Effect of Blended Cements Produced with Natural Zeolite and Volcanic Tuffs on Sulfate Resistance of Concrete

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Abstarct: In this study, influence of blended cements produced with different types of pozzolans on sulfate resistance of concrete was investigated. For this reason, Manisa Enli Mining crushing waste natural zeolite (clinoptilolite) and two different types of volcanic tuff supplied from Eskişehir and Nevşehir region were used in blended cement production According to mechanical performance of these blended cements, sulfate resistance experiments were carried out in accordance with ASTM C 1012 code. The mechanical properties of the blended cements were determined on 40x40x160 mm mortar specimens. The 25x25x285 mm mortar bar specimens were produced in order to determine the length changes of the specimens under sulfate attack. Mortar bar specimens were cured in 10% Na_2SO_4 solution for 6 months. The length changes and mechanical properties of the mortar specimens with different types of blended cements showed that, zeolite and volcanic tuffs reduces the ettringite formation when compared with ordinary CEM I 42.5 reference specimens.

Introduction

Concrete is one of the most widely used construction material, owing to its good durability to cost ratio. However, when subjected to severe environments its durability can significantly decline due to corrosion of embedded reinforcement and/or degradation of the concrete (Roy et al., 2001). The most important parameter on concrete performance is the properties of cement used in concrete production. It is possible to achieve environmental and economical benefits with utilization of pozzolanic mineral additives in cement production. The durability problems in concrete and reinforced concrete structures exposing to aggressive environment effects, lead to the damages in structures before the expected service life. One of the significant concerns in the design of durable concrete is sulfate resistance.

Deterioration of concrete by sulfate attack is commonly observed in structures exposed to soils or groundwater containing a high concentration of sulfate ions (Irassar et al., 2000). Sodium sulfate reacts with calcium hydroxide to form calcium sulfate (gypsum). This reaction proceeds to a greater or lesser extent, depending on the conditions (Neville, 2004). Ettringite formation is considered to be the cause of most of the expansion and disruption of concrete structures involved in the sulphate attack (ACI, 1994). The penetration of sulfate ions into the concrete, the calcium monosulfoaluminate crystals in the paste may convert into gypsum or ettringite; this results in a change to a larger molar volume. These volumetric changes cause expansion and internal stresses, which ultimately weaken and destroy the paste bonds, deteriorating the concrete (Tikalsky et al., 2002, Topçu, 2006).

To mitigate this attack, concrete codes recommend a concrete mixture with low water/cement ratio and containing a sulfate resistant Portland cement. The lowered availability of C_3A can reduce the damage caused by sulfate attack due to a direct reduction in the quantity of ettringite that can form. Also, ettringite formation in chloride-rich environments is not associated with expansion and cracking (Santahanam et al., 2006). In addition to the C_3A content, C_3S/C_2S ratio of cement is also found to be an effective parameter in the sulfate resistance (Cao et al.,1997, Ramyar & İnan, 2007). Cements containing higher C_3S content, upon hydration produce significantly higher quantity of calcium hydroxide which may directly react with sulfate ions of high concentration (>8000 ppm) to cause gypsum corrosion (Rasheeduzzafer et al., 1990). Gypsum corrosion reduces the cohesion stiffness and strength of the hydrated cement paste.

Under the new specification, various materials can be used freely, but the material design methods of various cementitious materials must be established to satisfy the performance requirements of concrete (Sakai et al., 2005). Pozzolanic materials have been widely used as substitutes for Portland cement in many applications because of their advantageous properties which include cost decrease, reduction in heat evaluation, decreased permeability, alkali aggregate-expansion control, decreased chemical resistance, reduced concrete drying shrinkage and the improvement in the properties of fresh concrete (Shi & Day, 2001). Amorphous silica present in the pozzolanic materials combines with lime and forms cementitious materials. These materials improve the durability of concrete and the rate of gain in strength and can also reduce the rate of liberation of heat that is beneficial for mass concrete (Khandaker & Hossain, 2003). Nevertheless, the use of natural and artificial pozzolans as blend materials for cement has been constantly increasing in order to reduce energy consumption and CO_2 emission without causing any degradation to cement properties.

