Trakia Journal of Sciences, Vol. 7, Suppl. 2, pp 229-233, 2009

Available online at:
http://www.uni-sz.bg
ISSN 1313-7050 (print)
ISSN 1313-3551 (online)

Original Contribution

AN INVESTIGATION INTO THE EFFECT OF MAGNESIUM SULFATE IN ZEOLITE-SUBSTITUTED CEMENTS

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ABSTRACT

This study comparatively examines the effects of $MgSO_4$ in terms of the rate of zeolite admixture in paste specimens produced with PC42.5 R cement substituted with different ratios of zeolite. An examination of the chemical and physical changes of the specimens cured in water and $MgSO_4$ solution reveals that 15% zeolite admixture is appropriate. Compression strength of control specimens, 15% zeolite-substituted superplasticizers cured in water, was slightly higher than that of the specimens cured in $MgSO_4$ solution. This indicates that the pozzolanic activity was high and 15% admixture rate made the zeolite-substituted specimens resistant against $MgSO_4$ solution. Consequently, zeolite binds the portlandite, $Ca(OH)_2$, in cement and subsequently, is converted into Calcium Silicate Hydrate (C-S-H) composites; thereby, it prevents corrosion in cements, decreases permeability of concrete, and gives resistance against sulfate environments.

Key Words: zeolite, cement, corrosion

INTRODUCTION

Limestone, clay or marn are mainly used in cement production. Furthermore, in cases where the raw material mixture has insufficient iron oxide content, iron ore or pyrite ash are also used as a constituent of raw material mixture as a compensation. Similarly, when the amount of silica is insufficient, high-silica sand or a pozzolanic material is used as a constituent of raw material to compensate for this. Like other binding materials, cement, a hydraulic binding material, is composed of alkaline elements such as CaO and MgO and of elements such as SiO_2, Al_2O_3 and Fe_2O_3. The rates of alkaline and hydraulic elements determine the quality of a binding material.

By adding pozzolan into cement, it is possible to change its properties and its purposes and places of use. One of these pozzolans is zeolite. Presently, Japan, Italy, New Zealand, USA, Canada, and Bulgaria are known to have pure zeolite deposits with large reserves (KIBAROĞLU, 2007). A report by TUBITAK – NAM reports that Turkey has a natural zeolite reserve of about 50 billion tons (KOCAKUSAK, 2001).

Zeolites, alkali, and alkaline-earth have a crystalline structure and are defined as hydrated alumino-silicates. They are termed as “boiling stones” as they form bubbles to give out their water content when heated (SPO, 1996). Zeolites usually contain hydrated aluminum silicate; some potassium, sodium, calcium; and at times, barium and strontium etc. Zeolite crystals are glassy, white, transparent, and sometimes colored. They have a hardness of 4–6 and a density of 2–2.5 g/cm^3. They melt leaving a silica residue in acids and froth in the blowpipe. Hot mineral waters play a significant part in zeolite formation. Losing a considerable portion of their water content at 100^{o}C and higher temperatures, zeolites absorb 4–14% moisture from air. They lose their transparency as they give out water. However, most of them restore their transparency when they absorb water, which demonstrates the fact that crystal composition does not change with water loss. In other words, water passes through the net-like structure again as if passing through the fine holes of a sponge

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(SAYAR, 1960 and UNSAL, 2001).

Used in various chemical industries as catalysts, adsorbents, and ion exchangers, natural zeolites can also be used as light building blocks and light aggregates in general (YUCEL, 1990). As they contain a high amount of reactive SiO_2 and Al_2O_3, natural zeolites also have a pozzolanic quality, reacting with slaked lime $Ca(OH)_2$ and water to form binding products. Therefore, they can be used as natural pozzolans in cement or concrete as well. Experiments conducted in China have revealed that a natural zeolite specimen composed of clinoptilolite mineral had a pozzolanic activity between silica fume and fly ash (POONE, LAM, KOU, LIN, 1999).

Addition of natural pozzolans into cement and concrete components improves concrete properties such as workability, impermeability, and strength at late ages and increases the strength of concrete against external chemical factors such as alkali-aggregate reaction and sulfate effect.

