J. Civil Eng. Mater.App. 2020 (September); 4(3): 133-140

Journal of Civil Engineering and Materials Application

Journal home page: http://jcema.com

Received: 23 April 2020 • Accepted: 19 July 2020

Research

doi: 10.22034/jcema.2020.233594.1028

Iranian Eocene Green Tuffs as Natural Pozzolan for Use in Cement Industries

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ABSTRACT

Eocene Green Tuffs are widespread in Central Alborz in the north of Iran. In parts, they are used as natural Pozzolan. In this study, the Pozzolanic activities of tuff samples from Qazvin to Semnan in Alborz Mountain were examined. The Pozzolanic activity patterns vary in different beds and even change laterally. Chemical examination of the samples indicated that they all belonged to the acidic rock group and were consistent with related standards. The Pozzolanic activity was calculated for samples using a hydraulic factor, thermal analysis, and ion concentrations. Data obtained based on the thermal analysis presented a range of Pozzolanic activities for tuffs with similar chemistry and appearance. It was found in this research that mineralogy and texture controlled Pozzolan activity. Tuffs with high activity had glass in their matrix, but weathering and recrystallization reduced the activity. Petrographical examinations play an essential role in evaluating the availability of tuffs as natural Pozzolan in Central Alborz.

Keywords: **Natural Pozzolan; Petrography; Pozzolanic activity; Alborz Mountains; Plateau of Iran**

1. INTRODUCTION

Natural Pozzolans are silicate rocks and deposits widely assessed in construction and building materials [1,2]. Ancient Greeks and Romans were the first people who used them in combination with lime to make natural cement. Nowadays, Pozzolanic cement is a mixture of Portland cement and Pozzolan. Natural Pozzolans have become important because of their role in concrete durability [3, 4] and reducing CO_2 emission. Iran is geologically situated in an organic belt, and volcanic rocks capable as natural Pozzolan are common in many parts of the country. One of the known sources for Pozzolans in northern Iran is Eocene Green Tuffs [5]. The Eocene marine volcano-sedimentary sequence in the southern flank of Alborz Mountains in Iran is ~3-4 km thick. It extends along the length of the Central Alborz (Figure 1) with the greatest outcrop in the west and tapers, while becoming less continuous towards the east [6-8].The Alborz Mountain Range consists mainly of late Precambrian to Eocene sedimentary and Paleogene andesitic volcanic and intrusive rocks. Eocene Green Tuffs are a part of the Karaj Formation. The formation mainly consists of calc-alkaline, volcanic, and volcaniclastic rocks and shales [6, 9-12] which are deposited in an arc and back-arc setting, probably formed during its extension [13-15]. The Karaj Formation is uncomfortably overlain by shallow marine rocks, basalt, and conglomerate of the earliest Oligocene age. Eocene Green Tuffs are very similar in outcrops; however, the Pozzolanic activity patterns vary in different beds and even change laterally. In this study, the Pozzolanic activities of different tuff samples taken from Qazvin to Semnan in Alborz Mountain Range were examined (Figure 1). The study mainly aimed at finding relationships between Pozzolanic activities of tuffs and their chemical and petrographical properties.

Figure 1. Location of Central Alborz (quadrangle) in Iran and main localities

2. MATERIALS AND METHODS

Green tuffs in Central Alborz make distinctive sequences of thin to thick beds (Figure 2). Their main color is pale green, and the beds are similar in the field scale (Figure 3). Tuffs are faulted and folded in many places, and it is difficult to follow specific layers in the sequence. By examining geological maps [12] and satellite images, 102 Eocene tuff samples were collected, and 80 samples were chosen for petrography. Mineralogical and textural properties of thin sections of samples were identified under the polarizing microscope. Tuff samples were classified, and samples from different rock types were selected for more investigations. 7 rock samples crushed and grounded with ball mill to obtain particles as small as 5µ in Shahid Beheshti University in Tehran. Major element analyses for selected samples were carried out by the XRF method at Kharazmi University in Tehran. X-ray diffraction data characterized by Iran Mineral Processing Research Center. Pozzolanic activities of the same samples were determined in Road, Housing and Urban Development Research Center in Tehran (Iran).

