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CONCRETE MADE WITH ZEOLITE AND METAKAOLIN: A COMPARISON ON THE STRENGTH AND DURABILITY PROPERTIES

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ABSTRACT

An experimental investigation was carried out to evaluate the mechanical and durability properties of concrete mixtures containing natural zeolite (NZ) and metakaolin (MK) in binary blended system up to 20% replacements. Concrete mixtures were evaluated for compressive strength, penetration of water under pressure and water absorption in 30 minutes and 24 hours at various ages up to 90 days. Water to binder ratio and total cementitious materials content were kept constant for all mixtures as 0.4 and 400 kg/m3 respectively. The results showed that despite the observed decrease of compressive strength of proposed composites, they gained enough strength at the later ages similar to that of normal concrete. Moreover, the results confirmed the beneficial effects of zeolite and metakaolin on the durability indexes of concrete which lead a green and environment-friendly concrete.

Keywords: Concrete; durability; metakaolin; natural zeolite; water absorption; permeability

1. INTRODUCTION

Portland cement industry is responsible for approximately 7% of global CO_2 emission [1]. Partial replacement of Portland cements by one or more additives to obtain blended cements not only provides reduction in CO_2 emission and energy saving in cement production, but also supplies more durable cementitious systems to construction industry.

The extent of the benefits provided by use of blended cements increases with increasing

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content of additives in blended Portland cements. However, the content of additives in blended Portland cements, especially for natural Pozzolans and metakaolin, is limited by some factors such as increase in water requirement and decrease in rate of strength development of the cementitious systems. It has been found that the blended cements containing some volume (20% by weight) of natural Pozzolans posses lower 28-day compressive strength when compared to the reference Portland cement, although they show similar strength values at 91 days of age [2,3]. Therefore production of high-volume natural Pozzolan blended cements which are able to compete against ordinary Portland cement requires natural Pozzolans exhibiting significantly high strength activity.

Natural Zeolite is a popular type of natural pozzolan which has been widely utilized in constructions since ancient times [4]. Zeolite group of minerals currently include more than forty naturally occurring species, and is the largest group of silicate minerals [5]. Clinoptilolite, heulandite, analcime, chabazite, and mordenite are the most common types of natural zeolite minerals on the earth. It is known that they show considerable pozzolanic activity despite their distinct crystalline structure. Pozzolanic activity of natural zeolites has been principally attributed to dissolution of zeolitic crystals of three dimensional framework structures under the attack of hydroxyl ions available in hydrating cementitious system [6–11]. Application of natural zeolite in the manufacture of pozzolanic cements began from the first decades of the 20th century and shows a growing trend in recent decades [4]. It is reported that in the construction of the Los Angeles aqueduct with 240 mile long in 1912, about 25% of cement was replaced by zeolitic tuff leading to economic benefits [12]. Recently, the most important utilization of natural zeolite in cement and concrete industry is reported in China. As mentioned by Feng and Peng [13] in 2005, the total quantity of zeolite consumed for this purpose was as much as 30 million tons per year in China. Zeolitic tuffs are also used as pozzolanic material in some cement plants of Russia, Germany, Slovenia, Cuba, Serbia and Spain [4]. Moreover, utilization of natural zeolite as a pozzolanic material is growing in Iran in recent years [14-20]. There is no general agreement on the effects of zeolite on the mechanical properties of concrete at early ages, while higher strengths have been reported at later ages compared to ordinary Portland cement concrete. Tokushige et al., [22] observed that the compressive strength of mortars containing zeolite increased markedly with progress of the age. Najimi [19] investigated the properties of concrete containing natural zeolite (clinoptilolite type) as SCM by replacing 10 and 15 percent of cement and using water to cementitious materials ratio (w/cm) of 0.5. It was observed that the compressive strength of concrete containing natural zeolite was lower than that of control concrete after 7 days of curing, whereas it was equal or slightly higher than control concrete at 28 days curing Poon et al. [21] used natural zeolite as part of cement and investigated the effect of w/cm ratio on the pastes. In general, zeolite in cement pastes with a lower w/cm ratio contributed more to the strength of the pastes.

