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The Flow Properties of Some Chemical Additives Used in Modification of Natural Zeolite for Cement Concrete

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Aim: To assess the effectiveness of water-reducing additives in relation compressive strength of cement pastes.
Methodology: Experimental study, Materials used were natural zeolite from Egypt, with a grain size up to 0.08 mm, containing zeolite (clinoptilolite) - 75%, and ratio Si / Al content is 4.8-5.4; Portland cement CEM I 42.5 R., and a modified viscometer with an internal diameter of 25 mm and 50 mm height was used. Changes in water demand was evaluated by value of flowing on the border of gravity spread test.
Results: Natural zeolites with low W/S ratio (water solid ratio) equals to 0.4 was well plasticized at low dosages (0.25%) of additive Melflux. The most effective form of chemical additives was SP-3, which at the dosage of 0.6% reduces the W/S ratio of zeolite pastes by 20%. In addition, Melflux

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was chosen as the most effective in cement systems, although it is less efficient in natural zeolite, but the amount accepted is 5%, also Melflux was compared with pure cement paste in range from 0.1 to 0.75% by weight of solids, which determines need of concrete with high strength. **Conclusion:** Cement paste containing natural zeolite exhibit improved resistance to water requirement by using chemical additives. However, adding natural zeolite in presence of additive Melflux decreases water demand of mixtures which directly increase the compressive strength of cement paste.

Keywords: Nature zeolite; water requirement; chemical additives; cement concrete.

1. INTRODUCTION

High quality of concrete can be achieved with a reasonable selection of all components and their high degree of compatibility. New generation of concretes is considered as concrete with additives. Compatibility of all important components, particularly the content of additives in the mixture is essential to get concrete with high quality. Incompatibility in the "cement - additive" results from inconsistency of the functional additives due to imposition of physical and chemical and colloid-chemical effects [1].

One of factors characterizing this feature of concrete, is the type of cement. For decades, many researches focused on the role of shaping and physicochemical properties of concrete and also the role of mineral additives like zeolite and pozzolan [2-6].

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents and catalyst [7-10]. A pozzolan is a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties, it has been proven, that use of pozzolanic additives for cements increases their resistance to corrosion, due to its highly waterproof property, decreased content of $Ca(OH)_2$ and low presence of capillary pores in its matrix [11]. In addition, it hinders the penetration of aggressive media by ions from entering hardened concrete [12].

Considering economic and technological benefits of using a high quality of concrete, new functional mineral additives is required for construction sectors [12]. Zeolites is an example which have unique properties [13-17]. Natural zeolites are a group of hydrated tektoaluminosilicates, with a specific hierarchical structure [2]. It has characteristic features regards framework of TO_4 tetrahedra, which linked together via shared oxygen atoms, and also presence of voids filled ions and water molecules that gives it great freedom of movement [18-19]. Clinoptilolite is the most abundant and economically important type of natural zeolites. Based on literature data [20-22]. It's concluded, that Clinoptilolite has pozzolanic properties in presence of water, and reacts with calcium hydroxide to form a product having excellent binding properties (C-S-H).

Determinant of pozzolanic activity is quantity and rate of binding of $Ca(OH)_2$ by active ingredients of pozzolan (SiO_2+Al_2O_3). Clinoptilolite similarly as diatomite or volcanic tuffs, belongs to the group of pozzolan of moderate activity relative to the $Ca(OH)_2$, compared to the less active siliceous or calcareous fly ash, gaize and highly active metakaolinite or silica fume [3].

Zeolites represent a group of aqueous aluminosilicates of alkali and/or alkaline earth metal framework with an open porous microstructure. The crystalline lattice of zeolites built of four-five-six-membered rings or more formed silicon-oxygen tetrahedra [4]. Some amount of silicon atoms replaced by aluminum atoms. As a result, the crystal structure in space inside zeolites form a system of interconnected channel environment and cavities [23]. Open frame-cavity structure of zeolites $[AlSi]O^{4-}$ has a negative charge, compensatory counterions (metal ions, etc.) and easily dehydrating water molecules. In this regard, zeolites may act as an active mineral additives cement systems, and their specific open microstructure characterized by selective adsorbents [6,24,25]. However, this material is also important that it is compatible with known effective chemical modifiers [26].

