

## **Effect of Four Iranian Natural Pozzolans on Concrete Durability against Chloride Penetration and Sulfate Attack**

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### **ABSTRACT**

Sulfate attacks and chloride corrosion are the most important problems concerning the durability of concrete structures in hot regions of the Persian Gulf and Oman Sea. Natural pozzolans are natural mineral admixtures which can improve concrete durability against sulfate attacks and chloride corrosion. This paper presents the results of experimental study on the effect of natural pozzolans: Jajrood Truss, Eskandan Pumice, Abyek Tuff, and Khash Pumice, on the ordinary structural concrete durability. Concrete specimens were made of three pozzolan replacement levels, and Rapid Chloride Penetration test, Electrical Resistance test, and Half Cell Potential test were conducted at different ages. In addition, strength reductions and mass changes of concrete specimens immersed in sodium sulfate solution and expansion of concrete prisms immersed in sodium sulfate solution and magnesium sulfate solution were studied. Generally, the results indicate that natural pozzolans have positive effects on concrete specimen resistance to the chloride ions penetration and bars corrosion in comparison with concretes containing ordinary cement.

### **INTRODUCTION**

Nowadays, pozzolanic materials are widely used as supplementary cementing material in Portland cements and may replace part of the clinker in order to enhance the performance of the hydrated cement. Such composite or blended cements are employed for their advantageous properties which include cost reduction, ecological benefits, decreasing in permeability, enhancement of durability and etc. So, different types of pozzolanic materials such as natural volcanic pozzolans are used in concretes.

Natural volcanic pozzolans are one of the oldest construction materials known to humanity. Natural volcanic ash is formed during volcanic eruptions. Ash is created when solid rock shatters and magma separates into minute particles during explosive volcanic activity. A layer of volcanic ash tends to become cemented together to form a solid rock can be used as natural pozzolan [Shi and Day 2001]. "Trass", "Pumice" and "tuff" are three types of natural pozzolanic material consisting of mineral materials and consolidated volcanic ash. The pozzolanic activity of these materials is related to their siliceous ingredients and to their physical effects. [Ramezani pour and Ghazimoradi 1992, Mehta and Monteiro 2006]

According to Anwar Hossain's investigation [Anwar Hossain 2003] volcanic ashes had very similar compositions and had silica content of about 60%. He showed an increase in setting

times with the increase in volcanic ash content. Based on the results, he concluded that strength got reduced by 21% (1-day), 18% (3-days) and 9.5% (7 and 28-days) when volcanic ash content varied from 0 to 20%.

According to some performed studies [Tasdemir 2003, Ozer and Ozkul 2004, Yetgin and Cavdar 2006, Rahmani and Ramazanianpour 2008] in the early days, although the cements containing natural Trass cement less compressive strength in comparison with portland cement, this strength difference decreases gradually in the following days. Especially in applications where the durability of concrete or is more important than strength, the durability properties can be provided without reducing the minimum strength desired by related standards, by adding a relatively high amount of natural pozzolan to the cement.

These observations are in agreement with the findings of Anwar Hossain, where he has reported the addition of pumice to cement causes a reduction in compressive strength compared to normal concrete. [Anwar Hossain 2003]. He [Anwar Hossain 2005] examined concrete specimens incorporating different percentages of volcanic ash (VA) up to 30% as cement replacement. Based upon the experimental study, he concluded that blending cements with 20% VA produced the best performance showing lower porosity and higher chloride ion resistance under seawater attack.

Hossain and Lachemi [Hossain and Lachemi 2006] compared the performance of volcanic ash (VA) and finely ground volcanic pumice (VP). 0 and 20% VA or VP concrete specimens were immersed in magnesium–sodium sulfate solution. The results show that VA/VP based blended cement concrete specimens showed higher and faster rate of deterioration than plain cement concrete specimens.

In this paper, the effect of various amounts of four natural Iranian pozzolans (Jajrood Truss, Eskandan Pumice, Abyek Tuff, and Khash Pumice) on compressive strength, water penetration, sorptivity, rapid chloride permeability test (RCPT) and electrical resistivity at different ages are investigated. In addition, strength reductions and mass changes of concrete specimens immersed in sodium sulfate solution and expansion of mortar prisms immersed in sodium sulfate solution and magnesium sulfate solution were studied.

