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Araştırma Makalesi / Research Article

EXAMINATIONS OF THE INTERNAL STRUCTURE OF ZEOLITE-BLENDED CEMENTS

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Abstract: *Pozzolans are mineral-based materials that are not cementitious on their own, but gain cementitious properties when they are combined with lime and cement and react with water. Studies are in rapid progress to enhance performance in concrete made with pozzolanic cements. In this experimental study, cement paste specimens of 40x40x160 mm were cured in water and then kept in $MgSO_4$ solution to examine their 7- and 28-day compressive strengths and XRD and SEM images. An examination of the chemical and physical changes in the specimens cured in water and MgSO4 solution revealed that the specimens blended with 15% zeolite and containing superplasticizers had a slightly higher compressive strength than the specimens cured in $MgSO_4$ solution. This points out to the high pozzolanic activity and to the fact that 15% admixture rate made zeolite-blended specimens resistant against $MgSO_4$ solution. Consequently, zeolite is converted into Calcium Silicate Hydrate (C-S-H) composites after binding the portlandite, $Ca(OH)_{2,}$ content in cement. Therefore, it could be argued that cements prevent corrosion, decrease the permeability of concrete, and improves its resistance against sulfate environments. The most characteristic aspect of the study is that the specimens were placed in $MgSO_4$ solution on the 1^{st} day.*
In this work, images which have different frame length are modeled by KLT (Karhunen Loeve Transform). PSNR is used as the performance criteria. It has been shown that, short frame length performs better than long frame length in image data compression.

Keywords: *Cement, Puzzolan, SEM, XRD, Zeolite*

INTRODUCTION

A pozzolan is described as "a silicious or aluminous material, which in itself possesses little or no cementation value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious properties" (ASTM C 125, 1994; ASTM C 618, 1994). TS 25 and ASTM C 618 standards report on the limit values for the physical and chemical properties that natural pozzolans should possess to be used in concrete production as a suitable admixture (ASTM C 618, 1994; TS 25, 2008).

Designated as "boiling stones" by Cronstedt in 1756 since they form bubbles to give out their water content when heated, zeolites are defined as hydrated alumino-silicates of the alkali and alkaline earth metals with crystalline structure (DPT, 1996).

Zeolites have been used in various industrial areas for over forty years. They are usually employed as light building stones and light aggregates in construction sector, as an additive in paper industry, and as a soil regulator and fertilizer additive in agricultural sector (Yucel, 1990). A report by TUBITAK – NAM states that Turkey has a natural zeolite reserve of about 50 billion tons (Kocakusak, 2001).

The experiments carried out on a natural zeolite specimen commercially available in China and composed of clinoptilolite mineral demonstrated that the tested material was a pozzolanic material, with a reactivity between that of silica fume and fly ash (Poone, Lam, Kou, Lin, 1999).

Mehta reported that blended Portland cements containing 10%, 20% and 30% natural pozzolan produced similar or higher compressive strength than the reference Portland cement and were much more resistant against alkali-silica reaction and sulfate effect (Mehta, 1981).

Studies on concretes containing natural zeolite have also demonstrated that zeolite improves concrete properties and can be used in the production of high-performance concrete. In high-strength and flowing concretes with zeolitic mineral admixture, adding 10% zeolite instead of cement and around 31–35% superplasticizers into the mixture produces a concrete strength of 80 MP and a slump value of 18 cm. This increases the compressive strength of normal Portland cements by about 10% to 15%. Moreover, no bleeding or segregation occurs in concrete (Feng, Li, Zang, 1990). It has also been demonstrated that natural zeolite admixture enhances the compressive strength of concrete and prevents unfavorable expansions due to alkali-aggregate reaction (Feng, Jia, Chen, 1998).

Natural zeolites are used in Portland cement and in concrete as light aggregates, in wastewater treatment, in separating oxygen and nitrogen in air, in fixing petrol catalysts, and in cleaning and drying gases as absorbents (Mumpton, 1976).

