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An Investigation on Production of Blended Cement with Natural Building Stone Waste Resistant to Sulphate Effects

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Abstract

In this study, the cements produced by the additive materials from Isparta city, Turkey and its region which gives puzzolanic activity are compared with normal Portland cement. In this comparison sulphate resistance and other cement properties are examined.

The natural additives which undergone various procedures are blended with clinker and gypsum under different proportions, which are main cement compounds. Prepared mortar specimens cured in the water for 28 days and then they were exposed to three different proportions of sodium sulphate solution for 125 days. Afterwards performances of cements are determined with compressive strength. Also the prepared specimens for during 3 months period and there are cured under moist atmosphere volume expansion are measured and continuously monitored.

The results show that, diatomite blended cement having more porous structure than andesite powder were more affected by sulphate attack. As in the normal standard tests, by adding 10 % of these materials gave similar strength values with 42.5 Portland cement, at later periods of time.

INTRODUCTION

Sulfate attack is one of the most important problems concerning the durability of concrete structures. Under the sulfate environment, cement paste undergoes deterioration resulting from expansion, spalling and softening [1, 2].

Sulfate attack occurs in concrete when concrete is in contact with a source of sulfate ions, which can be groundwater, soil, or rainwater. Sulfate attack usually manifests itself by cracking and spalling of concrete accompanied by expansion and/or loss of strength. The resistance of concrete to sulfate attack is determined by several factors, such as water/cement ratio, permeability, and cement characteristics, which include fineness and cement composition [3]. The sulfates found in groundwater are often a combination of calcium, sodium, and magnesium sulfate. Owing to the low solubility of calcium sulfate (~2 g/l at 20 °C), the highly soluble sulfates (Na2SO4, MgSO4, FeSO4) present in soil predominate in the groundwater solution[4].

It is generally recognized that addition of pozzolan reduces the calcium hydroxide in cement paste and improves the permeability of concrete. This helps to increase the resistance of concrete to the attack of sulfate and other harmful solutions. The increase in the service life of the structure made from the blended cement containing pozzolan would further reduce the amount of Portland cement use[5].

In the study conducted by Kilinçkale [6], pozzolan cements produced by adding pozzolans such as silica fume, rice husk ash, blast furnace slag, fly ash, trass in 20% replacement for Portland cement. On the 28th day of production, the produced specimens had been stored in water, in $MgSO_4 \cdot 7H_2O$ (5%) solution. Compressive strengths of the mortars stored in water for 28 days are silica fume, rice husk ash, and control, 43.3, 40.1, and 31.0 MPa, respectively. The highest loss of compressive strength is 20% and the highest gain of weight is 4.2%, occurring in blast furnace slag mortar in $MgSO_4$.

In a study blended cements containing corncob ash (CA) and ground granulated blast furnace slag (GGBFS) were investigated by Binici et al.[7]. Different amounts of additives (20 and 40%) were incorporated into these blends in equal amounts. Their sulfate resistance was determined by compressive strengths after 24 months under sulfate conditions. The micrographs showed that these additives provide more condense structures of cement hydration and excellent sulfate resistance. Thus, CA and GGBFS additives in cement production can contribute to the cement durability.

Binici and Aksoğan [8] reported the results of study on the sulfate resistance of blended cement combination of reference Portland cement with high volume ground granulated blast-furnace slag (GGBS) and natural pozzolan (NP). The exposure solutions were tap water containing 5% magnesium sulfate solution and 5% sodium sulfate solution. It was observed that the sulfate resistances of blended cements were significantly higher both against sodium sulfate and magnesium sulfate attacks than references cement. Final strength reductions for finer mixes attacked by magnesium sulfate were marginally lower than those attacked by sodium sulfate.

In the study was conducted by Al-Dulaijan [9], the maximum deterioration, due to sulfate attack, was noted in Type I cement followed by silica fume and Type V cements. The performance of Type V, Type I plus silica fume and Type I plus fly ash was not significantly different from each other. The enhanced sulfate resistance noted in the Type I cement blended with either silica fume or fly ash indicates the usefulness of these cements in both sulfate and sulfate plus chloride environments.