## **EXPERIMENTAL INVESTIGATION**

### **Materials**

The materials used in the current investigation were locally sourced and they satisfied the requirements of respective national standards. The volcanic pumice used in this investigation were collected from the Eskandan and Khash area. The sources of Truss and Tuff were Jajrood and Abyek, respectively. The natural pozzolans collected from the source were dried and sieved.

Type I cements were used as plain cements as well as to manufacture blended cements. Blended cements were produced in the laboratory by thoroughly mixing cement and natural pozzolans. Table 1 presents the results for typical chemical compositions of the type I Portland cement and natural pozzolans.

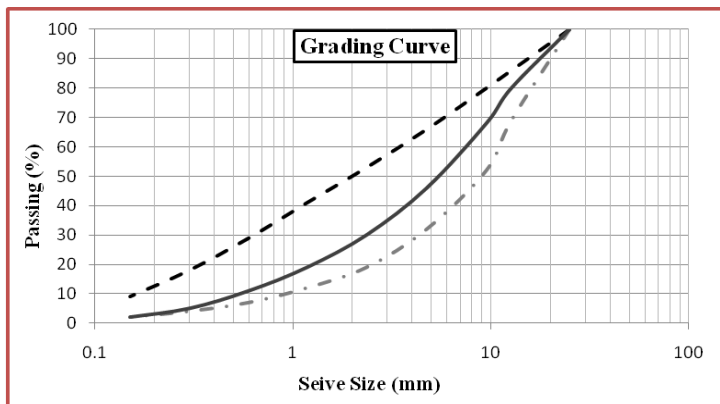
For all mix designs, coarse aggregates were crushed calcareous stone with a maximum size of 25 mm and fine aggregate was natural sand. The coarse aggregates have a specific gravity and a water absorption of 2680 kg/m<sup>3</sup> and 1.75%, respectively, and the fine aggregate has a water absorption of 2.56% and a specific gravity of 2560 kg/m<sup>3</sup>. The gradings of the coarse

and fine aggregates according to the ISIRI Standard (Institute of Standards and Industrial Research of Iran) are presented in Figure 1.

Potable water was used for casting and curing of all the concrete specimens. A high range water reducing (HRWR) admixture based on modified polycarboxylic-ether, with a specific gravity of 1.05 was employed to achieve the desired workability in all concrete mixtures.

**Table 1. Chemical Composition and Physical Properties of Cement and Natural Pozzolans**

Chemical Composition	Cement	Tuff	Pumice-A	Pumice-E	Truss
SiO <sub>2</sub>	21.57	62.64	73.91	67.70	65.74
Al <sub>2</sub> O <sub>3</sub>	2.87	15.19	13.32	15.80	12.24
Fe <sub>2</sub> O <sub>3</sub>	2.65	4.47	1.37	3.39	2.05
CaO	61.6	6.83	1.13	3.90	2.87
SO <sub>3</sub>	0	0.38	0	0.33	0
MgO	3.95	1.71	0.68	0.99	0.96
Na <sub>2</sub> O	0.12	2.77	1.83	2.95	1.92
K <sub>2</sub> O	0.57	2.09	4.14	2.00	2.02
LOI	2.28	2.88	3.15	2.30	8.50
Physical Properties					
Specific Gravity	3.18	2.66	2.60	2.54	2.50
Fineness (cm <sup>2</sup> /g)	3300	4500	3400	3500	3500



**Fig. 1. The Grading of the Aggregates**

## Mixture proportions

A total of 13 concrete mixtures were made; Mix design parameters of concrete such as binder content (cement+pozzolan=350 kg/m<sup>3</sup>) and water/binder=0.50 were the same for all the concrete mixtures. Slumps were kept constant at 70 ± 10 mm. Superplasticizer was used at very low dosages for mixtures to achieve similar slumps. The concrete production was carried out in a mixer of 60 liters capacity. The mixture proportions for concrete specimens are summarized in Table 2. After casting, the concrete specimens were covered with a wet towel for 24 hours and cured under laboratory conditions. Then, they were demolded and cured in lime-saturated water at 23 ± 2°C to prevent possible leaching of Ca(OH)<sub>2</sub> from these specimens.