In a study on zeolite formation, Hay established that zeolites are often non-metamorphosed rocks and are found in three fourths or more of sea bottom and in modern ocean basins as sediments. Zeolites are usually sedimentary rocks by their natural formation and the group of analcime, chabazite, clinoptilolite, crionite, heulandite, laumontite, mordenite, phillipsite, and natrolite are minerals (Hay, 1976).

Smolka and Schunger (1976) underline the fact that modern tuffs, a type of zeolite, are used in the production of light bricks and lining of high chimneys and natural clinoptilolite is also considerably used in ammonium removal from urban sewage (Smolka, Schwuger, 1976).

Albayrak et al. examined the influence of zeolite on autoclave aerated concretes. In such concretes in which quartzite is used instead of zeolite, a marked increase was observed in the thermal conductivity of autoclave products, while their compressive strength improved by 1.22–3.34 N/mm^2 (Albayrak, 2006).

The most important field of application for zeolite as pozzolan is its use as hydraulic cement in environments with continuous exposure to ground water corrosion. The most striking example of use of zeolite material is the construction of a water canal of 386 km in length in the US in 1912. The use of zeolite-blended cement for about 25% of the amount of Portland cement required for construction resulted in a profit of around $ 1.000.000 (Kibaroğlu, 2007).

MATERIAL and METHOD

The following materials and equipment were used in the study:

Cement: PC 42.5 R (CEM I 42.5 R) cement obtained from Mersin CIMSA cement factory was used in the study. Table 1 presents the chemical and physical analyses of the cement.

Zeolite: In the fineness experiments on zeolite obtained from Izmir ENLI Mining Corporation performed in the laboratories of OYSA Cement Factory, Blaine fineness was found to be 6000 cm^2/g. Other physical and chemical properties of zeolite are presented in Table 2.

Standard Sand: The standard sand of Pinarhisar Cement Factory, which contains 90% SiO_2 and conforms to TS EN 196-1, was used in all mortar mixtures in the study (TS EN 196-1, 2002).

Superplasticizer Concrete Admixture (SP): The chemical composition of the superplasticizer obtained from Sika Construction Chemicals Inc. is Sikament-FF-N naphthalene formaldehyde sulphonate. The amount used was 0.9% of cement weight. Depending on the desired performance, it is used in concretes within the range of 0.8–3.0% of binder amount (800–3.000 g for 100 kg binder). It is liquid with a PH value of 9 and a specific weight of 1.22 kg/l.

Table 1. Chemical and physical analysis of the cement

Specimen	PÇ 42.5	Standard:			
	Typical Analysis	(TS EN 197-1) CEM 42.5/R			
Report Date	03.11.2004				
CHEMICAL PROPERTIES		Results	Test Method	Standard Values in TS EN 197-1 CEM 42.5/R	
				Minimum	Maximum
Ignition Loss	%	2.90	(TS EN 197-1)	-	5.00
Insoluble Matter	%	0.50		-	5.00
Sulfur Trioxide	%	3.60	XRD	-	4.00
Chloride	%	0.0060	(TS EN 196-1,2)	-	0.10
PHYSICAL PROPERTIES					
Starting setting time	Min.	150	(TS EN 196-1, 3)	60	-
Volume expansion	Mm	0.5		-	10.0
2-day Compressive Strength	N/mm	26.0		20.0	-
28-day Compressive Strength	N/mm	47.0		42.5	62.5

Table 2. XRD (X- Ray Diffraction) analysis of zeolite

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O
* %	3.4	67.9	11.5	1.8	1.2	0.9	2.4	0.4

* Given values represent the mean of ICP and laboratory tests.

Methods

The study was carried out in an experimental format. The experiments were based on TS 25 , TS EN 197-1 and ASTM C 109 (ASTM C 109, 1993) standards. Care was taken about material mixture design and laboratory conditions for the validity and reliability of the experiments.