It has been demonstrated that Portland cements substituted with 10%, 20% and 30% natural pozzolan have higher compressive strength than normal Portland cement (MEHTA, 1981); that it enhances concrete properties and can be used in high-performance concrete production (FENG, LI and ZANG, 1990); and that natural zeolite admixture prevents undesired expansions that may result from the alkali-aggregate reaction of concrete (MEHTA, 1981and FENG, JIA, CHEN, 1998).

A part of a master's thesis (FEN YILDIRIM, 2007), this study examined the effects of $MgSO_4$ in paste specimens produced with PC 42.5 R cement substituted with different ratios of zeolite. The characteristic of the study is that the prepared specimens were cured at the earliest age (24^{th} hour) in $MgSO_4$ solution to reveal the effect of sulfates on hydration process. Corrosive effects of sulfate solutions on cement paste increase with sulfate density and corrosion mechanism may also vary.

MATERIALS AND METHODS

Materials

Cement: PC 42.5 R (CEM I 42.5 R) cement produced by Mersin ÇİMSA cement factory was used in the study.

Zeolite: In the fineness experiments on zeolite obtained from Izmir ENLİ Mining Corporation performed in the laboratories of OYSA Cement Factory (OYSA, 2006). Blaine fineness was found to be 6000 cm²/g and other physical and chemical properties are presented in Table 1.

Superplasticizer (SP): Superplasticizer obtained from Sika was used as an additive in the amount of 0.9% of cement weight. Sikament-FF-N naphthalene formaldehyde sulfonate was the superplasticizer used whose technical information is as follows: pH 9, liquid, density 1.22 kg/l, proposed amount of cement weight 0.8-3.0%.

Methods

The study was carried out in an experimental format. The experiments were based on TS-25, TS 197-1 and ASTM C 109 standards, and care was taken about material mixture design and laboratory conditions for the validity and reliability of the experiments.

EXPERIMENTAL

Material Mixture Design

Specimens were prepared in 40x40x160mm casts with cements substituted with 0%, 15%, and 30% zeolite in weight. A certain fluidity rate was taken as a standard in all mixtures and this value was determined to be between 105%-115% (ASTM C 109). Three specimens were prepared for each paste specimen, some with and some without SP (Table 2).

Curing of Specimens

The admixture was premixed with a total amount of water before application and this solution was used to prepare concrete mortars. Concrete mortar mixtures were prepared in accordance with ASTM C 109. The samples were cured in 95% humidity at 20±2 C° in the laboratory for 24 hours and they were taken from the water bath and placed into sulfate ($MgSO_4$) solutions.

Table 1. *XRD (X-Ray Diffraction) Analysis of Zeolite*

	Cao		**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**
% (OYSA, 2006)	4.45	65.61	11.02	2.26	0.64	0.88	1.52	-
% ICP (ROTA, 2005)	3.4	71	11.8	1.7	1.4	-	2.4	0.4
% ICP (ENLI, 2007)	2.18	67.11	11.84	1.47	1.15	-	3.44	0.38

Table 2. *Material Mixture Design*

Mixture Nr	Mixture	Mixture and Amounts (Kg/m^3)						Flow (%)
		Quality	PC	ZEO	SK	SU	SA*	
1	0% Zeo (PC-Control)	Without SA	1400	-	-	560	0	110
2		With SA	1400	-	-	560	14	111
3	15% Zeo	Without SA	1190	210	-	560	0	111
4		With SA	1190	210	-	560	11.90	108
5	30% Zeo	Without SA	980	420	-	560	0	111
6		With SA	980	420	-	560	9.80	112

RESULTS AND DISCUSSION

Corrosive effects of sulfate solutions on cement paste increase with sulfate density and corrosion mechanism may also vary with density. It might take years to reveal the adverse effects of sulfate solutions on cement-based mortars and concretes. Therefore, experimental methods that provide quick results are needed to evaluate the sulfate resistance of cements and admixtures. Considering that cements/ concretes poured on sulfated surfaces or in water will be immediately placed under the effect of sulfates, paste samples produced here were placed in 7% $MgSO_4$ solutions at the 24^{th} hour. Figures 1 and 2 graphically present the compressive strengths of the samples kept in the solutions for 7 and 28 days. Mixing and compression of the paste samples were carried out in time-adjusted automatic machines.