**Table 2. Mixtures Proportions of Concretes**

Mix.	w/b	Replacement	Cement (Kg/m <sup>3</sup> )	Pozzolan (Kg/m <sup>3</sup> )	Water (Kg/m <sup>3</sup> )	Aggregate (Kg/m <sup>3</sup> )
Control	0.5	0	350	0	175	1750
P10	0.5	10	315	35	175	1750
P15	0.5	15	297.5	52.5	175	1750
P20	0.5	20	280	70	175	1750
A15	0.5	15	297.5	52.5	175	1750
A20	0.5	20	280	70	175	1750
A25	0.5	25	262.5	87.5	175	1750
K15	0.5	15	297.5	52.5	175	1750
K20	0.5	20	280	70	175	1750
K25	0.5	25	262.5	87.5	175	1750
T15	0.5	15	297.5	52.5	175	1750
T20	0.5	20	280	70	175	1750
T25	0.5	25	262.5	87.5	175	1750

## LABORATORY TESTING

Concrete cubes of 100×100×100 mm dimension were cast for compressive strength. They were tested for compressive strength after 7, 28, 91 and 180 days of water curing. The results obtained are reported as an average of three tests.

The electrical resistivity meter was used to measure the surface resistivity at the ages of 7, 28, 91 and 180 days. Special specimens (75 x 75 x 250 mm) were used at each test age. The electrical resistivity test for concretes was carried out by the four-point Wenner array probe technique. The probe array spacing used was 40 mm. The resistivity measurements were taken at four quaternary longitudinal locations of the specimen.

The water penetration test, which is most commonly used to evaluate the permeability of concrete, is the one specified by BS EN-12390-8:2000. In this test, 150 mm concrete cubes, after 91 and 180 days of water curing, were dried under laboratory conditions for 24 h. Water was applied on one face of the specimen under a pressure of 0.5 MPa. This pressure was maintained constant for a period of 72 h. After the completion of the test, the specimens were taken out and split open into two halves. The water penetration profile on the concrete

surface was then marked and the maximum depth of water penetration in three specimens was recorded and considered as an indicator of the water penetration.

The rapid chloride permeability test was conducted in accordance with ASTM C-1202 at 91 and 180 days. Two specimens of 100 mm in diameter and 50 mm in thickness conditioned according to the standard were subjected to a 60-V potential for 6 h. The total charge passed through the concrete specimens was determined and used to evaluate the chloride permeability of each concrete mixture.

The sorptivity was measured on 100 mm concrete cubic specimens, which were dried in a 50 °C oven for 14 days. After mass stabilization, the specimens were coated with the epoxy resin on their lateral surfaces only, in order to ensure uniaxial water absorption. The specimen was rested on rods to allow free access of water to the surface and the tap water level was kept no more than 5 mm above the base of the specimen. The masses of the specimens were measured after 0, 3, 6, 24 and 72 h of absorption. The sorptivity coefficient (S) according to BS EN-480-5:1997 was obtained using the following expression:

$$\frac{Q}{A} = c + S\sqrt{t} \quad (1)$$

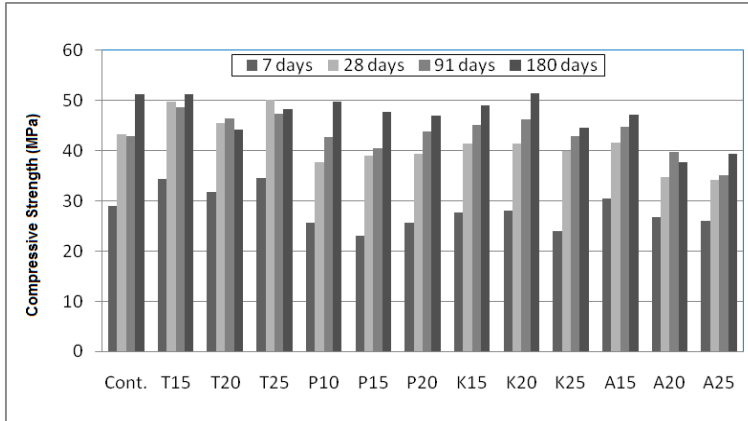
where Q is the amount of water adsorbed; A is the cross section of specimen that was in contact with water; t is the time (second); c is the constant coefficient; and S is the sorptivity coefficient of the specimen (m/s<sup>1/2</sup>).