The other pozzolan that used in this investigation was metakaolin. Metakaolin (MK) is a supplementary cementing material that conforms to ASTM C 618, Class N pozzolan specifications and it is considered as a pozzolanic material which is without direct cementitious value, but will, in the presence of moisture, reacts chemically with calcium hydroxide (CH) to form compounds possessing cementitious properties. It is obtained by the calcinations of kaolin at a temperature ranging between 500 ˚C and 800˚C. The material is a fine, white, clay mineral that has been traditionally used in the manufacture of porcelain. The Meta prefix in the term is used to denote change. In the case of MK, the change that is taking place is dehydroxylation, brought on by the application of heat over a defined period of time. MK is a silica and alumina based product that, on reaction with $Ca(OH)_2$, produces calcium silicate hydrates (CSH) gel and others hydrate products at ambient temperature. MK has been known to enhance strength [23] and pore-refinement [24] at relatively early ages. A relationship between strength and sorptivity has been demonstrated by Gopolan [25] for fly ash concrete. He reported that for concrete of a particular composition cured under given conditions, strength varies in a linear manner with sorptivity. Khatib and Clay [26] showed that there was a systematic reduction in absorption by capillary action with the increase in MK content in concrete. The absorption by total immersion, however, tended to increase slightly with the increase in MK content. Between 14 and 28 days curing, there was a slight increase in absorption by total immersion and by capillary rise for all MK concretes. An increase in the total pore volume led to an increase in water absorption. Tasdemir [27] indicated that the sorptivity coefficient of concrete decreases as the compressive strength of concrete increases.

It was also shown that the sorptivity coefficient of concrete is very sensitive to the curing condition. The effect of curing condition on the sorptivity coefficient of concrete seems to be higher in low strength concretes. Razak et al. [28] reported that metakaolin and silica fume was found to enhance the overall near surface characteristics of the concrete. The inclusion of metakaolin and silica fume greatly reduced the initial surface absorption, water absorption and sorptivity of concrete in varying magnitudes. Güneyisi and Mermerdas [29] indicated that the inclusion of MK greatly reduced sorptivity and chloride permeability of concrete in varying magnitudes, depending mainly on replacement level of MK (0–20%), w/b ratio (0.35 and 0.55), curing condition, and chloride exposure period. It was found that under the inadequate or poor curing, MK-modified concretes suffered a more severe loss of compressive strength and permeability-related durability than the plain concretes.

The aim of this paper is to study the effects of application of 20% metakaolin and 20% zeolite as supplementary cementitious material on the concrete's compressive strength and durability properties.

2. EXPERIMENTAL PROGRAM

2.1 Materials

Locally available Portland cement Type II meeting the requirements of ASTM C150 [31], and two types of supplementary cementitious materials (SCM) including zeolite (NZ) and metakaolin (MK) were used in this investigation. The chemical compositions of these binders are presented in Table 1.

Both fine and coarse aggregates were obtained from local sources in south of Tehran. Coarse aggregates with specific gravity of 2.65 and maximum size of 19 mm and fine aggregate with specific gravity of 2.56 were used in this study concrete.

The grading curves of coarse and fine aggregates are shown in Figures 1 and 2. Carboxylate-based super plasticizer was used for the concrete mixtures in order to improve the workability of fresh concrete. The cement used was commercially available ASTM Type II Portland cement with a specific gravity of 3.14 and a fineness of 290 m^2/kg. The source of NZ (Clinoptilolite type) used in this project was the mines from north of Semnan, Iran. Quantitative X-ray diffraction phase analysis of NZ of the mine had shown 90–95% zeolite in the mineralogy composition [30]. NZ had a specific gravity of 2.20, a fineness of 320 m^2/kg and an average particle size of 16.84 lm. The total content of SiO_2, Al_2O_3, and Fe_2O_3 in the zeolite was found to be approximately 83% which is more than the minimum requirement (70%) specified in ASTM C 618 for natural pozzolans.