MATERIAL MIXTURE DESIGN and SPECIMEN PREPARATION

Material Mixture Design

Specimens were prepared in 40x40x160mm casts with cements blended with 0%, 15%, and 30% zeolite by weight. The flow rate was determined to be between 105%-115% in all specimens. Three paste specimens were prepared for each paste specimen, some with and some without SP (Table 3).

Table 3. Material mixture design

Mixture Nr	Mixture	Mixtures and Amounts (kg/m^3)					Flow (%)
		Property	OC	ZEO	SU	SA	
1	0% Zeolite (PC-Control)	Without SP	1400	-	560	0	110
2		With SP	1400	-	560	14	111
3	15% Zeolite	Without SP	1190	210	560	0	111
4		With SP	1190	210	560	11.90	108
5	30% Zeolite	Without SP	980	420	560	0	111
6		With SP	980	420	560	9.80	112

Curing of Specimen

The admixture was premixed with total amount of water before application, and this solution was used for preparation of concrete mortars. Concrete mortar mixtures were prepared in accordance with ASTM C 109. The samples were cured in 95% humidity at 20+-2C in the laboratory for 24 hours, and they were taken out of the water bath and placed into sulphate ($MgSO_4$) solutions.

EXPERIMENTAL RESULTS AND DISCUSSION

The paste specimens with and without SP blended with 0%, 15%, 30% zeolite were subjected to 7- and 28-day compressive strength tests, the results of which are given in Figure 1.

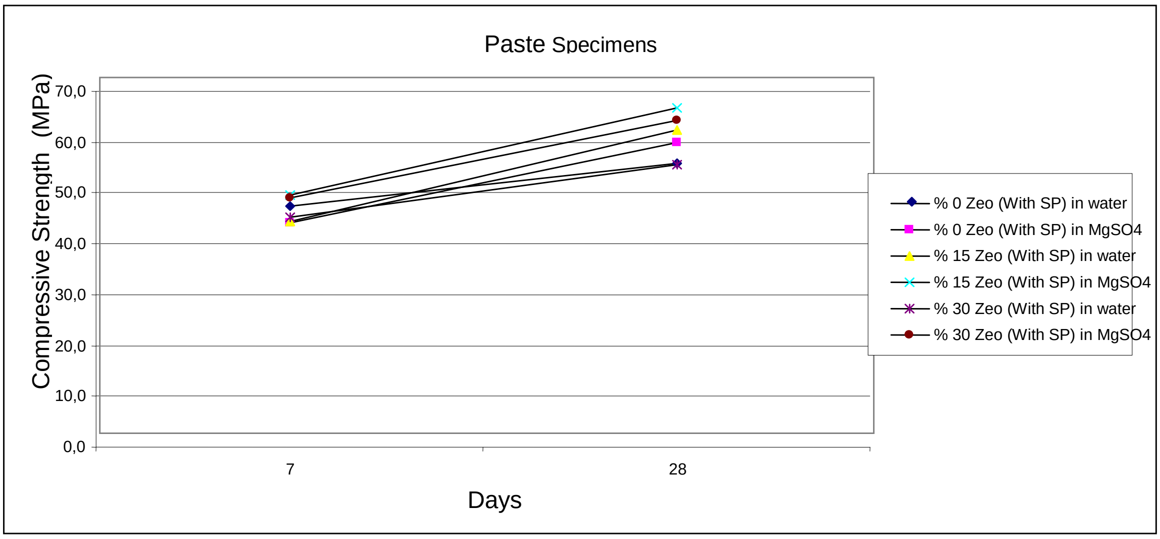

Figure 1. Compressive strength of paste specimens with SP

As seen in Figure 1, the 7-day compressive strength values of paste specimens with SP blended with 0%, 15%, 30% zeolite were higher than the reference 2-day compressive strength values in TS EN 197-1 cement standard (Lim. 20≤), while the compressive strength values of all 28-day zeolite-blended specimens with and without SP (Lim. 42.5≤) met the TS EN 197-1 standard. An examination of the cement paste specimens revealed that the 28-day compressive strength of paste specimen with SP blended with 15% zeolite was above the compressive strength value for the control specimen (62.3MPa). Therefore, studies on internal structure were based on the specimens with SP.