Concrete cylinder specimens 100×200 mm were cast with centrally conventional rebar of 12 mm diameter and 200 mm height to evaluate the reinforcement corrosion. The steel bars used in the specimen were coated with epoxy resin at the top (50 mm), i.e. half was in the concrete and another half was exposed to the air or solution and at bottom (25 mm). The steel bars were coated at the bottom due to break down of the passive film and at top due to the change in the medium; the chances of initiation of corrosion from both places are high. These concrete specimens were demolded and cured for 28 days in lime-saturated water at 23 ± 2°C. After completion of curing, the concrete specimens were partially immersed in 5% sodium chloride solution in a tank such that the top of the specimen was out of the solution. Then, the corrosion potentials (also referred as half-cell potentials) readings were taken at 21, 90 and 180 days. All measurements are performed according to ASTM C876 using a saturated calomel electrode (SCE). Four half-cell potential measurements are made manually on each specimen. For each mixture, triplicate specimens were used for this technique.

The sulfate exposure testing procedure was conducted by immersing concrete specimens after the specified initial curing in a water tank containing 5% sodium and magnesium sulfate solution at 23±2 °C (ASTM C1012-04). Some control concrete cubes were kept in the lime-saturated water solution tank at 23±2 °C for the compressive strength reduction determinations. The pH value of sulfate solution was kept constant in range of 6 to 8 by adding sulfuric acid. The degree of sulfate attack was evaluated by measuring the expansion of concrete prisms and compressive strength of concrete cubes. Sulfate expansion and weight change measurements were conducted up to 26 weeks. The concrete specimens utilized in the sulfate attack in this study were: 25×25×280 mm concrete prisms were used to measure the change in length and 100 mm cubes were used to measure the reduction in compressive strength with respect to strengths of control specimens cured in lime-saturated water solution. Stainless steel locating discs were mounted using epoxy resins at the ends of the concrete prisms to allow accurate measurements of length change. Three concrete specimens were cast and tested for each test condition to obtain average values.

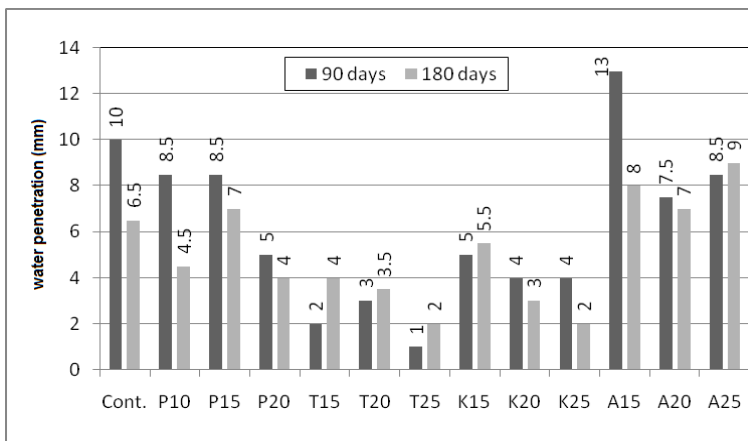
## RESULTS AND DISCUSSIONS

The compressive strengths of concrete specimens are shown in Figures 2. The comparison of the data shows that after 180 days of water curing, the highest compressive strength was 51.2 MPa for K20 concrete, while for CTL concretes, the compressive strength were 50.5. From the figures, it is found that natural pozzolans replacements reduced the compressive strengths of concrete. On the other hand, the strength increases with age. Tasdemir showed that cements including trass pozzolan decrease the strength of concrete and Anwar Hossain reported similar results for the pumice pozzolan.