Agarwal and Gulati [10] investigated use of fly ash, slag, silica fume and marble dust as replacement of cement on the compressive strength and cost effectiveness of low w/c ratio super plasticized Portland cement mortars The blending of industrial wastes in mortars was also studied. In their experimental study, cement mortars (1:3 and 1:6) incorporating various proportions of industrial wastes were designed to have a flow of 110 ± 5%. The compressive strength of mortars with and without super plasticizer was determined at 1, 3, 7, 28 and 180 days and their cost effectiveness was analyzed.

Ergun [11] paper describes the procedures and results of a laboratory investigation of mechanical properties carried out on the concrete specimens containing diatomite and Waste marble powder (WMP) as partial replacement of cement in concrete. According to his experimental test results, the concrete specimens containing 10% diatomite, 5% WPM and 5% WPM +10% diatomite replacement by weight for cement had the best compressive and flexural strength and the replacement of cement with diatomite and WMP separately and together using a super plasticizing admixture could be utilized to improve the mechanical properties of the conventional concrete mixtures.

In this study, the cements produced by the additive materials (pumice, diatomite, fly ash, andesite dust) from Isparta-Turkey and its surroundings which give pozzolanic activity are compared with normal Portland cement. In this comparison sulfate resistance and other cement properties are examined. The natural additives which undergone various procedures are blended with clinker and gypsum under different proportions, which are main cement compounds.

EXPERIMENTAL RESULTS AND DISCUSSION

The Effects of Used Waste Materials on Standard Consistency Water Demand

Table 1 shows the quantities of water required to produce cements of a standard consistency when using waste materials as mineral additives. In addition, Figure 1 shows the relationship between the amount of additives and the amount of water required to produce a cement of standard consistency in the manufactured cements.

As shown in Table 1, more water was required to produce the standard consistency in the diatomite blended DC1, DC2 and DC3 cements, andesite blended AC1, AC2, AC3 cements that were directly proportionate to the amounts of additive used. According to the table, the most water was required by the diatomite-blended cements. This may be due to the porous microstructure and specific gravity of the diatomite. As the specific gravity of diatomite is lower than other materials, volume of the diatomite blended in the cements would be higher, thus increasing the amount of water required for standard consistency.

Table 1 The Composition of the Blended Cement and Water Demand of Cement Mortar

TYPES OF PUZZOLANS (%)	TYPES OF BLENDED CEMENTS						
	RC	DC1	DC2	DC3	AC1	AC2	AC3
Clinker	96	66	56	46	66	56	46
Gypsum	4	4	4	4	4	4	4
Diatomite	0	10	20	30	-	-	-
Pumice		10	10	10	10	10	10
Andesite	-	-	-	-	10	20	30
Fly Ash	-	10	10	10	10	10	10
Amount of water (gr)	235	272	285	337	261	275	286
Amount of water (%)	52	60	63	75	58	61	64

Another reason for the increase in the water requirement with increased amounts of andesite is the existence of more materials due to the rational increase of the substitute materials in terms of weight in total amount of bounding materials in the mix. Therefore, the existing porous structure of these materials is also involved in further amount of composition of cement. Thus, some of the water added for standard consistency is absorbed and stored within the pore structure of these materials.

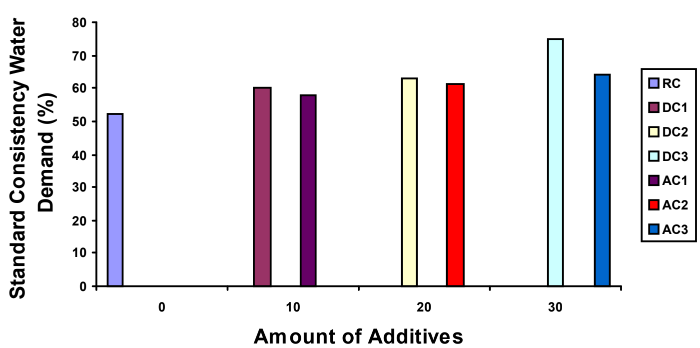

Figure 1 Relationship between the Amount of Additives and Standard Consistency Water Demand.

The Effects of Used Waste Materials on Setting Time

Table 2 shows initial and final setting periods for ten cement types made of diatomite, pumice, andesite, fly ash and clinker. It was seen that setting periods of all cements were in accordance with the ultimate values specified in TS EN 197-1 [12].Setting periods and the proportions of the materials used are shown in Figure 2.

