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Proposing a New Approach for Qualification of Natural Pozzolans

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Abstract. *Recognizing natural pozzolans and their qualities is one of the most important dilemmas in the field of cement and concrete. Although different methods have been published towards this aim, research shows some anomalies between the judgments of these methods. This paper aims to compare evaluation methods of natural pozzolans by considering their performance in concrete as a decision criterion in order to develop a guideline for their qualification. Therefore, firstly, the main available methods are described. Then, the pozzolanic activity of natural pozzolans is investigated using these methods and compared with the performance in concrete. Finally, a guideline is proposed, based on the discussed methods.*

Keywords: *Natural pozzolan; Pozzolanic activity; Strength activity index; Frattini test; Insoluble residue.*

INTRODUCTION

Natural pozzolans are defined as natural materials containing reactive silica and/or alumina, which, alone, have little or no binding property, but when mixed with Portland cement, react with lime (produced by cement hydration) in the presence of water, and thus set and harden like cement. In fact, the unsuitable lime in concrete is replaced by some appropriate products and as a result some efficient properties are gained, such as resistance against chemical attacks, reducing expansion due to alkali-silica reaction and strength development in later ages. Moreover, replacing cement by pozzolans leads to a lower heat of hydration. Therefore, the application of pozzolans offers some advantages, such as saving energy in blended cement production, preserving the environment, enhancing durability against various kinds of chemical attack and decreasing the heat of hydration [1-4].

Human beings have used natural pozzolans from 6000-7000 years ago. Malinowski et al. [5] reported that the oldest example of a hydraulic binder, dating from 5000-4000 B.C., was a mixture of lime and natural pozzolan; a diatomaceous earth from the Persian Gulf. The next oldest report of its use was in the Mediterranean region where the pozzolan was volcanic ash produced from two volcanic eruptions between 1600 and 1500 B.C. [5].

The Iranian plateau is one of the richest natural pozzolan areas of the world. Different kinds of natural pozzolan including Trass, Tuff, Zeolite and the like can be found in this region. Despite extensive resources and many years of application of natural pozzolans in the Iranian Plateau, a standard method for evaluation of pozzolan has not yet been established, although the quality of pozzolans has often been evaluated according to ASTM C618 [6]. Besides, some researchers and engineers have rarely applied other methods, such as thermo-gravimetric analysis and the Ferretini test. However, recent research manifests some discrepancies between these methods [7-9].

This paper is considered to prepare a guideline for the evaluation of pozzolans by the following steps.

First, the available methods regarding the determination of pozzolanic activity are presented and discussed, and the most applicable methods are selected. The results of selected tests for 4 different natural pozzolans are presented. Then, the results of concrete mixtures, which have been produced for better judgment, are illustrated. Finally, a guideline

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for investigating the quality of natural pozzolans is presented by considering the effectiveness, ability and easiness of the methods.

DIFFERENT METHODS OF NATURAL POZZOLANS' EVALUATION

The evaluation and quality control of natural pozzolans are carried out using different methods [6-15]. These methods are on the basis of physical/chemical properties, crystallography, mineralogy and determining $Ca(OH)_2$ consumption in thermal analysis or a saturated calcium hydroxide solution.

ASTM C618

ASTM C618 [6] presents the chemical and physical requirements and specifications of fly ash and natural pozzolan as supplementary cementitious materials where the standard testing procedure of ASTM C311 [10] is incorporated [7].

Briefly speaking, in this method, the foremost important criteria for pozzolanic activity are the sum of chemical components, that is SiO_2+ Fe_2O_3+Al_2O_3, and the strength index, which is defined as; a ratio of compressive strength for mortar with 20% natural pozzolan as a supplementary cementitious material to the compressive strength of control mortar [6,10].