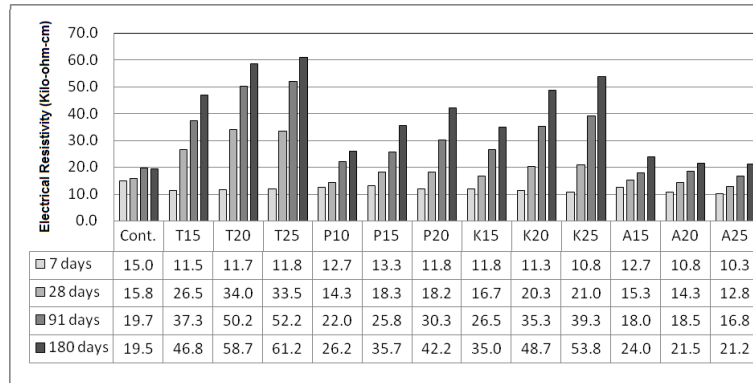
**Fig. 2. The Effect of Natural Pozzolans on the Compressive Strength (MPa) at Various Ages**

The average test results for the water penetration depth of the concretes are illustrated in Figure 3. At 90 days, except for A15 concretes, the other specimens provided lower water penetration depth than the normal concretes. For example, P20 and T20 provided a water penetration depth close to 5 mm and 3 mm, while normal concrete provided 10 mm water penetration depth. As expected, the lower depth was obtained at 180 days for all concretes. Nevertheless, at this age, the water penetration depth varied from 1 to 9 mm, which is relatively low.



**Fig. 3. The Effect of Natural Pozzolans on the Water Penetration (mm) at Various Ages**

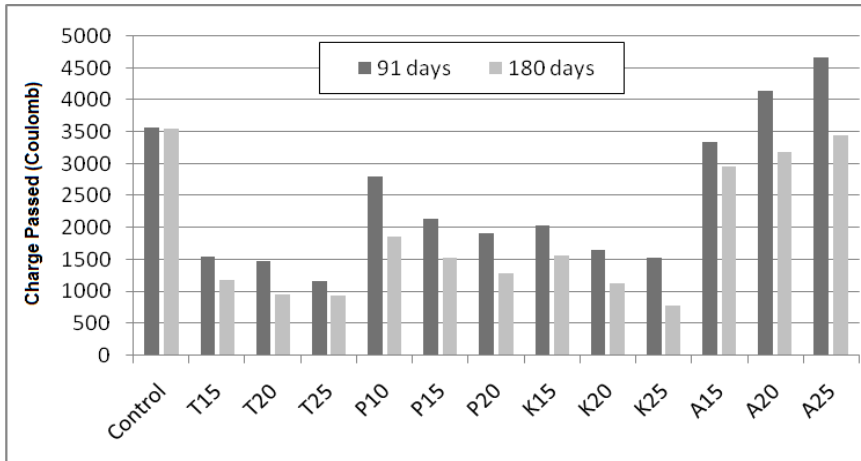
The average test results for the electrical resistivity of various concretes are presented in Figure 4. The electrical resistivity of the concretes varied in the range of 10 to 60 kΩ-cm for different types of concrete. As can be seen, the presence of the pozzolans increased the electrical resistivity of concretes. It is due to the reduced porosity and pore refinement produced by the pozzolans. The resistivity usually increases with lower porosity and smaller pore size, as the flow of ions through the pore spaces is hindered. In addition, the use of the pozzolans reduces the amount of hydroxyl and alkali ions, which are the main ions that carry charge. Therefore, the electrical resistivity was greatly increased in the presence of the pozzolans. A similar study on the pumice was noticed in an earlier research [Anwar Hosain 2005].