Table 2 Setting time values and volume expansion values of cements

SETTING TIMES	TYPES OF BLENDED CEMENTS						
	RC	DC1	DC2	DC3	AC1	AC2	AC3
Initial setting times (hours : min.)	3:40	2:36	2:32	2:38	2:43	2:34	2:18
Final setting time (hours : min.)	4:05	3:01	3:12	3:03	3:23	3:12	2:54
Volume expansion values (mm)	1	1	0	0	0	0	0

Generally, in all blended cements, initial setting periods show a tendency to decrease with increased use of waste material additives. A similar situation is also valid for the completion of setting. The shortest initial setting period was recorded as 2 hours and 18 minutes in 30% andesite blended AC3 cements.

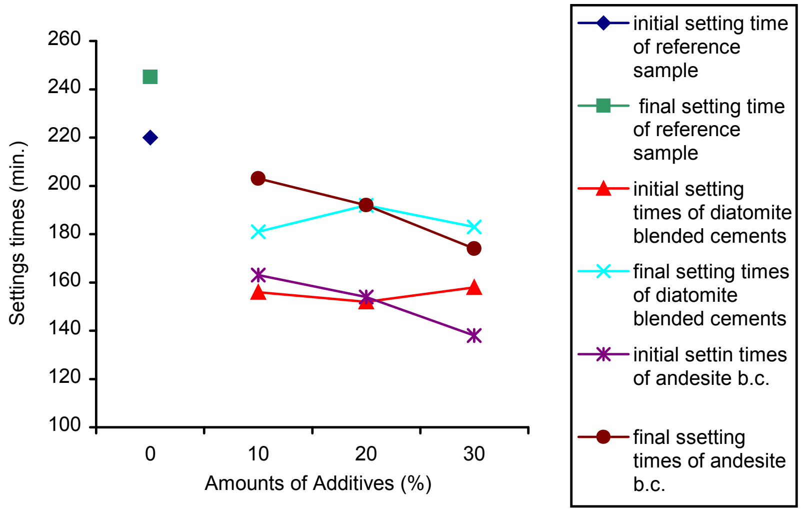

Figure 2 Relationship between setting periods and the proportions of the materials used

When diatomite, andesite are examined in terms of the setting periods, it is observed that andesite blended cements initiate and final setting later than diatomite cements. Another point of note is that additive ratio and setting period in diatomite blended cements increase directly proportionally to each other, while the exact opposite occurs in andesite blended cements. The relationship between the increase in the additive ratio and setting period in the diatomite blended cements may be explained by the transfer of normal consistency water from the pores and its diffusion into the cement paste [13].

The Effects of Used Waste Materials on Volume Expansion

Table 2 shows the setting periods together with the volume expansion test results for the cements made of diatomite, pumice, andesite, and fly ash. As shown, the obtained data was in accordance with the standards because the expansion volumes are below the ultimate value specified in TS EN 197-1. Therefore, the additives used could be said to make the desired contribution in terms of the volume expansion.

The Effects of Used Waste Materials on Specific Weight

Table 3 shows the specific gravities of the diatomite, pumice, andesite, and fly ash blended cements. Specific gravities of the cements show a decrease according to the rational increase in the diatomite, andesite amounts in the cements. Only the specific gravity of clinker and gypsum blended RC cement (96% clinker, 4% gypsum) is higher than that of the andesite, and diatomite blended cements. Another comparison is that the specific gravities of andesite blended cements show approximately similar values, while diatomite blended cements seem to have lower specific gravity than others, due to the low specific gravity of diatomite.

Table 3 Blaine values and specific weight of blended cements

PROPERTY	TYPES OF BLENDED CEMENTS						
	RC	DC1	DC2	DC3	AC1	AC2	AC3
SPECIFIC WEIGHT (g/cm^3)	2.86	2.44	2.26	2.10	2.64	2.60	2.44
AMOUNTS OF THE MATERIALS (gr)	105.74	90.21	83.55	77.64	97.50	96.12	90.21
BLAINE FINENESS (cm^2/gr)	2733	4677	5778	6686	3981	4398	4115

The Effects of Used Waste Materials on Chemical specifications of Cements

Table 4 shows the chemical compositions of diatomite, pumice, andesite, and fly ash blended cements. Numeric data for the chemical characteristics of the cements are in accordance with the ultimate values specified in the Table. In other words, all of the various types of blended cements conform to TS EN 197-1 in terms of the chemical constituents.