Frattini Test

In this method, according to EN 196-5 [11], test samples are prepared, consisting of cement and natural pozzolan, and mixed with distilled water. After preparation, samples are left for 8 days in a sealed plastic bottle in an oven at 40°C. It should be noted that the number of days in the oven can be increased depending on the pozzolans. After the abovementioned times, samples are vacuum filtered through a 2.7 μm nominal pore size filter paper and allowed to cool to ambient temperature in sealed Buchner funnels. The filtrate is analyzed for $[OH^-]$ by titration against dilute HCl with a methyl orange indicator, and for $[Ca^{2+}]$ by pH adjustment to 12.5, followed by titration with a 0.03 mol/l EDTA solution using the Patton and Reeder indicator [7,12].

Results are presented as a graph of $[Ca^{2+}]$, expressed as equivalent CaO, in mmol/l versus $[OH^-]$ in mmol/l. As seen in Figure 1, in the diagram for assessing pozzolanicity (a plot of CaO versus OH), a unique predefined curve demarcates pozzolanic and non-pozzolanic areas. Test results lying below this curve indicate removal of Ca^{2+} from the solution, which is attributed to pozzolanic activity. Results lying on or above the line indicate zero pozzolanic activity and results above the line correspond to no pozzolanic activity. It should be noted that this procedure assumes that no other source of soluble calcium is present in the system, as the leaching of calcium would invalidate this approach [7,12].

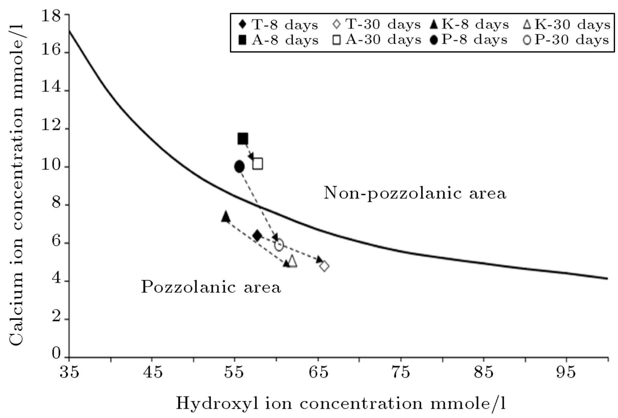


Figure 1. Results of Ferratini test at 8 and 30 days in 40°C.

Thermo-Gravimetric Analysis

Pozzolanic activity (that is the lime binding capacity of pozzolans) can be measured by thermo-gravimetric analysis. This method is based on the thermal decomposition of crystalline calcium hydroxide at a temperature range of 400 to 500°C to calcium oxide and water. By applying the above mentioned temperatures, the calcium hydroxide is decomposed and the resulted water is evaporated. The weight reduction, resulting from water evaporation in the test, is very low for suitable pozzolans and high in weak pozzolans.

Since a constant combination of pozzolan and lime has not been established, and also there is no criterion for judgment, this method is not used in the guideline.

Determination of Insoluble Residue

The Insoluble Residue (IR) test, according to EN 196-2 [13], determines the amount of insoluble residue ingredients. This test can be carried out by two methods, or better described under two conditions. In the first (here named as method I), hydrochloric acid and sodium carbonate are used, while the second (here termed as method II) utilizes hydrochloric acid and potassium hydroxide as a stronger condition for solution.

Mineralogical Analysis

Mineral components of pozzolans are identified by the XRD method semi-quantitatively. The amount of non-crystalline (amorphous) silica, playing a major role in pozzolanic activity, is determined through the identification of the amount of crystalline minerals. It should be noted that there is a remarkable relation between IR and XRD, as the insoluble residue content indicates the amount of soluble and insoluble minerals detected in XRD. Another method being used for the identification of crystalline and non-crystalline minerals in pozzolan is petrography, which can be performed using a petrography-microscope.

EVALUATION OF NATURAL POZZOLANS

Four natural pozzolans from different parts of the Iranian plateau were selected to be investigated in this research, i.e. Trass of Tehran (T), Abyek from Qazvin (A), Khash of Zahedan (K) and Pars pumice from Tabriz (P). The selected tests, i.e. ASTM C618 tests, IR, XRD and Frattini test were carried out on these pozzolans.