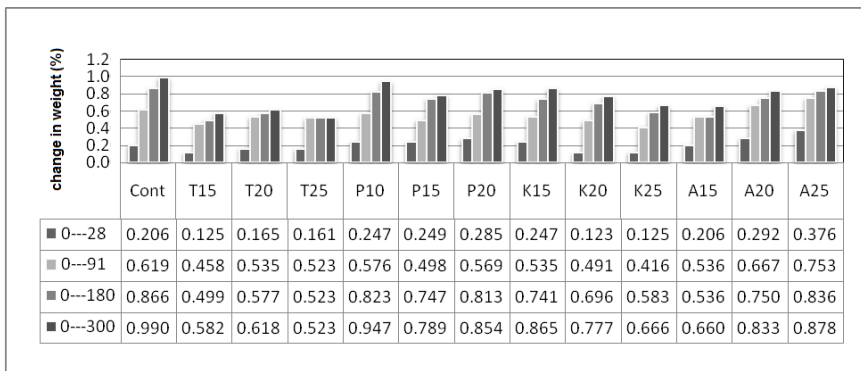
**Fig. 4. The Effect of Natural Pozzolans on the Electrical Resistivity (kΩ-cm) at Various Ages**

Usually there is a risk of temperature rise in using RCPT test for mortar specimens. For this experiment, the temperature rise is not large, as the strength of concretes used is reasonably high at around 20–50 MPa. Figure 5 presents Coulomb values for each mixture over the test duration of 6 hours. Results show that, one natural pozzolan, using pozzolanic material significantly enhances the resistance to chloride penetration compared with the control concrete, on average around 2~3 times higher for various specimens. At the age of 91 days, the normal concretes showed the value of 3500 coulombs while the charge passed through the T20 and K25 concrete were around 1500 coulombs. However, in the Abyek Tuff concrete, the charge passed increased by adding more pozzolan to the mixture. With a continuous moist-curing of up to 180 days, the charge passed through all concretes was reduced. Anwar Hossain showed that blending cements with 20% pumice produces the best performance showing lower porosity and higher chloride ion resistance. [Anwar Hossain 2005]

Table 6 summarizes the results of the lost strength of concrete mixtures after 180 days than normal concrete. In addition, Figure 6 shows weight loss of concrete in sodium sulfate solution than normal concrete cured in saturated limewater at various ages. It suggests that the use of the pozzolans improved the quality of concrete through the reduced porosity and densification of its pore structure. The physical and chemical modification of the pore structure of concrete occurs in the presence of the pozzolans due to its microfilling and pozzolanic effects. This results in the pore refinement and porosity reduction leading to a dense pore structure in both bulk paste matrix and transition zone of concrete that contributes to reducing the sulfate attack.



**Fig. 5. The Effect of Natural Pozzolans on the Rapid Chloride Ions Permeability (Coulomb) at Various Ages**



**Fig. 6. Weight Reduction (%) of Concrete Specimens in Sodium Sulfate Solution at Various Ages**

**Table 6. Mixture Proportions and Fresh Concrete Properties of Mixtures**

	Cont.	T15	T20	T25	P10	P15	P20	K15	K20	K25	A15	A20	A25
28 days	-12.1	-4.5	0.0	-0.5	-4.6	-11.9	-4.0	-8.1	-8.7	-2.9	-4.6	-1.0	-3.3

The corrosion potentials of concrete are reported in Table 3. From the results, it was inferred that corrosion resistance was found to increase by adding pozzolanic materials. It means, the results of corrosion potential indicate that the replacement of pozzolans refined the pores. Thereby permeability and corrosion were reduced. It seems that the pozzolanic reaction product fills the pores existing between cement grains and results in dense calcium silicate hydrate. Both microfilling and pozzolanic effects of pozzolans play an important role to refine the pore structure in bulk paste matrix. The pore refinement occurring due to the secondary reaction between SiO<sub>2</sub> and Ca(OH)<sub>2</sub> makes the microstructure of concrete denser and improves the interfacial bond between aggregates and binder paste. As a result, the durability of concretes and their corrosion rates are improved.



**Table 3. The Effect of Natural Pozzolans on the Corrosion Potential (mV) at Various Ages**

	Cont.	T15	T20	T25	P10	P15	P20	K15	K20	K25	A15	A20	A25
28 days	590	306	319	367	247	482	165	167	280	202	405	308	269
91 days	578	240	236	360	205	300	180	160	214	189	370	231	270
180 days	-587	-162	-241	-312	-567	-535	-114	-105	-324	-420	-266	-403	-428

Table 4 shows the influence of the different amounts of natural pozzolans on sorptivity of concretes at the age of 91 and 180 days. In all three series T, P and K, sorptivity decreases with the period of curing and increases with pozzolan replacement. For example, after 91 days, the sorptivity coefficient for the normal mixture was 1.8 times as large as that for the K20 mixture; but this parameter for the A25 mixture was only 1.08 times as large as that for the normal mixture. The results of water depth show similar trends. The results indicate that pozzolanic concrete generally have lower depths of water than normal concretes. Water transportation in cementitious materials depends on capillary porosity, its connectivity and the pore structure (tortuosity and constriction or disconnection); these parameters are directly related to the progress of cement hydration and pozzolanic reactions.