Table 4 Chemical analysis results of blended cements

CHEMICAL CONSTITUENTS (%)	TYPES OF BLENDED CEMENTS							TS EN 197-1
	RC	DC1	DC2	DC3	AC1	AC2	AC3	
SiO_2	19.20	30.99	37.42	42.40	27.16	28.19	30.61	
Al_2O_3	4.23	5.48	5.38	5.22	6.50	6.71	8.14	
Fe_2O_3	3.44	5.82	5.86	5.89	6.96	7.96	9.75	
CaO	58.57	51.81	49.97	48.36	52.03	51.20	48.51	
MgO	3.00	3.81	3.19	2.45	4.53	4.20	4.10	
SO_3	3.18	2.37	2.18	1.97	2.41	2.81	2.05	<4.0
S.CaO	0.89	0.50	0.44	0.34	0.56	0.44	0.43	
CI	-0.001	0.004	0.005	0.004	0.005	0.013	0.005	<0.10
$CaCO_3$	-0.32	2.49	1.52	0.61	4.43	9.48	5.39	
[1] PKCACKAL	1.21	19.45	18.00	15.60	34.32	36.47	58.35	
[2] T. ADDITIVE	0.88	21.94	19.52	16.21	38.76	45.95	63.74	

The Effects of Used Waste Materials on Water Requirements of Cement Mortar

Table 5 shows the water requirements of the diatomite, andesite, pumice and fly ash blended cements and the control cement mortars, determined form the pour test specified in ASTM C 109. The amount of water required to achieve stable consistency in the manufactured cements (110 ± 5% pouring should be ensured according to ASTM C 109) is similar to the amount for the standard consistency. Therefore, the factors affecting the water requirement for standard consistency also have an effect on these cement mortars.

Table 5 Water requirements of blended cements

TYPE OF PUZZOLAN	TYPE OF BLENDED CEMENTS						
(%)	RC	DC1	DC2	DC3	AC1	AC2	AC3
Clinker	96	66	56	46	66	56	46
Gypsum	4	4	4	4	4	4	4
Diatomite	0	10	20	30	--	--	
Pumice	--	10	10	10	10	10	10
Andesite	--	--	--	--	10	20	30
Fly Ash	--	10	10	10	10	10	10
Water Requirement	24.86	32.86	38.29	43.71	29.43	31.43	32

As shown in the relationship between additive ratio and mortar water in Figure 3, mortar water shows an increase parallel with the increase in the additive ratio of the materials blended in the cements. There are two reasons for this; the first is that clinker has a lower specific gravity than other materials, and the second is that the waste materials used have a more porous structure than the clinker particles.

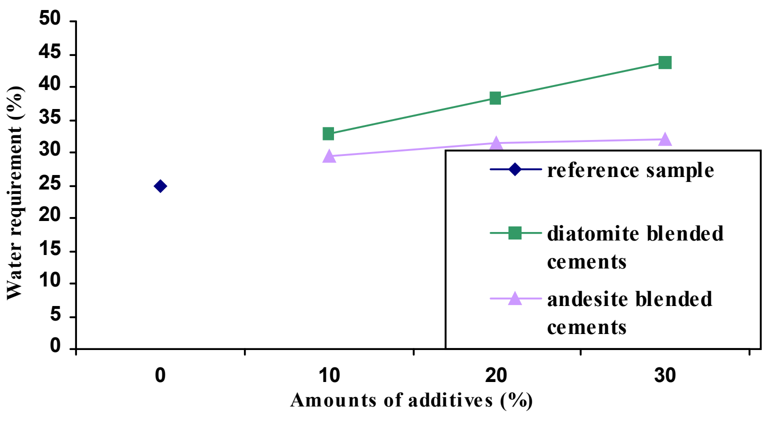

Figure 3 Relationship between additive ratio and water requirement of blended cement mortars

The effect of the specific surface area of the cement on the required water is similar to its effect on the quantity of water for standard consistency. This is clearly demonstrated in the relationship between cement fineness and standard consistency water, shown in Figure 4.