The use of active mineral additives for the manufacture of various concrete, mixtures and solutions inevitably involves the need of using highly effective additives of plasticizers action to regulate retechnologization properties of concrete mixtures and solutions [27]. However, there are a number of problems, one of which is "incompatibility". In this regard, the problem of choosing chemical additives for purpose of establishing its high water reducing activity in aqueous silicate and aluminosilicate systems have been solved that would be one of the components of high-strength concrete.

2. METHODS AND MATERIALS

2.1 Materials

Materials used in our study were natural zeolite from Egypt, manufactured by «Gawish import & export Egypt» with a grain size up to 0.08 mm, containing zeolite (clinoptilolite) - 75%, and ratio Si / Al content is 4.8-5.4; Portland cement CEM I 42.5 R. Chemical and mineralogical composition of raw materials has been shown in Table 1 and Table 2.

2.1.1 Chemical modifiers

In the current study four chemical modifiers were used first, (Polyplast SP-3 Powder) is superplasticizer easily soluble in water. It refers to anionic surfactants formed by condensation of naphthalene sulfonic acids with formaldehyde, and by neutralization with alkali (NaOH). Plasticizers SP-3 are additives that increase plasticity or fluidity of materials to which they are added, these include plastics, cement, concrete, wallboard and clay bodies. Second, (Melflux 2641 F) is Superplasticizer in a form of yellowish powder easily soluble in water with high performance superplasticizer for cement based construction materials. Third, (Micro Air 125) is additive used as water surfactant solution with microvacuolated designed for concrete mixes with high frost resistance and water resistance. Fourth, Polycarboxylate ether carboxine of alpha is transparent liquid additive.

2.2 Methods

The effectiveness of water-reducing additives were evaluated to reduce water demand, water-mineral pastes with control composition (without additives) with the same flow controlled with a modified viscometer were compared. Viscometer is a cylinder of stainless steel with an internal diameter of 25 mm and 50 mm height. Changes in water demand were evaluated by value of flowing on the border of gravity spread test.

Method used was consisted of the following as shown in Fig. 1 and Fig. 2, first under glass with 180x180 mm dimensions' fits paper coated with a circular scale, then glass and cylinder were moisturizing. A weighed sample of material is taken in a quantity to fully fill the cylinder.

2.2.1 Paste preparation

Amount of 60 Grams of Zeolite and cement were mixed with chemical additives in percent ranges from (0.2 - 0.75), as shown in Table 3. Then water was added to the different mixtures until flow of paste reached diameter of 6.6 cm and then the amount of water used and W/S were calculated and recorded as shown in Table 3.

Table 1. The chemical composition of portland cement and natural zeolite

Ingredient	Amount (%)							
	SiO_2	CaO	MgO	Fe_2O_3	Na_2O	$A1_2O3$	SO_3	K_2O
Cement	22,0	66,2	0,86	5,32	0,14	4,79	0,09	0,6
Zeolite	71.4	1.26	0.45	1.04	2.086	11.9	-	3.02

Table 2. Phase composition of raw materials

Phase composition of cement cylinder	**C3S**	**C2S**	**C3A**	**C4AF**	
Amount (%)	62	17	4	14	
Mineral composition of zeolite	**Clinoptilolite**	**Feldspar**	**Cristobalite**	**Clay mica**	**Quarts**
Amount (%)	75	3	7	4	traces

Table 3. The paste properties and water reducing activity of chemical modifiers in various systems

Composition	Additive type	W/S ratio	Amount of additive (%)	τ0,pa	Mass of powder (g)	Amount of water (ml)	Density (g/cm^3)
Zeolite	-	0.4	0	66.09	60	24	1709.14
Zeolite	SP-3	0.4	0.2	64.47	60	24	1642.18
		0.37	0.4	70.37	60	22	1783.54
		0.32	0.6	69.85	60	19	1770.2
Zeolite	Carboxine of alpha	0.42	0.2	68.63	60	25	1739.4
		0.383	0.4	68	60	23	1723.5
		0.375	0.5	71.56	60	22.5	1813.56
Zeolite	Air 125	0.383	0.25	66.31	60	23	1680.5
		0.367	0.5	72.51	60	22	1837.66
		0.333	0.75	69.54	60	20	1762.42
Zeolite	Melflux	0.383	0.25	68.25	60	23	1765.01
		0.377	0.5	66.27	60	22.6	1713.86
		0.367	0.75	64.95	60	22	1679.76
Cement	-	0.45	0	77.11	60	27	1994.07
Cement	SP-3	0.4	0.2	74.17	60	24	1918.08
		0.38	0.4	77.52	60	23	2004.81
		0.35	0.6	74.76	60	19	1933.28
Cement	Carboxine of alpha	0.37	0.2	66.13	60	22	1606.7
		0.350	0.4	65.55	60	21	1617.86
		0.32	0.6	68.9	60	20	1709.04
Cement	Air 125	0.45	0.25	72.46	60	27	1873.98
		0.43	0.5	70.61	60	26	1826.16
		0.42	0.75	76.89	60	25	1988.51
Cement	Melf	0.32	0.25	69.61	60	19	1800.22
		0.28	0.5	72.59	60	17	1877.31
		0.25	0.75	74.84	60	15	1935.51
Cement + (5%) Zeolite	-	0.42	0	65.86	60	25	1703.11
Cement + (5%) Zeolite	Melf	0.34	0.25	79.6	60	20.5	2058.56
		0.3	0.5	81.75	60	18	2114.19
		0.26	0.75	83.9	60	15.5	2169.76