Table 1: Chemical properties of binders

	Local cement	Natural zeolite	Metakaolin
Oxide composition % by mass			
CaO	63.25	1.68	3.38
SiO_2	22.42	67.79	74.3
Al_2O_3	4.68	13.66	17.8
Fe_2O_3	3.68	1.44	0.82
MgO	3.63	1.2	0.22
Na_2O	0.25	2.04	0.0
K_2O	0.75	1.42	0.39
SO_3	1.74	0.5	0.46
Loss on ignition	0.45	10.23	2.56

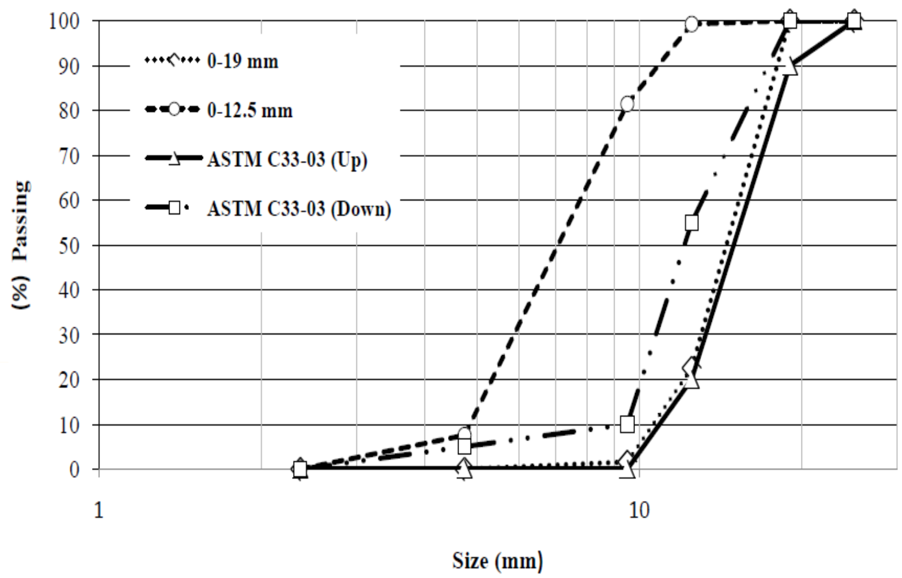

Figure 1. Grading curve of fine aggregates

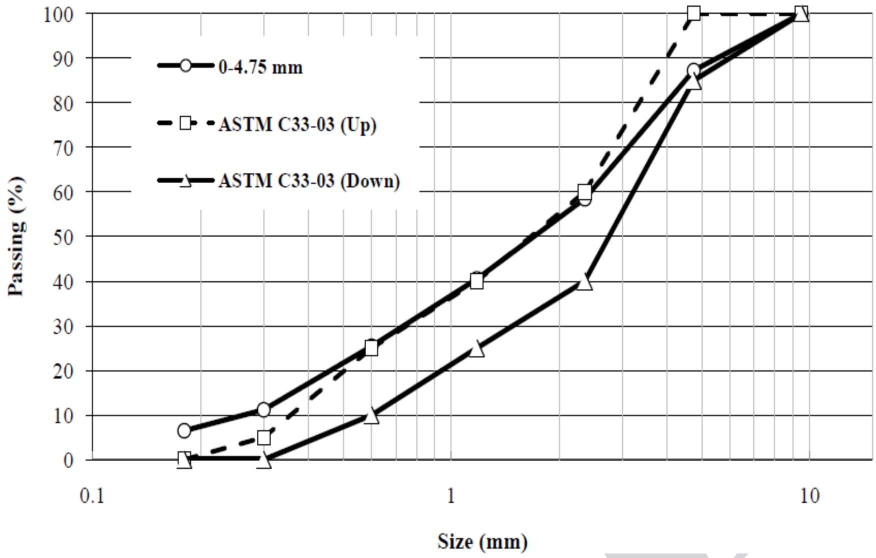

Figure 2. Grading curve of coarse aggregates

2.2 Mix proportions

In this study, concrete mixtures incorporating 20% replacement of NZ or MK at water to total cementitious materials ratio (w/cm) of 0.40 was considered. The cementitious materials content was kept at 400 kg/m^3.

Table 2: Mixture proportion

Mix ID	A/B	FA/CA	Mass of Ingredients (kg/m^3)					Superplasticiser (L/m^3)
			Water	Cement	Cement replacement		FA	
					NZ	MK		
Control	4.31	1.5	160	400	-	-	1060	1
M20	4.31	1.5	160	320	-	80	1047	1
Z20	4.31	1.5	160	320	80	-	1040	3

Note: The numeral in mix designation corresponds to the percentage of SCM present in the binder. For example M20 means that the concrete was prepared using MK (20%) and the rest was PC.

control mix (100% PC); A/B – aggregate–binder ratio; C_A – coarse aggregate; NZ –Natural Zeolite; MK –Metakaolin; F_A – fine aggregate.