Microstructural properties of the cement paste specimens were examined on a scanning electron microscope (LEO 435VP) by the secondary electron image method. The results of the examination are shown in Figures 2-7. As a result, it was observed that (calcium silicate hydrate (C-S-H), calcium hydroxide (portlandite), and calcium sulfoaluminate (ettringite), chief hydration products of cement, were produced in the examined specimens. In particular, ettringite formation in the specimens kept in water containing $MgSO_4$ was more marked than in other specimens.

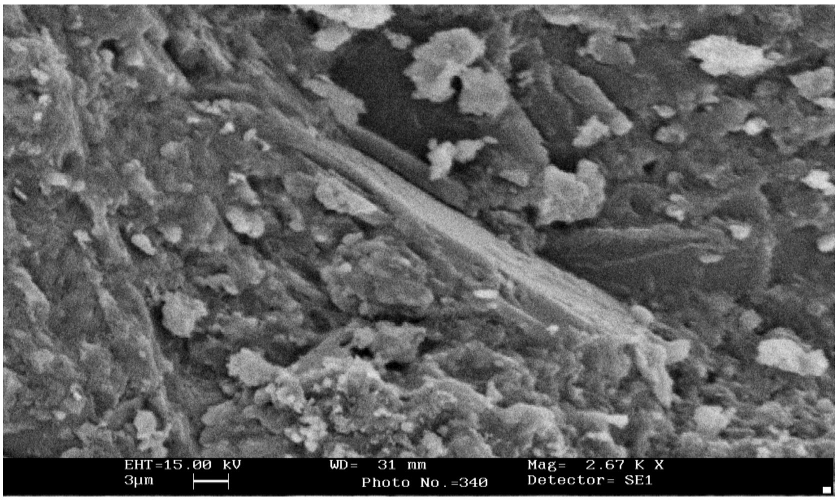

Figure 2. SEM image of the specimens with SP blended with 0% zeolite in aqueous medium

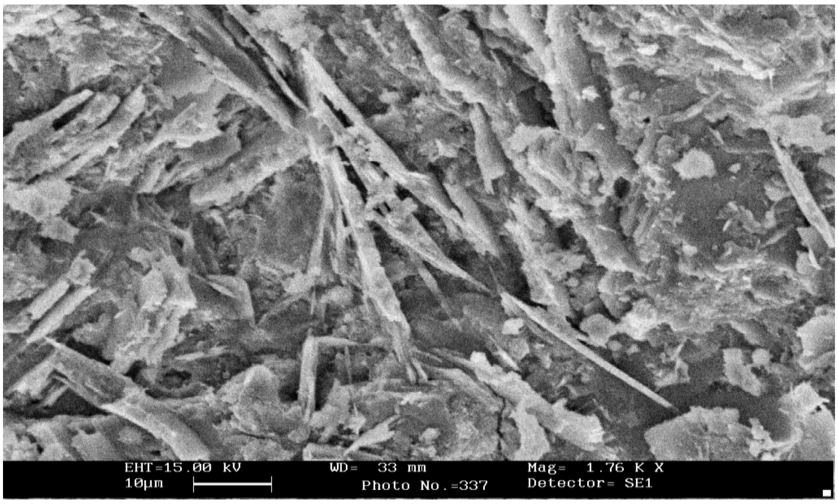

Figure 3. SEM image of the specimens with SP blended with 0% zeolite in $MgSO_4$ medium