2.2.2 Flow determination and limiting shear stress

After filling, the cylinder will take up and then diameter of paste flowing is measured by calipers. In every measurement the density of resulting paste was record.

The paste properties are respectively shown in Tables 3. Limiting shear stress was calculated by the formula:

$$\tau_0 = \frac{hd^2\rho g}{\kappa D^2}$$

Where:

- τ0 - limiting shear stress paste, Pascal;
- h and d respectively the height and the diameter of viscometer, m;
- ρ- is the density of the paste, kg/m3;
- K – coefficient taking into account the redistribution of stresses in viscoelastic bodies, equal to 2;
- D – diameter of flowing paste, m, (in this work, diameter is constant equal to 6.6 cm (0.066 m).

2.2.3 Determination of compressive stress

Compressive strength of cubes of concrete stones was assessed by machine known as P-5 after 28 days. Concreter cubes involved zeolite and chemical additives as shown in Table 3. Mixtures were poured in sequential concrete cast consisted of 6 pieces in a form of cubes and size of each cube was 20 mm. The compressive strength was determined by testing specimen's halves of samples-beams, made after the flexure tests (six pieces). In order to get results of flexure and compression of sample, load of the press plates is transferred to the sample, and the surface area of plates in contact with the sample, equal to 25 cm^2 as shown in Fig. 3.

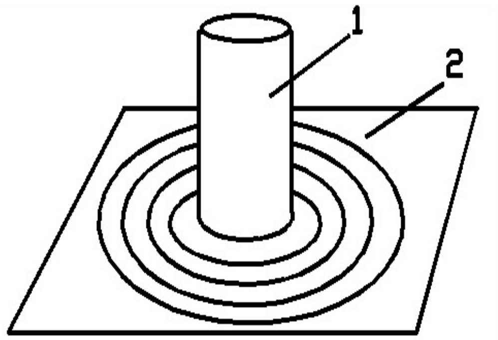

Fig. 1. Status of cylinder above glass plate
1-Cylinder (viscometer)
2. Glass plate in order to measure flow in

Fig. 2. Form of paste after lifting cylinder

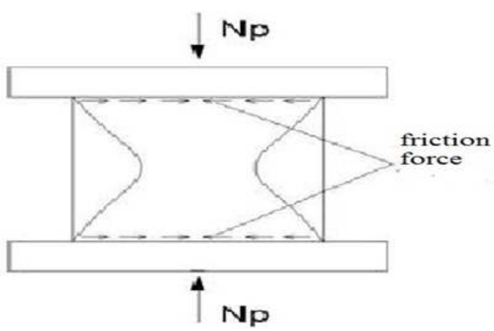

Fig. 3. Character destruction of cement stone with the compression test

3. RESULTS AND DISSCUSION

Interoperability additives for cement paste was determined by the change in water demand in the flowing of the water-mineral paste on the border of gravity spread test. The results shown in Table 3 and Figs. 1 and 2, that adding natural zeolite without calcium hydroxide in presence of additive Melflux decreases water demand of mixtures which directly increase the compressive strength of cement paste.

Fig. 4. Shows natural zeolites with low W/S ratio (water solid ratio) equal to 0.4 and plasticized well at low dosages (0.25%) of additive Melflux.

The most effective form of chemical additives was SP-3, which at the dosage of 0.6% reduces the W/S ratio of zeolite pastes by 20%.