Figure 2. Sequences of thin to thick beds of green tuffs in Karaj formation (Karaj- Chalos road).

Figure 3. Outcrop of Karaj green tuffs (Green tuffs are homogeneous and similar in different outcrops)

3. RESULTS AND DISCUSSION

3.1. LITHOLOGY AND PETROGRAPHY

Based on petrography, tuff samples are classified into three groups of crystal tuffs, lithic tuffs, and fine grain tuffs. Some units include fossil and other non-volcanic lithics and can be categorized as suffice. In hand, specimen tuffs are very similar and uniform (Figure 3). Plagioclase, quartz, and minor alkali feldspar, biotite, and opaque were observed in crystalline tuffs. Rock fragments in lithic tuffs are mainly volcanic. Plagioclase and quartz crystals are present in fine-grain tuffs. Matrix is made of glass and cryptocrystalline minerals in all groups. Secondary minerals such a calcite, quartz, and clay minerals are common in many different rock units. Figure 4 shows thin sections of 7 selected samples, and the same samples' mineralogy is summarized in Table 1. Moreover, Table 2 summarized the XRD results for semi-quantitative crystalline mineral contents of the tuff samples.

Table 1. Summary of petrography data for analyzed tuff samples.

sample	Petrography (%)	Location
CA89	**Plagioclase, Quartz, Glass shard, Fossil, Glassy-crypto crystalline matrix**	36° 00' 39" 51° 17' 35"
CA92	**Micro granular Quartz and Plagioclase, Glassy-crypto crystalline matrix**	33° 57' 46" 51° 21' 36"
CA94	**Feldspar + Pyroxene, Crypto crystalline matrix, Secondary Quartz + Biotite**	36° 01' 52" 57° 16' 10"
CA132	**Plagioclase, Glass shard, Quartz, Biotite, Crypto crystalline matrix, Secondary calcite and opaque**	36° 10' 27" 50° 21' 05"
CA150	**Plagioclase, glass Shard, Glassy-crypto crystalline matrix**	33° 41' 51" 52° 02' 52"
CA209	**Feldspar, Quartz, Crypto crystalline matrix**	35° 39' 13" 53° 34' 02"
CA214	**Feldspar, Quartz, Crypto crystalline matrix, Secondary Quartz and Clay minerals**	35° 39' 30" 53° 30' 23"

Table 2. XRD results for semi-quantitative crystalline mineral contents of the tuff samples

Pozzolan						
CA89	**CA92**	**CA94**	**CA132**	**CA150**	**CA209**	CA214
5	**6**	**15**	**16**	**4**	**29**	36
56	**49**	**39**	**35**	**52**	**31**	27
9	**7**	**13**	**11**	**6**	**9**	6
6	**4**	**9**	**7**	**7**	**8**	7
12	**15**	**9**	**13**	**17**	**10**	9
1	**3**	**2**	**3**	**2**	**7**	5
traces	**1**	**6**	**8**	**2**	**4**	7
traces	**traces**	**traces**	**traces**	**traces**	**traces**	traces
10 (Clinoptilolite)	**14 (Clinoptilolite)**	**6 (Mordenite)**	**5 (Smectite, Kaolinite)**	**9 (Clinoptilolite)**	**1 (Mordenite)**	2 (Mordenite)
clear	clear	traces	traces	clear	traces	traces