Results of ASTM C618

The chemical and physical properties of pozzolan, according to ASTM C618, are presented in Table 1. As observed, all pozzolans passed the requirements of class N of this standard. Pozzolan A presented the highest amount of $SiO_2+Al_2O_3+Fe_2O_3$. Pozzolans A and T showed the highest strength activity, while pozzolan K and P showed mediocre strength activity.

Results of Frattini test

In this method, according to EN 196-5 [11], twenty grams of test samples were prepared consisting of 80% cement (type II) and 20% natural pozzolan, and mixed with 100 ml of distilled water. The results of the Ferratini test, performed based on EN 196-5, are shown in Figure 1 for 8 and 30 days sealed in a plastic bottle in an oven at 40°C. According to EN 196-5, pozzolans T and K showed suitable pozzolanic activity. Pozzolan P did not show pozzolanic activity after 8 days, while it presented suitable activity after 30 days. Moreover, pozzolan A did not show pozzolanic activity after both 8 and 30 days.

Results of Insoluble Residue

The insoluble residue was measured according to EN 196-2 [13], and the test results are presented in Table 2. It should be noted that both aforementioned methods

Table 1. Chemical and physical properties of natural pozzolans according to class N of ASTM C618.

Requirements			Natural Pozzolans			
			T	A	K	P
Chemical Requirements	$SiO_2+Al_2O_3+Fe_2O_3$, %	min, 70.0	80.88	86.97	81.07	85.20
	Sulfur trioxide (SO_3), %	max, 4.0	< 0.10	< 0.10	< 0.10	0.56
	Moisture content, %	max, 3.0	2.48	0.52	0.18	0.85
	Loss on ignition, %	max, 10.0	8.49	2.92	1.88	2.59
Physical Requirements	Amount retained when wet-sieved on 45 μm sieve, %	max, 34	4	2	7	5
	Strength activity index, at 7 days, percent of control	min, 75	110	105	89	80
	Strength activity index, at 28 days, percent of control	min, 75	118	116	91.5	82
	Water requirement, percent of control	max, 115	106	94	100	104
	Autoclave expansion or contraction, %	max, 0.8	0.05	0.10	0.09	0.09
Pozzolan Condition		—	Pass	Pass	Pass	Pass

Table 2. Results for determination of insoluble residue, %.

Pozzolan	Method I		Method II
	Normal Amount of Na_2CO_3-Solution	Increased Amount of Na_2CO_3-Solution	
T	71.54	62.60	29.30
A	91.98	90.34	80.70
K	86.71	81.20	75.60
P	87.31	79.51	60.80

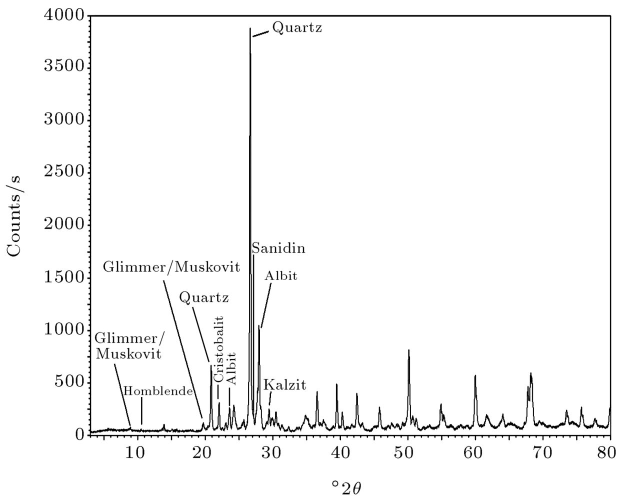
were used for measuring IR. Moreover, method I was done with a stronger Na_2CO_3 solution too, as the amount of alkaline disintegration solution was enlarged by factor 4.

As seen, pozzolans T and A showed the lowest and highest amount of insoluble residue, respectively. According to this test, the priority of pozzolan is recognized as T, P, K and A, which contained more soluble minerals.