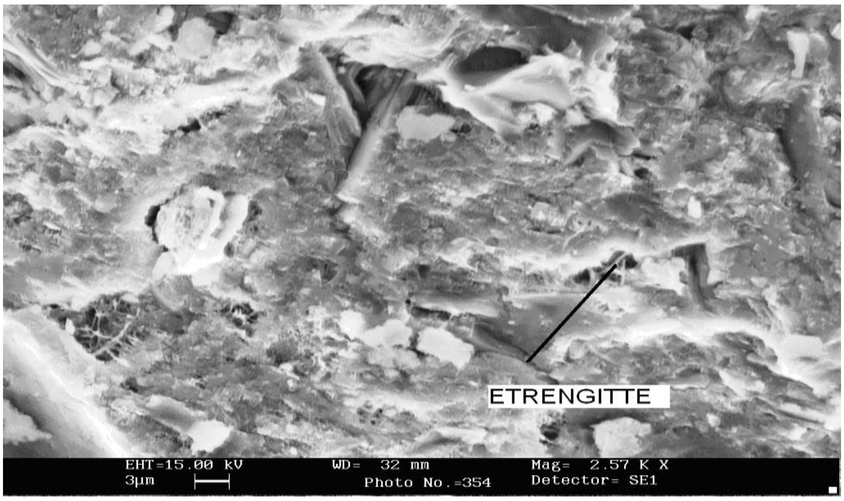

Figure 4. SEM image of the specimens with SP blended with 15% zeolite in aqueous medium

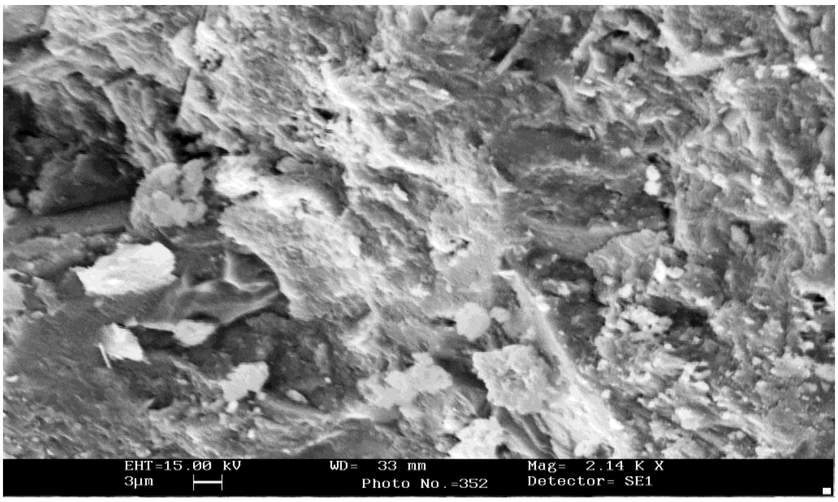

Figure 5. SEM image of the specimens with SP blended with 15% zeolite in $MgSO_4$ medium

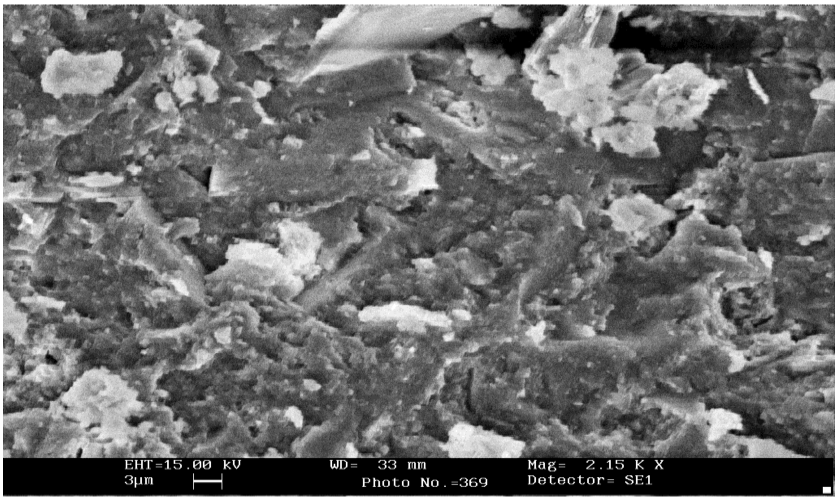

Figure 6. SEM image of the specimens with SP blended with 30% zeolite in aqueous medium