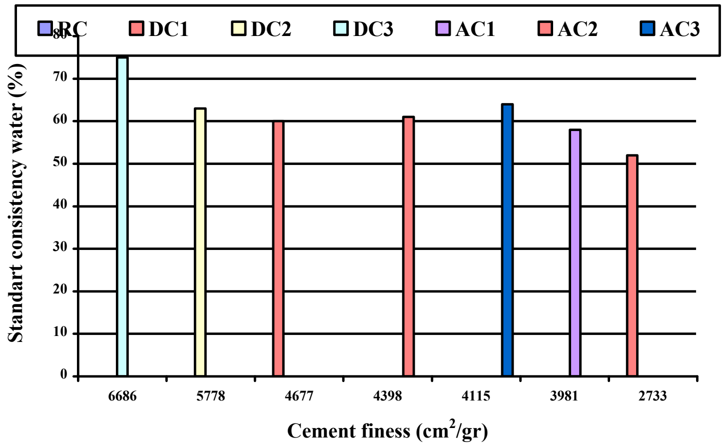

Figure 4 Relationships between cement fineness and standard consistency water

Diatomite mortars required more water than the andesite mortars, which had similar water requirements. This could be explained by the lower specific gravity of diatomites compared to the andesite. As the blending process is based on weight, more diatomites will be used for the same additive ratio and this means more mortar water will be needed. In addition, the water-increasing effect of the porous structure of diatomite should also be considered.

The Effects of Used Waste Materials on Compressive Strength

Samples were cured for 7, 28 or 56 days, either in water or Na_2SO_4 solution, and were then subjected to compressive strength tests in accordance with TS EN 196-1. Tables 6 and 7 show the compressive strength data of the samples kept in water and Na_2SO_4 solution, respectively.

Table 6 Compressive strength data of the samples were cured for 7, 28 or 56 days

Sample Ages (days)	Compressive Strength (N/mm^2) Data of the Samples Keep in Water						
	RC	DC1	DC2	DC3	AC1	AC2	AC3
7	28.5	27.1	26.05	17.41	20	16	11.7
28	47.4	41.4	41	31.55	32.2	26.2	19.2
56	49.7	43.7	43.85	34.25	34.9	28.7	22

- The relationships between compressive strength and sample ages and additive ratios are presented separately for each material in Figures 5 to 7.

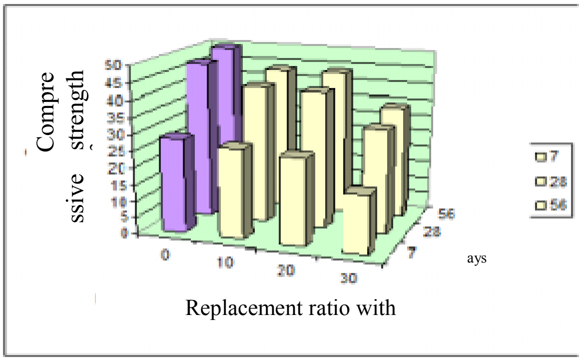

Figure 5 The relationship between compressive strength and sample ages and additive ratios of diatomite blended cements

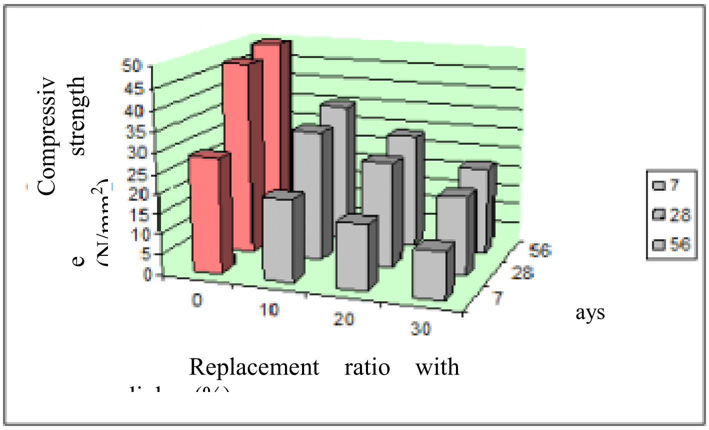

Figure 6 The relationship between compressive strength and sample ages and additive ratios of andesite blended cements