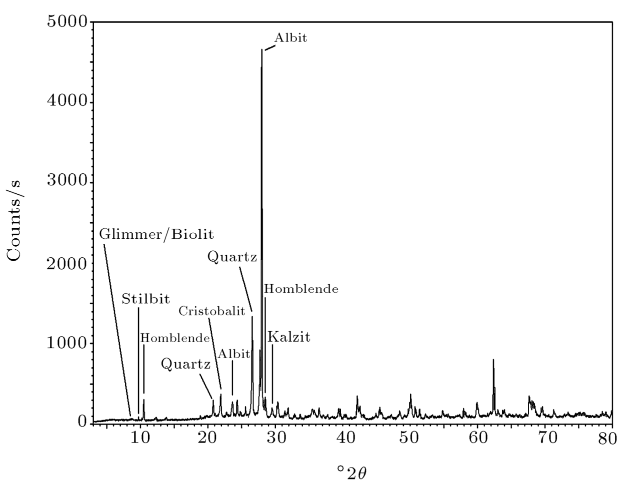
XRD Results

The results of semi-quantitative amounts of minerals can join with the results of the insoluble residue. Interpretation of insoluble results could become more sensible using XRD results. The XRD results of pozzolans A and P are presented in Figure 2. From XRD analysis, the following results can be drawn:

- Pozzolan A consisted of only 4% in acids slightly-dissoluble Calcite ($CaCO_3$), probably a small amount of glassy phases, and about 90% in acids and bases hardly-dissoluble crystalline mineral components, e.g. Quartz, Plagioclase (Sodium feldspar), Sanidine (Potasium-Feldspar), Mica, Cristobalite, Hornblende and Clay minerals. This amount can better describe IR of about 91.98%. Increasing the sodium carbonate solution by a factor of 4 in the dissolution process led to a small decrease of IR; as IR reached to 90.34%. This means, the disintegration process was limited to the dissolution of Calcite and probably some glassy mineral phases.
- Pozzolan P consisted of only 1% in acids slightly-dissoluble Calcite ($CaCO_3$), traces of a clay mineral and probably small amounts of glassy phases. Remarkable phases were the high amounts of 60% Plagioclase (Sodium Feldspar), 18% Cristobalite and 6% Hornblende. Analysis of the IR by EN 196-2, method I, showed values of about 79% to 87%. This means that only 13% to 21% of the pozzolanic mass was easily dissoluble. Surprisingly, in method II, the amount of IR was reduced to about 60%. Under these reaction conditions, partially Feldspars, Hornblende, Cristobalite and glassy phases were probably dissolved. It can be assumed that the majority of insoluble residue constituents were Plagioclase-Feldspars (60%). Since pozzolan P had a higher dissoluble amount in method II, it, speculatively, has a better performance at longer ages.



(a) Natural pozzolan A



(b) Natural pozzolan P

Figure 2. XRD results of natural pozzolans A and P.

Evaluation of Natural Pozzolans in Concrete

Since the performance of pozzolan in concrete is the best judgment criterion, the authors studied the performance of concrete containing natural pozzolans by using compressive strength (according to EN 12390-3 [16]) and water penetration (according to EN 12390-8 [17]). Table 3 presents the concrete mix proportions, corresponding compressive strength and water penetration depth.

As observed, after 28 and 90 days curing, concrete mixtures of pozzolan T and A had the highest and lowest compressive strength, respectively. Concrete mixtures of pozzolan P showed the lowest compressive strength at 7 days, but their compressive strengths were more than concrete mixtures of pozzolan K and A at 90 days. Moreover, the water penetration of concrete mixtures could be arranged as pozolan T, K, P and A after 28 days curing, while the priority was as T, P, K and A after 90 days curing. As a conclusion, pozzolan A had the lowest pozzolanic activity, while pozzolan T presented the highest pozzolanic activity. Moreover, pozzolan P showed better activity at longer ages. It

Table 3. Mixture proportions of concretes containing natural pozzolans.