Zeolites are crystalline alumina silicates with uniform pores, channels and cavities. They posses special properties like ion exchange, molecular sieves, a large surface area and a catalytic activity which makes them a preferable material for tremendous industrial applications (Breck, 1971). About 40 natural zeolites have been identified during the past 200 years; the most commons are analcime, chabazite, clinoptilolite, mordenite and philipsite. Worldwide production of natural zeolite was estimated at about 3-4 M ton on the basis of recorded production and production estimates (Virta, 2001). Rather than the known application areas, higher quantities of research (de Gennaro et al., 2004, de Gennaro et al., 2005) concerning the using of natural zeolite, especially clinoptilolite in concrete applications as pozzolanic cement, light weight aggregates and dimension stone is being increased in recent years. Zeolitic tuffs and amorphous silicate tuffs are the main natural pozzolans in the cement industry. The pozzolanic activity of zeolites depends on their chemical and mineralogical composition. The pozzolanic properties of zeolites are due to their reactive SiO_2 and Al_2O_3, which react with the $Ca(OH)_2$ liberated during the hydration of cement and convert it into C–S–H gels and aluminates. As a result, the micro-structure of hardened cement concrete is improved and the concrete becomes more impervious (Gervais & Ouki, 2002). On the other hand, some waste materials such as fly ash (FA) and ground granulated blast furnace slag (BFS) can be used as supplementary cementing material, or artificial pozzolan, in concrete industry. The reactivity of FA and BFS is supposed to be particularly influenced by the glass content and its composition.

In this study, influence of blended cements produced with different types of pozzolans on sulfate resistance of concrete was investigated. For this reason, Manisa Enli Mining crushing waste natural zeolite (clinoptilolite) and two different types of volcanic tuff supplied from Eskişehir and Nevşehir region were used in blended cement production. The first group single composition cements are produced by grinding different pozzolans replacing clinker, provided from Çimsa Cement Factory, at the ratios of 10, 20, 30, 40 and 45% together with gypsum stone in a ball mill. The second group composite cements are produced with 20-30% replacement ratios in binary replacement compositions. According to mechanical performance of these blended cements, sulfate resistance experiments were carried out in accordance with ASTM C 1012 code (ASTM C 1012, 2002). The mechanical properties of the blended cements were determined on 40x40x160 mm mortar specimens. The 25x25x285 mm mortar bar specimens were produced in order to determine the length changes of the specimens under sulfate attack. Mortar bar specimens were cured in 10% Na_2SO_4 solution for 6 months. The length changes and mechanical properties of the mortar specimens with different types of blended cements were determined and analyzed in order to obtain a durable cement composition against sulfate attack.

Experimental Study

The raw materials of blended cement compositions were supplied from different sources. Cement clinker, gypsum limestone and Eskişehir trass were supplied from Çimsa Eskişehir cement factory. Natural zeolite in clinoptilolite form was provided from Manisa Gördes region and Nevşehir Tuff was supplied from Nevşehir-İnli region. Chemical analyses of the materials were made by means of X-ray spectrophotometer (XRF) and the test results are given in Table 1. In this study, 24 different types of blended cement mixes with zeolite (Z), Eskişehir tuff (ET) and Nevşehir tuff (NT), replacement of 10, 20, 30, 40 and 45% by weight, 5% limestone for particle size arrangement and 3% gypsum were produced by intergrinding these materials in ball mill. These are defined as first group. According to compressive strength results of first group cements, the optimum replacement ratio of additives was found as 20 and 30% of clinker. Then the second group mixes were designed by means of 20 and 30% replacement ratio as binary composition. These blended cements were compared with reference to CEM I 42.5 ordinary Portland cement in experimental studies.

Chemical Composition	Clinker, %	Clinoptilolite, %	Eskişehir Tuff, %	Nevşehir Tuff, %
SiO_2	20.98	62.78	61.12	59.37
Al_2O_3	5.55	10.66	12.32	14.46
Fe_2O_3	3.85	4.20	6.51	6.99
CaO	65.85	2.37	4.28	5.82
MgO	1.12	1.10	5.88	4.99
K_2O	0.53	0.74	1.73	2.66
Na_2O	0.14	0.35	2.44	2.52
SO_3	0.97	-	0.1	-

Table 1: Chemical composition of the raw materials.