Superplasticizer was added in order to attain a slump of about 170 ± 5 mm. The mixture proportions and fresh concrete properties are respectively shown in Tables 2 and 3.

The dry materials were mixed first followed by the addition of water into the mixer. Finally, the superplasticizer was added to the mixture. Immediately after mixing, the concrete mixtures were consolidated by a vibrating table. After casting, all the specimens were left covered in the casting room for 24 h. The test samples were then remolded and moist cured at 23±1 ˚C until the age of tests.

To characterize the strength development and durability properties, the compressive strength and transport indexes including, water penetration depth, water absorption in 30 min and 24 hr and, were studied and their inter-relationships were discussed.

Table 3: Properties of fresh concrete

Mix ID	Slump (Cm)	Density (kg/m^3)	Air content (%)
Reference	19	2341	2.7
M20	17	2320	2.6
Z20	15	2310	3

3. RESULT AND DISCUSSION

3.1 Compressive strength

Compressive strength was measured on three 100 mm cube at the age of 3, 7, 28 and 90 days and the mean value were reported as the strength. At testing age, samples were removed from the curing tank and weighed. The samples were centrally placed in a compression testing machine and load was applied at a rate of 150 kN/min. The strength development results are shown in Figure 3 for reference, M20 and Z20 mixtures.

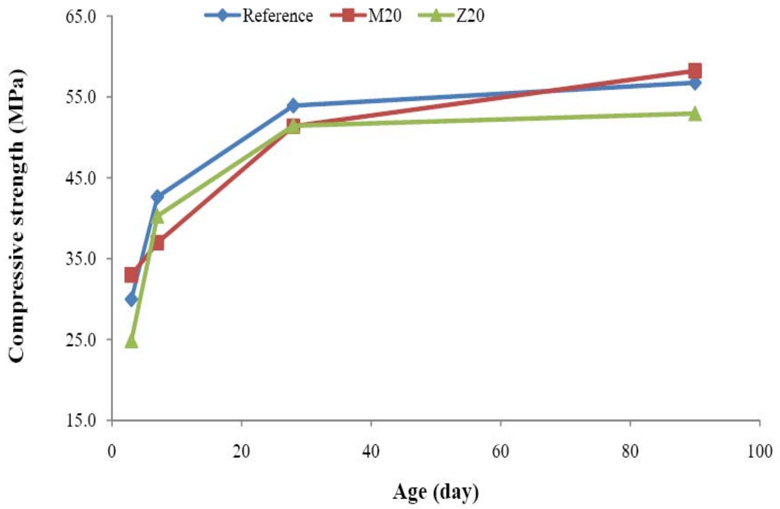

Figure 3. Compressive strength development for control, M20, and Z20

The results obviously demonstrated that application of metakaolin lead to an improvement of compressive strength in the later ages of 90 days while it was experienced a decrease in the earlier ages of 3, 7 days. The compressive strength of M20 was almost near the reference mixture with a minor decrease of 5%. In mixtures containing 20% NZ, compressive strength reduction was observed to be about 17% compared to reference concrete at age of 3 days. Such decreasing trends are about 6%, 5% and 7% at ages of 7 days, 28 days and 90 days respectively.

3.2 Depth of water penetration

Depth of water penetration was performed according to BS EN 12390-8 [32] test method at the ages of 28 and 90 days. Figure 4 shows results of water penetration depth (WPD) at the ages of 28 and 90 days. The results show that all of WPD of all mixtures are lower than 16 mm. which are in the acceptable ranges of standard. WPD of both reference and mixture containing 20% of zeolite decreased from 28 days to 90 days in which a decrease of about 17% and 27% could be observed respectively for reference and Z20. A different behavior could be seen for M20 as a mixture with 20% of metakaolin replaced with Portland cement. In this mixture, WPD increased about 30% by curing period from 28 days to 90 days.