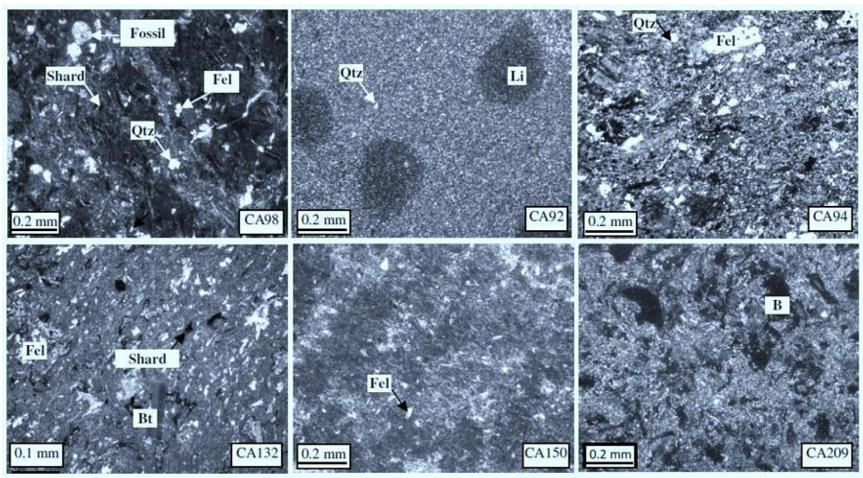

Figure 4. Thin section photomicrographs of analyzed tuffs. Mineralogy of the samples summarized in Table 1. Fel: Feldspar; Bt: Biotite; Qtz: Quartz; B: Bubble.

3.2. CHEMICAL ANALYSES

Chemical analyses for major elements were obtained by the XRF method (Table 3). Based on SiO2 content, all analyzed samples are in an acidic volcanic rock group. Iron is higher than expected in sample CA209, which is due to alteration and the presence of hematite in this sample (Table 1). Higher K in sample CA132 and sample 214 is reflecting the presence of secondary fine-grain muscovite (sericite) in their matrix.

Sample	SiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	MnO	P2O5
CA89	**76.06**	**14.33**	**1.13**	**0.36**	**3.05**	**2.12**	**2.63**	**0.20**	**0.05**	**0.06**
CA92	**76.01**	**13.57**	**1.35**	**0.76**	**1.59**	**4.34**	**1.94**	**0.18**	**0.04**	**0.03**
CA94	**69.85**	**15.42**	**2.95**	**0.81**	**5.22**	**0.55**	**3.94**	**0.40**	**0.08**	**0.14**
CA132	**74.52**	**12.55**	**2.25**	**0.44**	**0.73**	**0.95**	**7.57**	**0.30**	**0.03**	**0.09**
CA150	**77.02**	**11.90**	**1.39**	**0.46**	**1.72**	**4.50**	**2.32**	**0.18**	**0.01**	**0.05**
CA209	**72.54**	**11.90**	**4.73**	**1.97**	**1.19**	**3.45**	**3.58**	**0.51**	**0.10**	**0.06**
CA214	**78.01**	**11.36**	**1.28**	**0.46**	**0.70**	**0.28**	**7.49**	**0.17**	**0.01**	**0.10**

Table 3. The major oxides of selected samples in percent.

3.3. POZZOLAN ACTIVITY

For 7 selected samples, Pozzolanic activity was calculated using 3 methods: strength activity index, thermo-gravimetry (TG), and concentration of calcium ion Ca2+ (expressed as calcium oxide or CaO).The strength activity index was calculated for selected samples for two stages of 7 days and 28 days (Table 4). This factor was calculated for mortar with 20% Pozzolan. Based on ASTM C 618 [16] for acceptable Pozzolan quality, this index should be above 75 in each stage.

Sample	Strength activity index			Pozzolan activity (%) (thermal analyses)	
	30 Day	7 Day	quality	9 Day	quality
CA89	114.5	113	acceptable	26.83	high
CA92	105.5	105	acceptable	30.42	high
CA94	122	117	acceptable	21.97	medium
CA132	134.5	118	acceptable	21.29	medium
CA150	113	112.5	acceptable	30.57	high
CA209	106	104.5	acceptable	17.87	Low
CA214	112	106	acceptable	13.97	Very low

Table 4. Results of strength activity index and TG.

