3) it was determined that pozzolanic activity increases with the increase in SiO_2 rate. It was also thought that not only in non-crystalline form SiO_2 but also in crystalline form SiO_2 was increased the pozzolanic activity. The increase in the Al_2O_3 decreases the compressive strength. Also it is seen from the graph that the correlation coefficient is quite high (79%). Similarly, compressive strength decreased along with an increase in the Fe_2O_3 composition. Therefore, an increase in the sum of Al_2O_3 and Fe_2O_3 rates will decrease the compressive strength. As just seen, although an increase in the sum of these three elements increase the strength, this increase is in fact caused by SiO_2. This should be accepted as a finding that assist to reinvestigate the stipulation of the $Al_2O_3\% + SiO_2\% + Fe_2O_3\% > 70\%$ limit mentioned in TS 25. Therefore, the meaningfulness of the West European standard mentioned above [18], which was made a separate limitation about SiO_2 and other component rate, is seen. On the other hand,

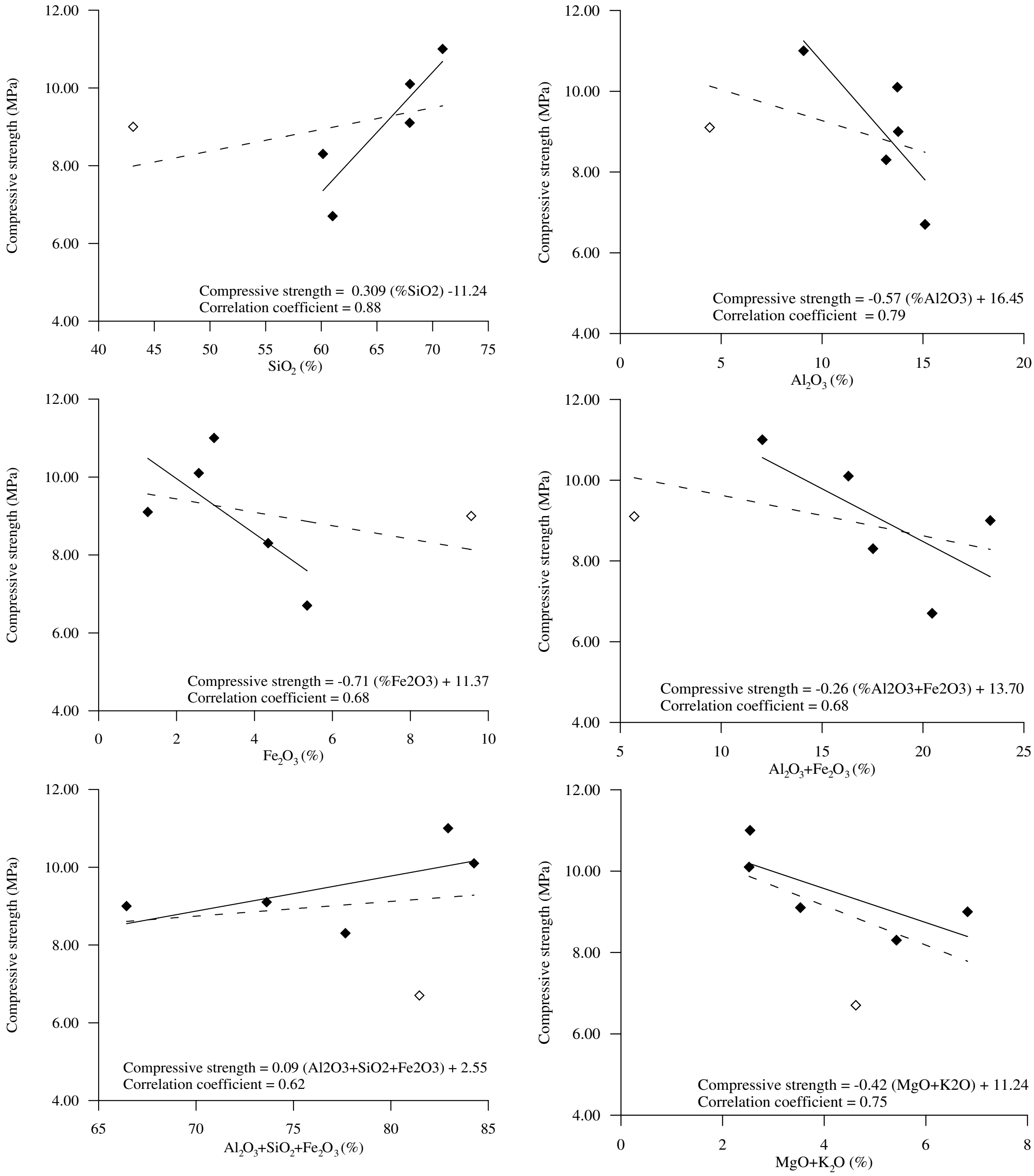

Fig. 3. The relations between components of pozzolan and compressive strength.

when the MgO and K_2O rate increased as a total, a decrease in the compressive strength is seen (Fig. 3). Here again, the relation is appearing with a high correlation coefficient (75%).