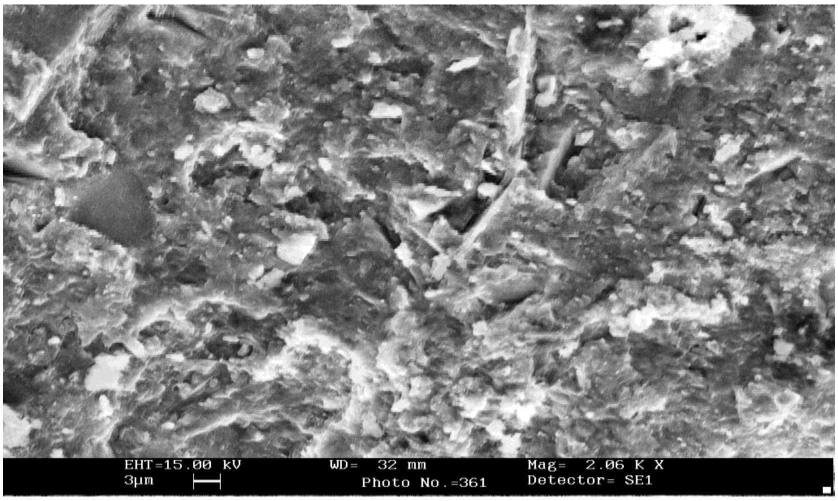

Figure 7. SEM image of the specimens with SP blended with 30% zeolite in $MgSO_4$ medium

The strength gained by the cement paste depends on the amount of C-S-H gels which occur as a result of the hydration of C_3S main components. Naturally, not all C-S-H gels occur at once. Production of C-S-H gels continues and the strength of cement paste increases throughout the hydration process (Erdoğan, 2007).

The mineralogical analysis results for the specimens with SP blended with 0%, 15%, 30% zeolite suggest that (Figure 8-13) portlandite and C-S-H gel in the specimens occur as a result of the hydration of cement phases, while quartz and feldspar minerals observed in some of the specimens were due to the raw materials used as admixtures in the cement (Report nr 0411)

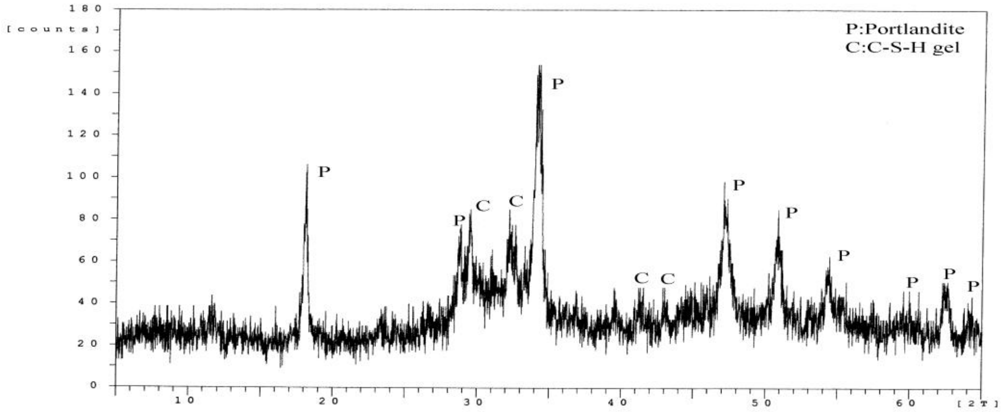

Figure 8. X-ray diffraction of the specimens with SP blended with 0% zeolite in aqueous medium