The pozzolanic activity was calculated using thermal analyses above 400 ˚C with STA-449 (Netzsch) for a mixture of Pozzolan powder and calcium hydroxide with the same Wt% for 9 days (Table 4). Pozzolan activity was divided into 4 quality groups: 1) Good quality group for upper 25%; 2) medium quality group for the range between 20-25%; 3) low-quality group for 15-20% and 4) very low-quality group for activity less than 15%.

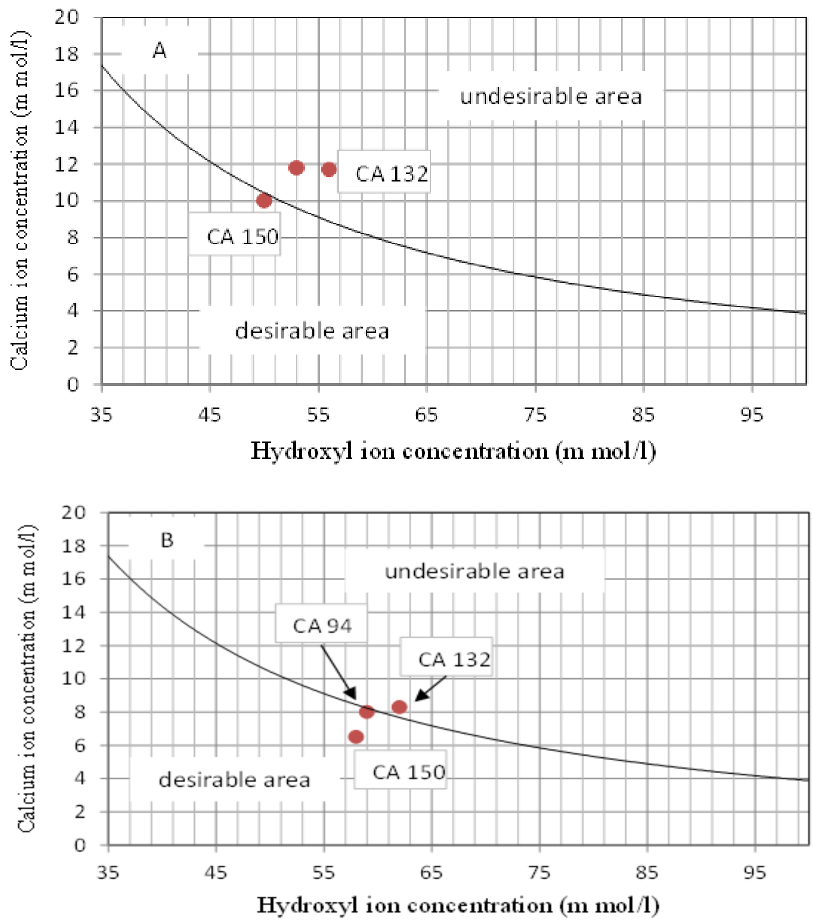

Figure 5. Concentration of Ca2+ (mmol/L) and OH- (mmol/L) for 3 selected tuffs from Central Alborz. A) after 9 days and B) after 30 days. Curve is based on EN 196-5 standard.

Figure 5 shows the concentration of Ca2+ (mmol/L) and OH- (mmol/L) for 3 selected tuffs from Central Alborz, after 9 and 30 days based on EN 196-5 standard. As seen in these Figures, (plots of CaO versus OH), a unique predefined curve demarcates pozzolanic and non-pozzolanic areas. The blended cement is satisfactory if the concentration of CaO in the solution falls below the curve.