Mixture Identification	Mixture Proportion			Compressive Strength (MPa)			Water Penetration Depth (mm)	
	Type of Pozzolan, Cement Replacement (%)	Cement (kg/m^3)	Pozzolan (kg/m^3)	7 Days	28 Days	90 Days	28 Days	90 Days
C	-	360	-	40	54	64	15	13
T-15	Tehran, 15	306	54	36	51	59	12	8
T-30	Tehran, 30	252	108	29	45	53	11	5
A-15	Abyek, 15	306	54	29	42	51	16	15
A-30	Abyek, 30	252	108	24	34	41	17	14
K-15	Khash, 15	306	54	30	45	56	14	10
K-30	Khash, 30	252	108	24	38	48	14	9
P-15	Pars pumice, 15	306	54	28	43	57	15	9
P-30	Pars pumice, 30	252	108	22	37	49	14	7

Note: the followings are valid for all mixtures:

w/cm = 0.5, water = 180 kg/m^3, fine aggregates = 870 kg/m^3 and coarse aggregates = 870 kg/m^3.

should be noted that pozzolan A also gave an unsatisfactory performance in previous research [18,19].

DISCUSSION AND GUIDELINES

As seen, the results of ASTM C618 showed the least conformity with concrete mixture results, whereas the Frattini test, the insoluble residue and recognizing crystalline and amorphous minerals presented a suitable agreement with concrete mixture results. Therefore, this guideline consists of four steps, which start from the easiest methods towards the most accurate (and maybe the most expensive) methods, as shown in Figure 3. Also, the steps are designed to evaluate natural pozzolans in a procedure using the following arrangement:

1. Evaluating pozzolans,
2. Measuring pozzolans in combination with cement,
3. Investigating the performance in concrete.

Step 1: Comparing with ASTM C618

The results showed that ASTM requirements are only useful to recognize whether a material can be pozzolan or not. Therefore, the first step is recognizing the ability of pozzolans by doing two major tests of ASTM; strength activity and summation of SiO_2, Fe_2O_3 and Al_2O_3. Since all the pozzolans and some non-active fillers satisfied ASTM requirements, one can consider that if one material cannot satisfy ASTM requirements, it is not a pozzolan.

Step 2: Determining Insoluble Residue and Minerals

Determining insoluble residue and studying the XRD of a pozzolan can be a suitable judgment for pozzolanic activity. In this step, firstly, the IR of natural pozzolans is measured according to method I of EN 196-2. If a pozzolan cannot satisfy the limitations, IR is evaluated again by method II of EN 196-2.

Step 3: Frattini Test

At this step, the Frattini test is carried out according to EN 196-5, except that, if one pozzolan cannot show pozzolanic activity, the time of the test should be continued for 30 days, because natural pozzolans usually react with $Ca(OH)_2$ later in comparison with other pozzolans.

Step 4: Evaluation of Natural Pozzolans in Concrete

Since the performance of pozzolans in concrete is the best judgment, this step is carried out as a final stage. The best percent of replacement, depending on concrete conditions, can be selected at this step too. Moreover, if some pozzolans show little differences in former steps, their quality can be judged at this step.