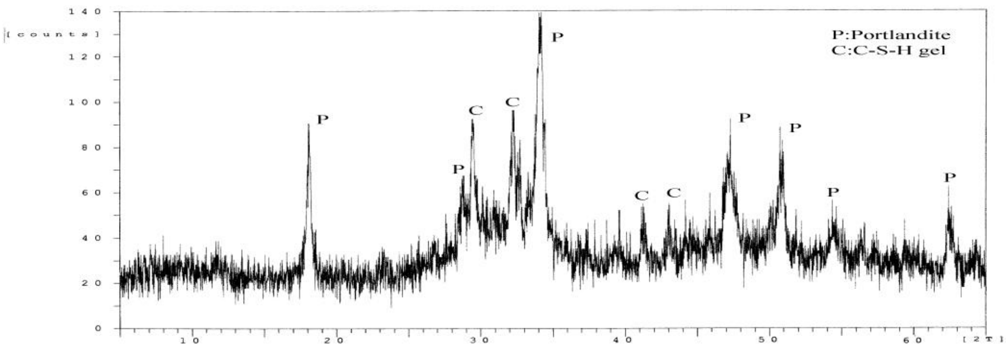

Figure 9. X-ray diffraction of the specimens with SP blended with 0% zeolite in $MgSO_4$ medium

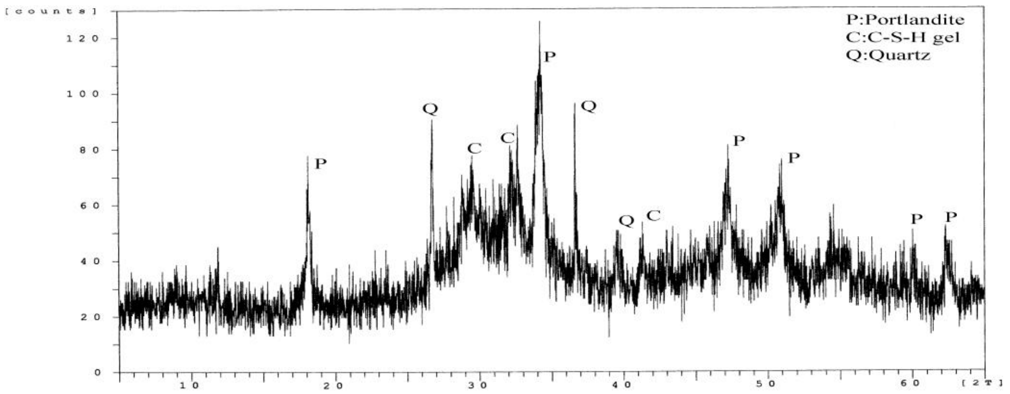

Figure 10. X-ray diffraction of the specimens with SP blended with 15% zeolite in aqueous medium

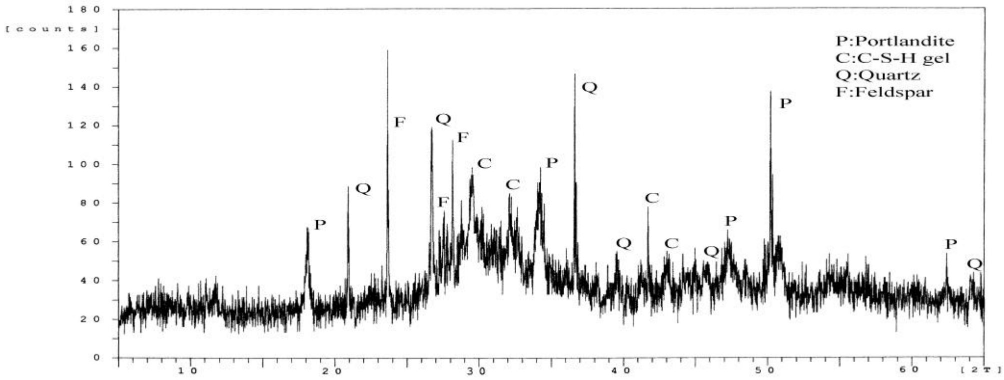

Figure 12. X-ray diffraction of the specimens with SP blended with 30% zeolite in aqueous medium