S/B ratio plays a significant role in mixtures. A decrease in the amount of calcium hydroxide with mortar porosity and pozzolan admixture with an optimum S/B ratio and a decrease in the possible ettringite amount caused by a higher of aluminum binding by the resultant hydrates delay solution penetration time in mortars and concretes. Care was taken to achieve a flow value between 105% and 115% to control S/B ratio.

When using fine-grained mineral admixtures in concrete, a certain percentage of the cement weight is usually decreased and substituted by fine-grained mineral admixtures. Specific weight of pozzolanic materials is lower than that of cement paste. Thus, the total volume of binding materials used in concrete (i.e., “cement+pozzolan” volume) increases, which results in an increase in the volume of binding paste in concrete. This helps obtaining a more fluent concrete with a better workability.

Compression velocity and amount that can be achieved in a Portland cement paste in concrete depend on the speed and amount of the formation of calcium-silicate-hydrate (C-S-H) gels which result from the reaction of the main components with calcium silicate in the cement with water. The more rapid the formation of C-S-H gels, the higher the strength. Strength acquisition of fine-grained pozzolanic admixtures in cement paste is possible by the reaction of these materials with calcium hydroxide, which forms as a result of the hydration of the main components with calcium silicate in cement. The reaction of pozzolanic materials with calcium hydroxide and water leads to the formation of new C-S-H gels and increased strength.

In case of an external sulfate attack in hardened concrete, some portion of calcium hydroxide found in the structure of hardened cement paste is replaced by gypsum. Subsequently, ettringite is formed as a result of the reaction among gypsum, calcium monosulfo-aluminate-hydrate and water, leading to expansion of concrete. Since a lower amount of Portland cement is used in pozzolanic concrete production when compared to concrete without pozzolan, the rate of C_3A in concrete is lower as well. Therefore, sulfate-resistance is better in concretes with fine-grained pozzolans and less C_3A.

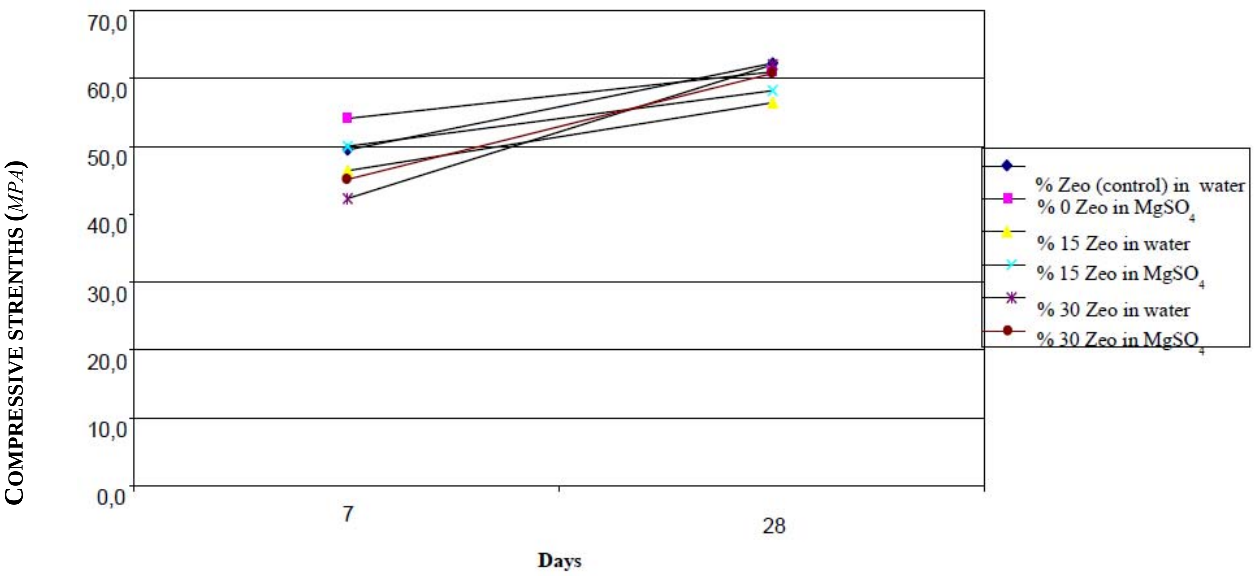

Figure 1. Compressive strengths of paste specimens without SP.