The compressive strength results for the samples showed:

- No high compressive strength value was obtained from the reference samples (RC) on days 7, 28 or 56.
- The highest compressive strength was obtained from the diatomite-blended group on days 7, 28 and 56 (respectively 27.1 N/mm2 for 10% diatomite, 26.05 N/mm^2 for 20% diatomite, and 17.41 N/mm^2 for 30% diatomite on day 7; and 41.4, 41, 31.55 N/mm2 on day 28).
- The highest strength was obtained from the 10% diatomite blended DC1 sample on days 7, 28 and 56; and from the 20% diatomite blended DC2 sample on day 56.
- The lowest compressive strength was obtained from the 30% andesite blended AC3 sample on days 7, 28 and 56.
- As in the previous flexural tensile strength tests, compressive strength was found to decrease with increased additive ratios. Such a decrease could be explained by the internal structures of the materials becoming more porous with increasing use of additives.

The Effect of Sulfate on Compressive Strength

- As expected, in the compressive strength tests to determine the effect of sulfate, the compressive strength values of the samples stored in Na_2SO_4 solution for 90 days were low compared to the strength values obtained from 28-day and 56-day replicate samples cured in water. According to the compressive strength values of cement mortar bars kept in sodium sulfate for 90 days, it was seen that: Reference samples (RC) showed the best performance in all solutions.
- Among the samples kept in the less effective solution (1500 mg/l), the highest strength against sulfate was 36.72 N/mm2, recorded in the 10% diatomite blended DC1 sample.
- Among the samples kept in the medium-level effective solution (9000 mg/l), the highest strength against sulfate was again obtained from 10% diatomite blended DC1 sample (34.4 N/mm^2), followed by 10% andesite dust blended samples.
- Among the samples kept in the highly effective solution (13500 mg/l), the highest strength against sulfate was obtained, respectively, by 10% andesite (AC1) and diatomite dust blended (DC1) samples.

According to the test results, such a loss of strength in the samples stored in sulfate could be explained by ettringite formation. Although ettringite formation may be the main reason for the strength loss in the hardened cement mortar, gypsum could also cause reductions in hardness and strength. Gypsum was indicated not affecting the strength as much as ettringite [9]. Besides, disruption in the hardened cement mortars, beginning with gypsum formation, resulted in hardness and strength loss, which became worse with expansion [14].

Table 7 Compressive strength values of cement mortar bars kept in sodium sulfate

Solution Levels	Compressive Strength (N/mm^2) Data of the Samples Keep in Na_2SO_4						
	RC	DC1	DC2	DC3	AC1	AC2	AC3
1500 mg/l	44.7	36.72	32.49	12.63	34.15	17.69	17.12
9000 mg/l	40.5	34.4	21.85	18.53	27.42	26.59	15.2
13500 mg/l	37.05	25.59	21.52	11.13	27.17	22.18	21.93

The Effects of Used Waste Materials on Shrinkage Tests

Samples to be subjected to shrinkage tests were chosen from samples cured in water and which showed relatively good performance in the compressive strength tests. PÇ 42.5, 10, 20 and 30%; diatomite blended (DC1, DC2 and DC3) samples; 10% andesite blended AC1 sample mortar bars were cured in drying rooms with 23±1 *°C* temperature and 50±5*%* relative humidity 13 weeks (125 days)in such a way that all samples would be subjected to the same air circulation. Figures 8 show the relationship between shrinkage and age of the mortar bar samples.

As shown in Figures 8, shrinkage values followed a fluctuating tendency. The results show that shrinkage values decreased with increased additive ratios in the diatomite group. After 125 days, the lowest shrinkage value (-0.079%) was found in the 30% diatomite blended DC3 sample. The highest shrinkage value (0.1371%) was found in the 10% andesite blended AC1 sample. Therefore, the 30% DC3 sample, which has the highest diatomite content, showed lower shrinkage value compared to, respectively, and the 10% andesite blended AC1 and the replicate sample RC, which all contained the lowest additive ratios. In conclusion, the use of increased diatomite content could be said to decrease the shrinkage of the cement. The fluctuating course of shrinkage observed in the samples is estimated to be derived from the curing facilities. As the amount of water used in the tests was determined by the "water requirement of the cement" test, the pores within the cement materials were completely waterlogged. In the advancing ages, it will be appropriate to control the environmental factors in a standardized way and to monitor the shrinkage during the consumption of water through evaporation and hydration. More detailed studies are required to accomplish this.