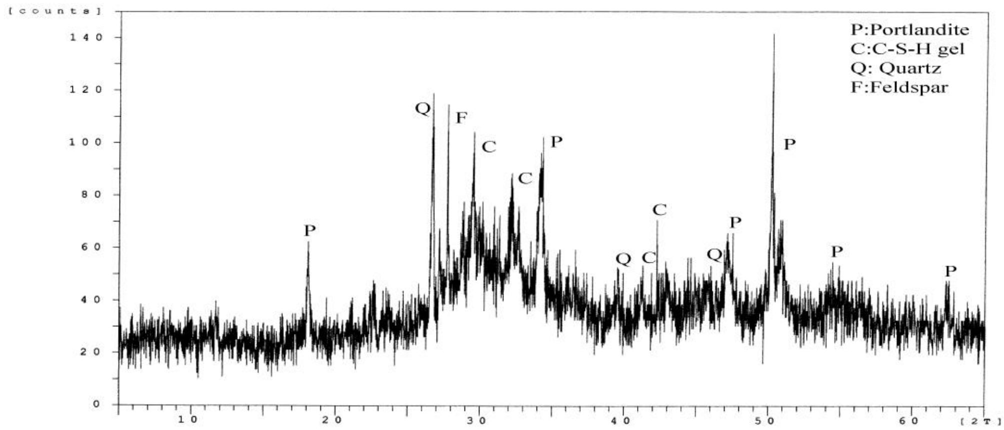

Figure 13. X-ray diffraction of the specimens with SP blended with 30% zeolite in $MgSO_4$ medium

CONCLUSIONS

When pozzolan is added into Portland cement, $Ca(OH)_2$ occurring as a result of cement hydration reacts with SiO_2 and Al_2O_3 and consequently, pozzolan acquires cementitious property. Free lime due to the hydration of Portland cement dissolves in water and has low strength, which is the greatest weakness of cement. Pozzolan added to cement binds free lime in cement, preventing its salvation and increasing its strength. This gradual but continuous binding process gives superiority to pozzolanic cement over Portland cement.

In this study, of the paste specimens produced by PC42.5 R blended with zeolite, those cured in water and MgSO4 solution were comparatively examined in terms of their chemical and physical (compressive strength) changes. An examination of consistency on the specimens showed that the amount of water was constant in paste specimens. In the specimens with and without SP blended with 15% and 30% zeolite, increasing amount of admixture increased the need for water. Care was taken to keep flow between 105%-110%. It is believed that the need for water increases with increasing amount of admixture, which might be influenced by the porous structure and high Blaine fineness of zeolite.

In the study, 15% zeolite admixture was taken as a basis for the paste specimens produced with PC 42.5 R cement. The compressive strength of the specimens with superplasticizer was found to be higher than that of the specimens without superplasticizer. The control specimens with SP, blended with 15% zeolite and cured in MgSO4 solution had slightly higher compressive strength when compared to the specimens cured in water. This indicates the high zeolite activity and (short-term) resistance of zeolite-blended cement specimen against $MgSO_4$ solution (Figure 1).

This finding is agreement with Mehta's (Mehta, 1981) argument that "Portland cements containing 10%, 20% and 30% natural pozzolan may produce similar or higher compressive strength than the reference Portland cement".

Considered along with Fen's (Fen, 2007) XRD and SEM examinations, the results of this study confirm the suitability of 15% zeolite admixture for Portland cement. The amount of portlandite in cement decreased when the admixture rate was increased to 30%. However, (Q) quartz was observed in the specimens blended with 30% zeolite, which points out to extra pozzolan material that remains after zeolite binds the portlandite occurring in the composition and converts into calcium silicate hydrate (C-S-H). Chemical C-S-H formation with zeolite admixture means that the harmful Ca(OH)2 in composition becomes useful (Fen, 2007). As a result, it is clear that the blended cements obtained will acquire properties that prevent corrosion, decrease concrete permeability, and enhance resistance against sulfated environments. As a conclusion, the use of 15% zeolite as admixture in PC 42.5/R cement and its production with SP will increase the cement's compressive strength.

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