The results show that the most important component increasing the pozzolanic activity of a pozzolan is SiO_2 oxide. Al_2O_3, Fe_2O_3, MgO and K_2O oxides decrease the pozzolanic activity. It is possible to say that there are two reasons of increasing strengths of pozzolans, 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. There are also standards as EN 196–5 about the determination of these properties [22]. Therefore, it is possible to say that the rocks those are used as pozzolan should be high proportion of SiO_2.

4. Conclusions

As seen from this study, it possible to easily find rich natural pozzolan resources in Northeast of Turkey (Trabzon–Bayburt district). The rocks that were taken from this region and investigated were volcanic origin and they showed pozzolanic property. They consisted of tuffs, except one, and they mostly fulfilled the TS 25 standard requirements for both pozzolanic activity and chemical composition. With this result, by using these natural pozzolan resources in cement production, important amounts of heat saving can be possible and this can help stopping global warming and excess CO_2 emissions, which are the common ecological problems of humanity.

Another result obtained from this study, the pozzolanic activities of natural pozzolans and hence their compressive strengths are directly proportional with the increase in SiO_2 ratio and inversely proportional to Al_2O_3 and Fe_2O_3ratios. Again it is seen that increase in the MgO and K_2O ratios decrease the pozzolanic activity. According to this, it is once again seen that the most important component of pozzolan is SiO_2 and it can provide contributions to pozzolanic activity in both crystalline form and non-crystalline form.

Acknowledgements

This study is funded by Karadeniz Technical University (Project No. 2002 118.001.1). Thanks to Trabzon Cement Factory for laboratory possibilities.

References

[1] Uzal B, Turanlı L. Studies on blended cement containing a high volume of natural pozzolans. Cem Concr Res 2003;33:1777–81.
[2] Rodriguez-Camacho RE, Uribe-Afif R. Importance of using natural pozzolans on concrete durability. Cem Concr Res 2002;32:1851–8.
[3] Çolak A. The long-term durability performance of gypsum – portland cement – natural pozzolan blends. Cem Concr Res 2002;32:109–15.
[4] Vu D, Stroeven P, Bui V. Strength and durability aspects of calsined caolin-blended portland cement mortar and concrete. Cem Concr Comp 2001;23:471–8.
[5] Çavdar A, Yetgin Ş. Tane inceliğinin traslı çimento özelliklerine etkisi. In: Ergin A, Özdemir G, editors. Türkiye İnşaat Mühendisliği XVII. Teknik Kongresi. Istanbul: Altan Press; 2004. p. 451–4.
[6] Yetgin Ş, Çavdar A, Değişiminin Tras Oranı. Traslı Çimentonun Bazı Özelliklerine Etkisi. In: Özturan T et al., editors. Advances in civil engineering 2004 6th international conference. Istanbul: Kansu Press; 2004. p. 1084–92.
[7] Canpolat F, Yılmaz K, Köse M, Sümer M, Yurdusev M. Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production. Cem Concr Res 2003;2324:1–5.
[8] Shannag M. High strength concrete containing natural pozzolan and silica fume. Cem Concr Comp 2000;22:399–406.
[9] Turanlı L, Uzal B, Bektas F. Effect of large amounts of natural pozzolan addition on properties of blended cements. Cem Concr Res 2005;35/6:1106–11.
[10] Rösler HJ. Lehrbuch Der Mineralogie. Berlin: VEB Deutcsher Verlag für Grundstoffindustrie; 1983.
[11] Massazza F. Puzolanlar. In: Puzolanlı Çimentolar ve Kullanım Alanları. Ankara: TCMA Press; 1989.
[12] Erkan Y. Magmatik Petrografi. Ankara: Hacettepe Üniversitesi Yayınları; 2001.
[13] Planungs Engineering Management (PEM), On investigations of Turkish natural pozzolans as cement admixtures, Planungs Engineering Management Report. Ankara, Düsseldorf, 1984.
[14] Türkmenoğlu AG, Tankut A. Use of tuffs from central Turkey as admixture in pozzolanic cements assessment of their petrographical properties. Cem Concr Res 2002;32:629–37.
[15] Aydın F. Değirmendere Vadisi (Trabzon–Esiroğlu, KD – Türkiye) Volkanitlerinin Petrolojisi ve Petrojenezi, Doctoral dissertation, Karadeniz Technical University, Trabzon, 2003.
[16] Erdoğdu K. Traslar ve Traslı Çimentolar. Ankara: TCMA R&D Institute Press; 2001.
[17] Leckebush R. Türkiye'de doğal puzolanların çimento katkı maddesi olarak kullanımı üzerine incelemeler. Ankara: TCMA Press; 1984.
[18] DIN 51043, Trass, Deutsches Institut für Normung, Germany, 1979.
[19] TS 25, Tras, Turkish Standards Institute, Ankara, Turkey, 1975.
[20] ASTM C311, Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete, ASTM, 2004.
[21] EN 196, Methods of testing cement, European Committee for Standardization, 1994.
[22] Locher W. Zement: Grundlagen der Herstellung und Verwendung. Dusseldorf: Verlag Bau und Technik; 2000. 89–106.