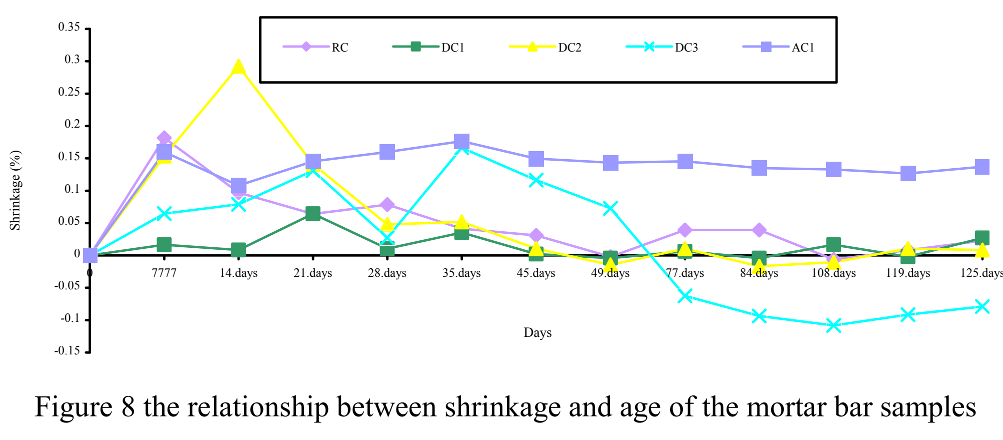

Figure 8 the relationship between shrinkage and age of the mortar bar samples

CONCLUSIONS

Within the scope of this study, blended cements were manufactured using fly ash, pumice and diatomite dusts obtained from the chimneys of thermal plants; andesite dusts obtained during the production of andesite paving stones. PC 42.5 and the reference cement RC were compared and the results are as follows:

Substitution of certain amounts of the cement with andesite dusts, diatomite increases the amount of water required to achieve a standard consistency in proportion to the amounts of these materials used. The observed increase is a linear function of the additive ratios.

In addition, the water required for standard consistency of the diatomite blended cements was slightly higher than that of the andesite cement, and the water requirements of the andesite blended cements for standard consistency were similar.

The use of diatomite, and andesite dust was found to reduce the initiation and completion of setting according to the amount used in the cement mix.

Test results met the condition that standard volume expansion should be less than 10mm. An increase in the diatomite or andesite dust ratios did not have a negative effect on the volume expansion.

The chemical compositions of the manufactured cements were in accordance with the proportions specified in TS EN 197-1.

Increased use of diatomite, and andesite directly increased the water requirements of mortars. The increase was slightly greater in the diatomite-blended cements, while the water requirements of the andesite blended cements were similar to the diatomite-blended cements.

Increased amounts of diatomite, and andesite in the cements reduced the compressive strength of the samples. In the advancing ages, considerable increases were observed in the compressive strength values due to the pozzolanic features of the materials. The 10% and 20% diatomite blended cements showed similar compressive strength characteristics to the RC reference cement.

However, during the 28-day compressive strength tests, only the 10% and 20% diatomite blended cements met the specification of pozzolanic cement type 32.5 (CEM IV B) according to standard TS EN 197–1. A similar inverse relationship between additive ratio and compressive strength was also observed in the sulfate solutions, but increasing the amount of Na_2SO_4 reduced the compressive strength of the samples. Samples with lower additive ratios (cements blended with10% additive) gave better results in these tests. In conclusion, compressive strength was lower in all additive groups compared to the samples cured in water.

Shrinkage tests were carried out with PÇ 42.5 (RC); 10%, 20% and 30% diatomite - blended DC1, DC2 and DC3 samples; and 10% andesite (AC1) samples. Test results showed that the addition of diatomite dust reduces the shrinkage of the cement according to the increase in the additive ratio.

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