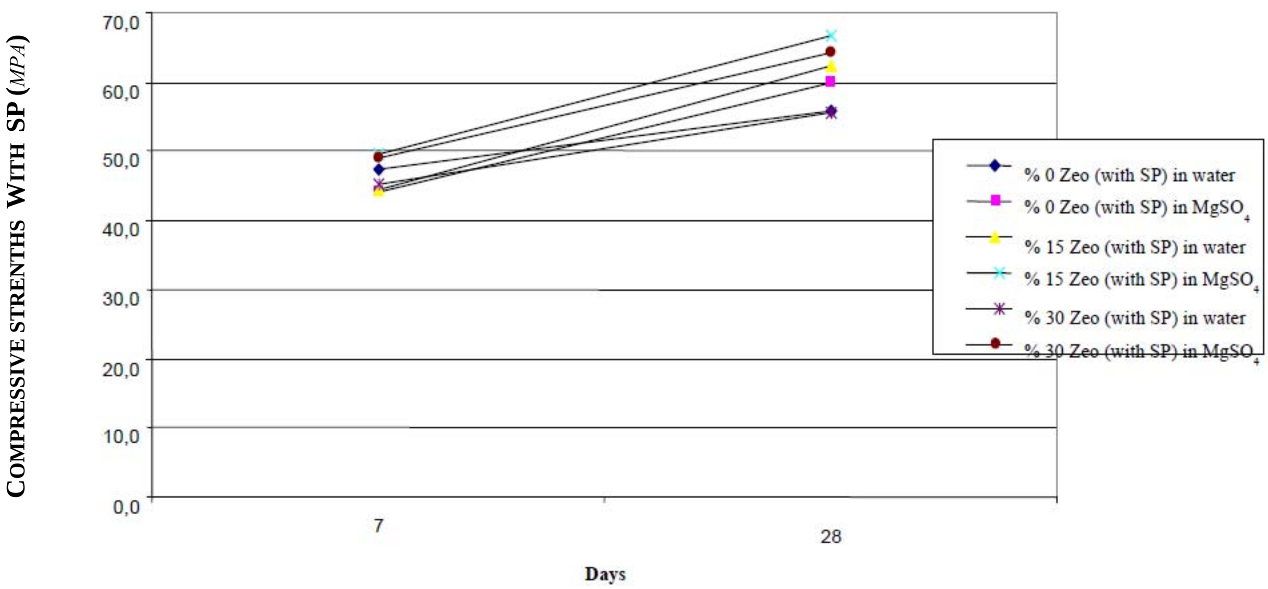

Figure 2. Compressive strengths of paste specimens with SP.

CONCLUSIONS AND SUGGESTIONS

The present study comparatively examined the chemical and physical (compressive strength) changes of specimens cured in water and MgSO4 solution on paste samples produced with PC42.5 R cement substituted with zeolite.

In the study, 15% zeolite admixture was taken as a basis in paste specimens produced with PC 42.5 R cement. Compressive strengths of superplasticizer-added samples were higher than those without superplasticizer admixture. Compressive strengths of 15%-zeolite-substituted control specimens with SP cured in $MgSO_4$ solution were slightly higher than the specimens cured in water. This demonstrates increased zeolite activity and resistance of zeolite-substituted cement specimen against $MgSO_4$ solution (Figures 1 and 2). This is in agreement with Mehta's statement that (MEHTA, 1981) "blended portland cements containing 10, 20 and 30% natural pozzolan produced similar or higher compressive strength than the reference portland".

The present findings along with Fen's

(FEN YILDIRIM, 2007) related XRD and SEM examinations confirm the suitability of 15% zeolite admixture in Portland cement. Increasing the admixture rate to 30 percent results in a decline in the amount of portlandite. However, the presence of (Q) quartz in cements with 30% zeolite admixture indicates that after zeolite binds the portlandite formed in the composition and is converted into calcium-silicate-hydrate (C-S-H), extra pozzolan remains in the environment. Chemical C-S-H formation with zeolite addition means that the harmful $Ca(OH)_2$ in composition is made useful (FEN YILDIRIM, 2007). As a result, it was concluded that the blended cements obtained acquired properties that prevent corrosion, decrease concrete permeability and enhance resistance against sulfated environments.

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