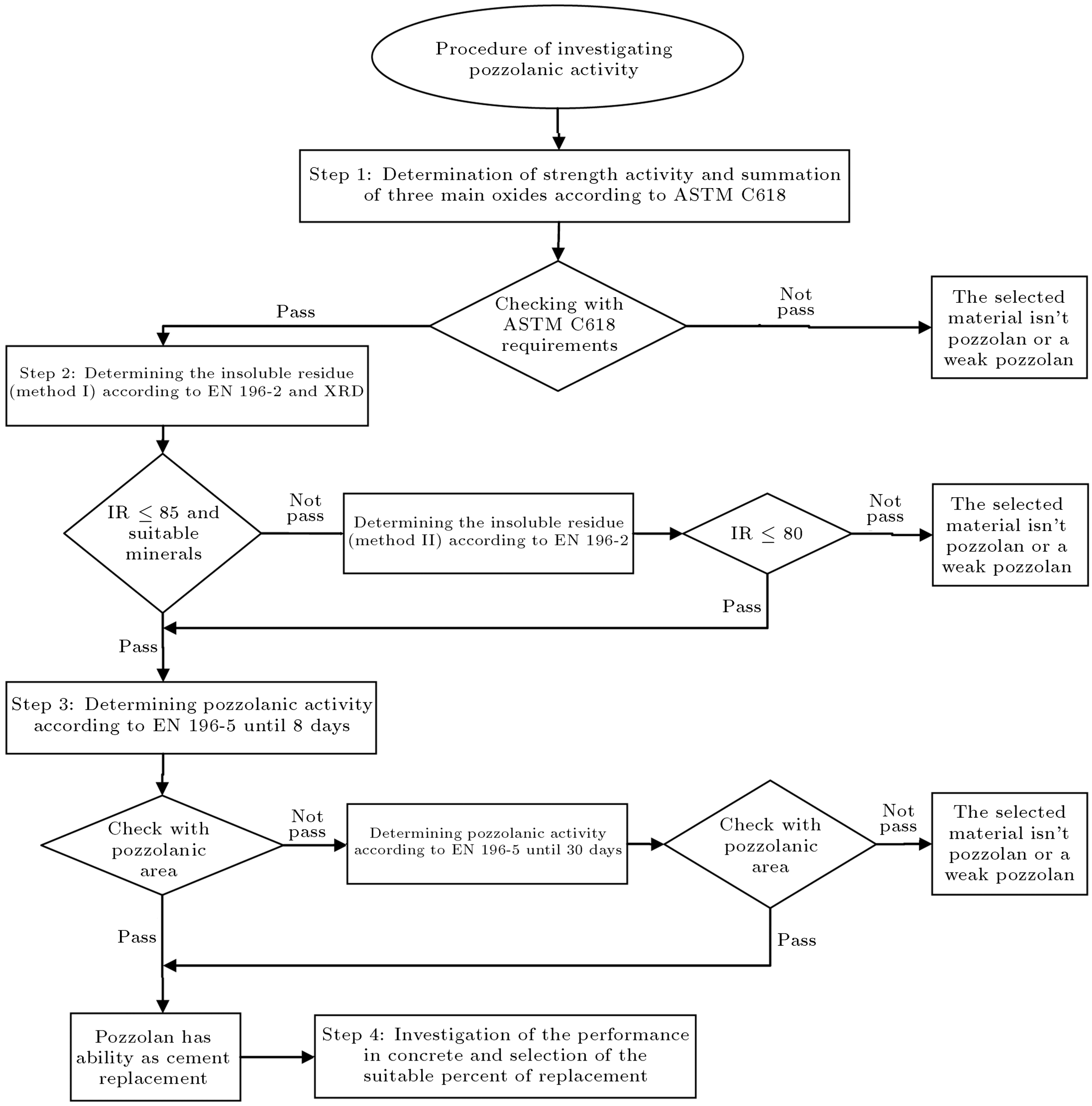


Figure 3. Flowchart of guideline (procedure of investigating natural pozzolans).

CONCLUDING REMARKS

From investigation of four different pozzolans, comparing their performance in concrete, and proposing a guideline, the following results can be drawn:

- Despite the high percent of SiO_2+Fe_2O_3+Al_2O_3 and the suitable strength activity of some natural pozzolans, they did not display a suitable performance in concrete. The method of ASTM C618 did not present a suitable conformity with the performance of natural pozzolans in concrete, whereas insoluble residue and the Frattini test showed better judgment.
- The criterion of ASTM C618 is easily accessible for some materials, so the ASTM requirements can be used as a first step towards recognizing natural pozzolans. If one material cannot pass ASTM requirements, it probably is not pozzolan.
- Recognizing pozzolanic activity using only one method is not suitable, so it is better to combine different methods for the evaluation of natural pozzolans.

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