3.4. DISCUSSION

Samples are rocks with high SiO2 and low Fe and Mg (Table 3), and based on ASTM C-618 Class N, all studied samples present requires chemical parameters for desirable Pozzolan. The hydraulic factor for samples is above 75, and as ASTM C 618 standard states, the quality of sample is acceptable to be used as natural Pozzolan. However, thermal analyses and Pozzolan quality test based on EN 196-5 standard present different levels of Pozzolanic quality for studied samples. The results of these two methods are in line with each other. According to thermal analyses, samples are arranged from very low Pozzolanic quality to high Pozzolanic quality (Table 4). Monitoring Ca2+ and OH- concentrations suggest that Pozzolan activity improved after 30 days, but like thermal analyses, sample CA-132 still is not suitable to be used as natural Pozzolan (Figure 5). The results in this study and previous works [17, 18] suggest that thermal analyses could evaluate the Pozzolanic activity of natural Pozzolans.Petrography of concrete is popular [19]. However, studies of natural Pozzolans are more based on chemical and mechanical relationships [e.g. 17] [20, 21] and few studies reported petrography of natural Pozzolans [22-24]. Petrographical examinations for studied samples indicate that despite the chemical similarities, the studied rocks are different in mineralogy and alteration. The 4 parameters calculated based on petrography are 1) fine-grain matrix to crystal ratio, 2) the amount of glass shard, 3) alteration, and 4) recrystallization.

The results of the study are summarized in Table 5. There are good agreements between petrographical factors and the results of thermal analyses. Increasing matrix/ crystal ratio and glass shards show a positive effect on Pozzolan activity (e.g. CA150 and CA92), but alteration and recrystallization reduce the Pozzolan activity (e.g. CA209 and CA214). Alteration to produce Fe bearing minerals such as chlorite, magnetite, or goethite and ankerite reveal more effect on Pozzolan activity than sericite (e.g. CA214). However, zeolite group minerals such as mordenite, clinoptilolite, and heulandite are present in samples with high Pozzolan activity (CA92 and CA94). Based on the data, the acidic green tuffs in Central Alborz that contain less than 10% crystals, glass shards in the matrix and, do not show alteration and recrystallization are more suitable to be used as natural Pozzolan.

Sample	Petrographical factors				Quality based on petrography	Quality based on thermal analyses
	Positive effects		Negative effects			
	Matrix /Crystal	Glass shard	Alteration	Recrystallization		
CA150	9/1	Low	-	-	Good	high
CA92	9/1	+	-	-	Good	high
CA89	9/1	-	-	-	acceptable	high
CA94	7/3	+	Low	Low	low	medium
CA132	6/4	+	Low	Low	low	medium
CA209	8/2	-	+	+	low	low
CA214	6/4	-	+	+	low	very low

Table 5. Petrographical factors for studied rocks. Samples ordered based on their quality on thermal analyses.

XRD data presented in Table 2 emphasized that the most active pozzolanic matter including the summation of Zeolite minerals and Calcites are found in the samples CA89, CA92 and CA150 are respectively, 11%, 17%, and 11% and the Minimum amounts are related to the samples CA209 and CA214 with 8% and 7 respectively. The results agree with the strength activity index and TG analysis.

4. CONCLUSION

Based on the results of the study, the following conclusions can be drawn:

- The main petrographical features of a good Pozzolan in different layers of green tuffs in Central Alborz are the presence of the glass shard and the absence of weathering to Fe minerals, recrystallization, and large crystals.

-Thermal analyses present a different range of Pozzolan activities for green tuffs with similar chemistry and appearance in Central Alborz.

-This research concludes that chemical analyses could not be used alone as the first identification factor of natural volcanic base Pozzolan in Central Alborz, while petrography is a powerful tool for the identification of Pozzolans in the first steps. Limited data is published so far in the literature about the petrography of Pozzolan, and this study encourages further research on petrographical properties of high-quality natural Pozzolans.

FUNDING/SUPPORT

Road, Housing and Urban Development Research Center.

ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from the Road, Housing and Urban Development Research Center.

AUTHORS CONTRIBUTION

This work was carried out in collaboration among all authors.

CONFLICT OF INTEREST

The author (s) declared no potential conflicts of interests with respect to the authorship and/or publication of this paper.

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