Comparative evaluation of chemical additives used in cement paste showed high efficiency additive Melflux in reducing W/S by more than 40% as shown in Fig. 5.

3.1 Compressive Strength

Since natural zeolite is an additive in cement, the effectiveness of reducing water demand of mixtures was evaluated, thereof in presence of additive Melflux as shown in Fig. 6. Additive Melflux in this experiment chosen as the most effective in cement systems, although it is less efficient in natural zeolite, but the amount accepted is 5%. Such a small amount of natural zeolite made due to conditions for obtaining high strength concrete [28].

As shown in Fig. 6 addition of a small amount (5%) of natural zeolite in cement reduces its water demand under the same flowing of test and reduces the effectiveness of chemical additives Melflux compared with pure cement paste in range from 0.1 to 0.75% by weight of solids, which determines need of concrete with high strength.

There have been several studies on the compressive strength of cement paste/mortar/concrete containing natural zeolites [29-31]. However, it is still difficult to predict the influence of natural zeolites as Supplementary Cementing properties of cement paste/mortar/concrete. Many parameters affect Materials on the the strength and durability, such as w/cm ratio, weight percentage of cement replaced with natural zeolites, the mineralogical and chemical composition of natural zeolites, a purity level of natural zeolites, its fineness, pozzolanic reactivity, etc. [11,14,32]. In the evaluation of rheological activity of various mineral admixtures for cement concrete [33], it has been found that natural zeolite from Egypt has a low water demand. This fact suggested that the introduction of natural zeolite from Egypt to Portland when replacing the part will not increase the water demand of the mixture and to a certain amount of it will not reduce the strength of the hardened stone. In this connection, in the beginning of our work we assessed the strength of the stone with different contents of zeolite, namely 5, 10, 15, 20, 30, 40 and 50%. Character destruction of cement stone with compression test shown in Fig. 3. Take control composition without zeolite (0%). results are shown in Table 4.

Table 4. Shows that adding 5% of zeolite into composition has increased the compressive strength by 23%. The results were as follows: the concrete containing 5% of natural zeolites has compressive strength increased up to about 5.5% and decrease of about 0.7% in the concrete containing 10% of natural zeolites, because of the sand that worsens the properties of concrete.

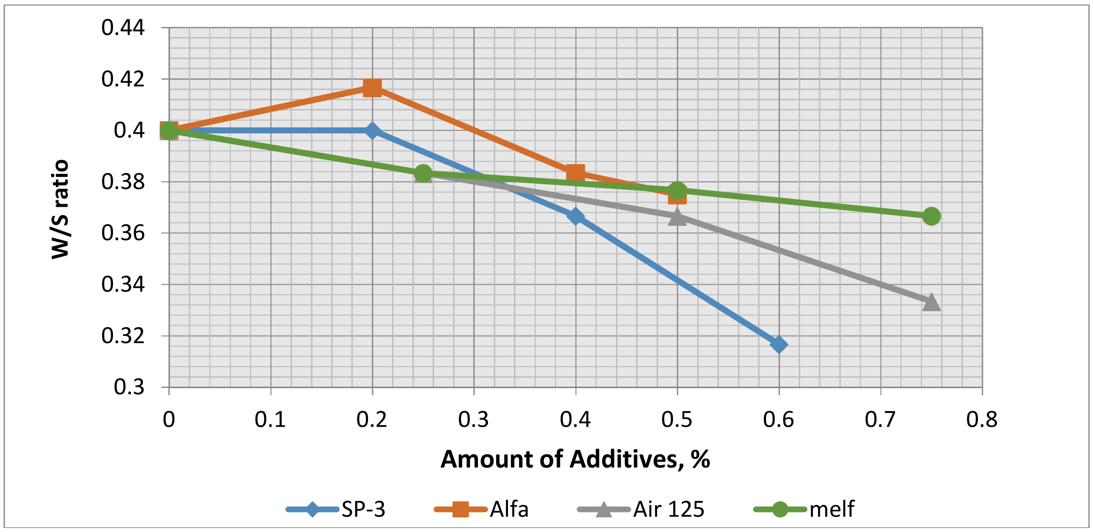

Fig. 4. Influence of type and quantity of chemical additive on water demand of natural zeolite powder