**Table 4. The Effect of Natural Pozzolans on the Sorptivity of Concrete ( $m/s^{0.5}$ ) at Various Ages**

		Cont	T15	T20	T25	P10	P15	P20	K15	K20	K25	A15	A20	A25
S ( $10^{-6}$ ) ( $m/s^{0.5}$ )	91 days	0.74	0.47	0.52	0.41	0.82	0.63	0.62	0.55	0.4	0.52	0.77	0.84	0.8
	180 days	0.54	0.47	0.47	0.46	0.52	0.47	0.45	0.46	0.37	0.43	0.59	0.69	0.66
Water height (mm)	91 days	45	17	6	13	40	25	20	15	18	8	45	60	50
	180 days	30	25	15	22	23	18	20	14	24	10	32	35	36

Table 5 shows test results for length change of the concrete bars. A larger expansion implies a lower resistance of mortar mixture to sulfate attack, and a smaller expansion implies a higher resistance to sulfate attack. After 26 weeks of immersion in sodium sulfate solution and magnesium sulfate solution, control mixture showed an expansion of approximately 0.05% and 0.06%; while other pozzolanic mixtures, -except A series- show expansion between 0.01% to 0.05%. This means that pozzolanic materials insignificantly have higher resistance to sulfate attack than the control mixture.

**Table 5. Length Change (%) of Concrete Containing various amount of Natural Pozzolans**

		Cont	T15	T20	T25	P10	P15	P20	K15	K20	K25	A15	A20	A25
Na <sub>2</sub> SO <sub>4</sub>	13 weeks	0.02	0.00	0.02	0.02	-0.01	0.01	0.04	0.02	-0.01	0.03	0.00	0.03	0.03
	26 weeks	0.05	0.01	0.06	0.03	0.01	0.04	0.05	0.03	0.00	0.04	0.03	0.05	0.10
MgSO <sub>4</sub>	13 weeks	0.05	0.06	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.02	0.06	0.02	0.04
	26 weeks	0.06	0.06	0.06	0.05	0.05	0.04	0.05	0.05	0.05	0.03	0.09	0.06	0.09

## CONCLUSIONS

In this study, the effect of various levels of natural pozzolans: Jajrood Truss, Eskandan Pumice, Abyek Tuff, and Khash Pumice, on the mechanical properties, durability and chloride-induced corrosion of the ordinary structural concretes was investigated. Based on the results of the present experiments, the following conclusions can be drawn out:

- The concrete specimens containing pozzolans, especially in late ages, have similar compressive strength compared with the control concrete (without pozzolans). So, they can be used as supplementary materials in concrete. However, the usage Abyek Tuff with more than 15% replacement is not recommended.
- In concrete containing Jajrood Truss, Eskandan Pumice, and Khash Pumice, sorptivity decreases with the period of curing and increases with the pozzolans replacement percentage. In addition, water penetration depth, electrical resistivity of concrete and chloride ion permeability is increased. However, usage of Abyek Tuff pozzolans showed much less resistance to chloride attack.
- The physical and chemical modification of the pore structure of concrete occurs in the presence of these pozzolans due to its microfilling and pozzolanic effects. This results in the pore refinement and porosity reduction leading to a dense pore structure in both bulk paste matrix and transition zone of concrete that contributes to increasing the corrosion resistance of concretes.
- Replacement of cement with Jajrood Truss, Eskandan Pumice, and Khash Pumice was found effective in improving the resistance of concrete to sulfate attack. The sulfate resistance of pozzolanic concrete increased with increasing the replacement level. Concrete containing Abyek Tuff showed weak durability to sulfate attack.

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