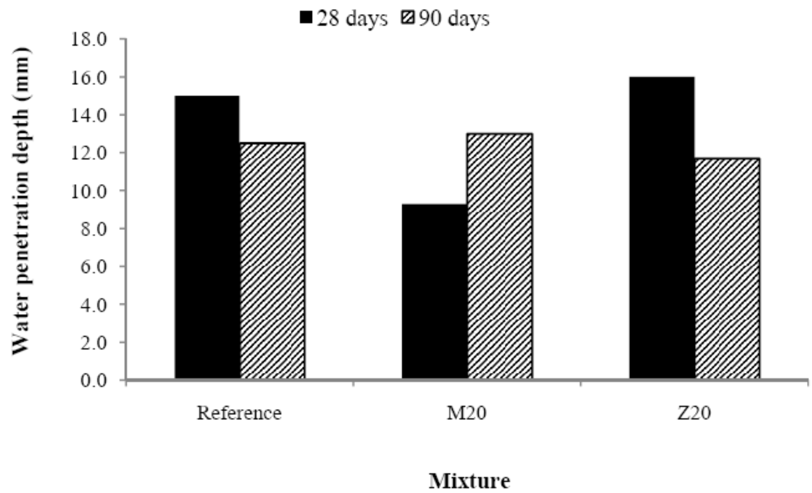

Figure 4. Water penetration depth at 28 days and 90 days

3.3 Water absorption in 30 min and 24 h

Three 100 mm cube specimens were used for this test. Water absorption (WA) tests were performed in oven-dried for 72 h. The absorption of each specimen was measured by calculating the increase in mass resulting from immersion in water for 30 min and 24h as a percentage of the mass of the dry specimen. Figures 5 and 6 show the results of WA in 30 min (WA-30) and 24 h (WA-24) respectively. WA-30 experienced a decreasing trend by curing time from 28 days to 90 days while WA-24 increased for reference concrete and M20 and N20 decreased by increasing curing time. In this regard, utilizing 20% of MK, increased the WA-30 around 56% while it was decreased up to 24% after 28 days and 90 days of curing respectively. However, in the case of NZ, WA-30 increased up to 80 % after 28 days and reached to the WA-30 value similar to reference concrete. Such findings showed that the application of MK and NZ lead to favorable effects on concrete’s 30 min. absorption properties.

Moreover, as depicted in Figure 6, application of zeolite decreased the water absorption of concrete after 24 hour up to 9% and 14% after 28 and 90 days respectively. However, metakaolin addition increased the abortion properties of concrete after 24 hour at the age of 28 days up to 23% and it was decreased up to 12% at the age of 90 days. These results showed that zeolite improved the WA-24 and metakaolin replacement increased the WA-24 and at the later ages, decreased the WA-24.