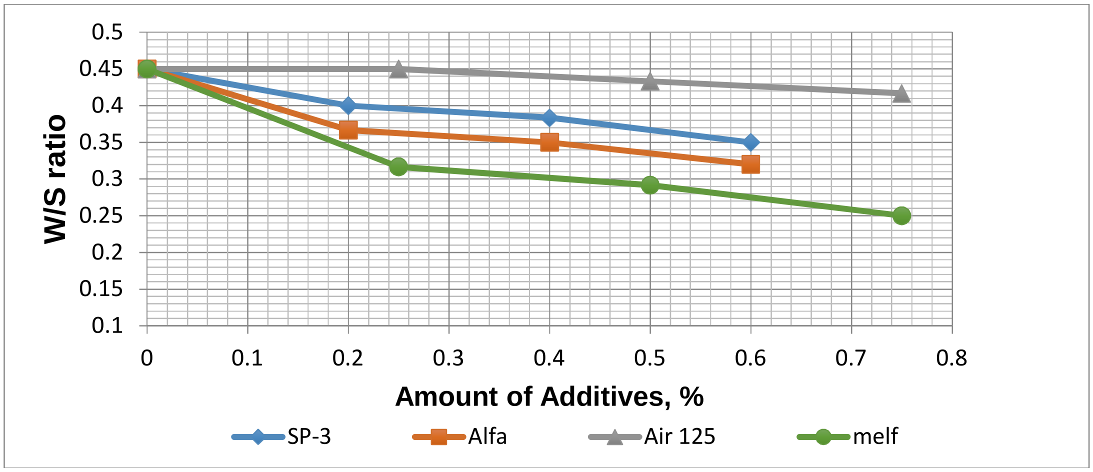

Fig. 5. Influence of the type and quantity of chemical additive on water requirement of cement paste

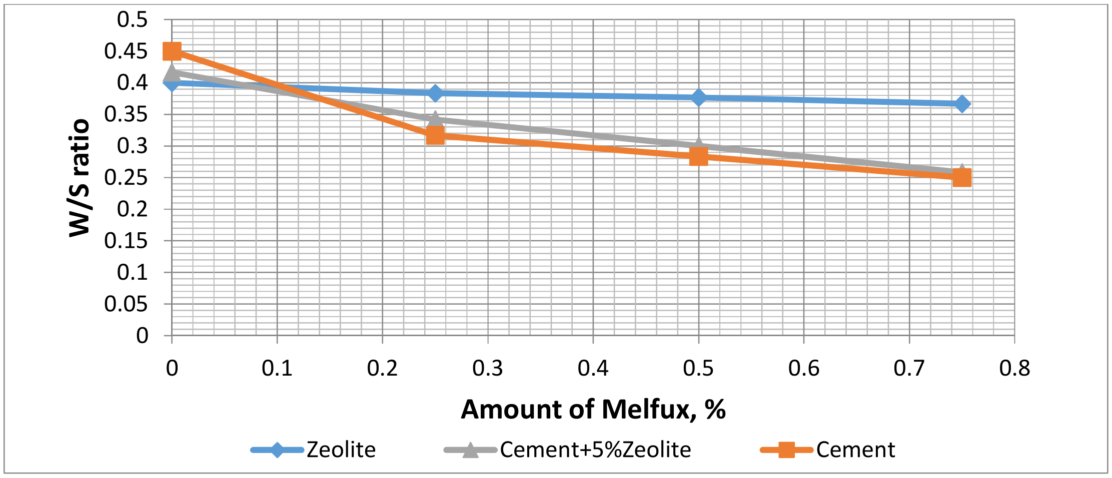

Fig. 6. Effect of additives Melflux on W/S mineral pastes

Table 4. Changes in strength of cement stone with zeolite from Egypt

Mix, %		w/s	Compressive strength after 28 days, kg/cm^2
Cement	Zeolite		
100	0	0.3	654.4
95	5	0.3	796.25
90	10	0.3	690
85	15	0.3	600.6
80	20	0.3	557
70	30	0.3	566
60	40	0.3	474.36
50	50	0.3	360.63

4. CONCLUSION

Cement paste containing natural zeolite exhibit improved resistance to water requirement by using chemical additives. However, adding natural zeolite in presence of additive Melflux decreases water demand of mixtures which directly increase the compressive strength of cement paste.

5. RECOMMENDATIONS

Due to specific features of natural clinoptilolite, it can be successfully used as a valuable mineral additive to cements, and it's recommended for researchers to study another different property such as compressive strength versus proportion of binder.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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