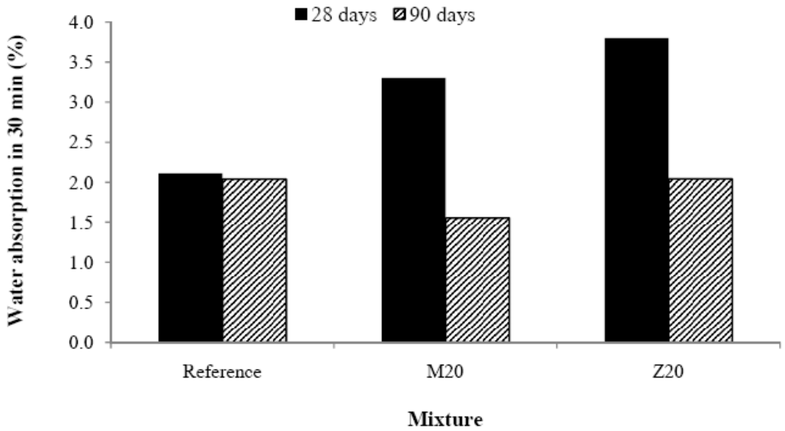

Figure 5. Water absorption in 30min at 28 and 90 days

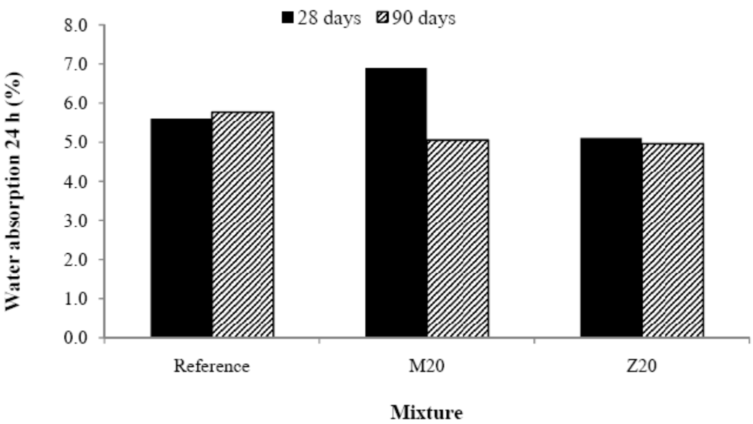

Figure 6. Water absorption in 24h at 28 and 90 days

3.4. Discussion

Figure 7 shows the compressive strength of under studied concrete mixtures. Comparison of the results showed that despite the beneficial effects of MK at 3 days, at the ages of 7 and 28 days, the strength decreased and then at the later age of 90 days it upgraded even a small increase than reference concrete. On the other hand, zeolite replacement at level of 20% instead of Portland cement, lead to decrease of compressive strength at all ages of curing. Such phenomena could be related to the pozzolanic activity of metakaolin and zeolite at different ages. The noticeable point could be deduced that M20 and Z20 produced a concrete mixture with a similar strength compared to reference concrete while they use lower pollutant Portland cement.

The results of water penetration and water absorption confirmed the beneficial effects of zeolite and metakaolin on the durability indexes of concrete by replacement up to 20 %. These generous effects might be attributed to the pozzolanic reactions developed in the concrete mixtures incorporated such supplementary cementitious materials with the following formula:

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2\ H_2O \rightarrow CaH_2SiO_4\ 2\ H_2O$$

The product of general formula (CaH_2SiO_4 2 H_2O) formed is a calcium silicate hydrate, also abbreviated as C-S-H in cement chemist notation, the hyphenation denotes the variable stoichiometry. The ratio of Ca/Si, or C/S, and the number of water molecules can vary and the above mentioned stoichiometry may differ which here is the governing factor of the findings of the research.

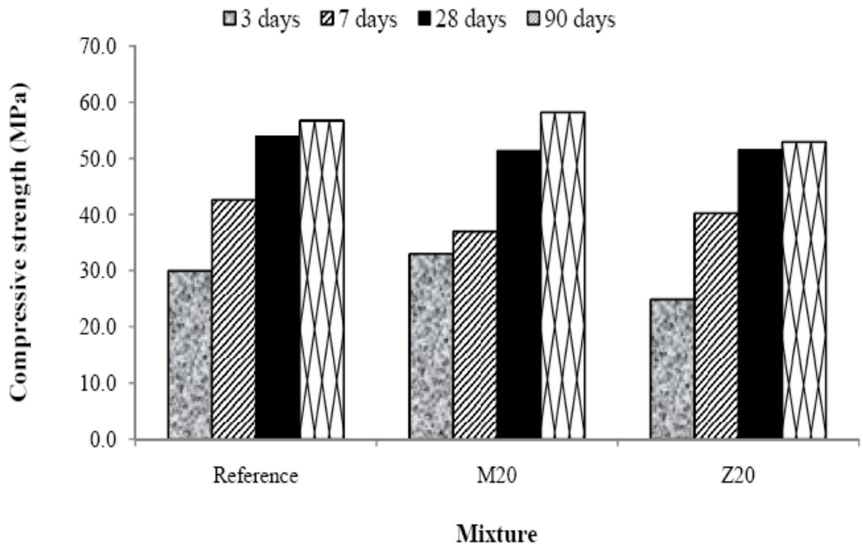

Figure 7. Compressive strength of reference, M20 and Z20 mixtures

4. CONCLUSION

On the base of the findings of this experimental investigation, the following results could be drawn:

1. Despite the observed decrease of compressive strength in metakaolin concrete at the early ages, its strength was upgraded to even more than normal concrete.
2. Zeolite contained concrete led to a decrease on compressive strength at all curing ages, however, its strength reduction is not impressive.
3. Concrete mixtures with replacement level up to 20% with metakaolin or zeolite (M20 and Z20) produced blended concrete with a similar strength compared to reference concrete at 90 days while they use lower pollutant Portland cement.
4. Utilizing 20% of MK, increased the WA-30 while it was decreased up to 24% after 28 days and 90 days of curing respectively.
5. The results of water penetration and water absorption confirmed the beneficial effects of zeolite and metakaolin on the durability indexes of concrete by replacement volume up to 20 %.
6. The generous effects on the durability might be attributed to the pozzolanic reactions developed in the concrete mixtures incorporated metakaolin or zeolite as supplementary cementitious materials.

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