The prepared cement mortars with the produced cements were cast in 40x40x160 mm prismatic moulds according to TS EN 196-1. The mortar specimens were removed from the moulds after 1 day and were then cured in lime saturated water at 20±1°C until the age of considering strength test. At the end of the curing period (2, 7, 28 and 180 days), mortar specimens were subjected to compressive strength test (TS EN 196-1, 2002).

Mortar bars were prepared according to ASTM C 1012 in dimension with 25x25x285 mm and 40x40x160 mm in order to determine the effects of sulfate on different types of produced blended cements. After the initial curing period, specimens were demolded and cured in lime saturated water (23 ± 1.7 °C) until the mortar cube specimens gained a compressive strength of 20 MPa as described by ASTM C 1012 (Sahmaran et al., 2007). Upon reaching a compressive strength of 20 MPa, the performance of cements under sulfate-attack were determined weekly through expansion measurements of mortar bars with which are immersed in 10% Na_2SO_4 solution for one year. During this curing cycle, compressive strength and ultrasound pulse velocity tests were carried out to determine the mechanical and physical properties of different blended cement mortars.

Results and Discussion

Compressive Strength

The aim of this study is to determine the strength development and sulfate resistance of different pozzolan blended cements. The mechanical performance of produced blended cements was determined by compressive strength test. The considered test results are given in Table 2. The compressive strength test results showed different behaviors depending upon the replacement ratio of pozzolans and age of the mortar specimens. In the early stage of cement hydration, $Ca(OH)_2$ from the hydrating paste was incorporated into the pozzolan structure and led to the formation of hydration product type C-S-H and hydrated aluminate phases (Topçu et al., 2008). According to compressive strength results the early age strengths of blended cements were reduced with increasing amounts of replacement ratio. At the age of 28 days, the compressive strength values of zeolite blended cements were higher than reference CEM I 42.5 cement up to 40% replacement ratios. Moreover at 180 days, the compressive strength of BFS, FA and zeolite blended cements reached approximately 57 MPa depending on the pozzolanic reaction of the considered mineral additive. This result was higher than the reference ordinary Portland cement mortars (50 MPa). According to mechanical testing results, it may be stated that long term strength performances of natural zeolite (clinoptilolite) and Eskişehir tuff blended cements were better than reference CEM I 42.5 type cement. A comparison based on strength development indicates that the replacement of zeolite and volcanic tuff is the most effective method in blended cement production.

Sulfate Resistance

According to compressive strength test results, the optimum usage of mineral additive in blended cement mixtures was found as 30% replacement ratio. For this reason the sulfate resistance tests were carried on 30% blended cements. The volume expansion of mortar bars was measured with 0.001 mm sensitive comparator for 6 months in order with ASTM C 1012 code. According to ASTM C 1157 the expansion limits of hydraulic cements were 0.10% and 0.05% at 26 weeks as moderate sulfate resistant and high sulfate resistant, respectively (ASTM C 1157, 2000). Also 0.10% expansion limit was suggested for high sulfate resistant cements. Volume expansion of different cement mortars which immersed in 10% Na_2SO_4 solution for 26 weeks are given in Fig. 1.

Cement Code	Compressive Strength, MPa			
	2 Days	7 Days	28 Days	180 Days
CEM I 42.5	22.00	30.43	45.25	50.69
ZBC-10	12.31	22.56	46.90	57.15
ZBC-20	11.23	20.38	48.28	54.89
ZBC-30	10.97	18.56	45.37	53.06
ZBC-40	7.25	17.25	39.65	50.65
ZBC-45	6.95	15.03	38.13	48.38
ETC-10	11.60	28.80	44.65	51.06
ETC-20	9.68	26.81	42.31	50.93
ETC-30	10.31	24.18	40.47	48.78
ETC-40	8.80	20.52	36.46	44.38
ETC-45	6.00	16.50	35.34	43.25
NTC-10	11.93	21.25	42.96	47.65
NTC-20	11.18	16.87	42.71	45.13
NTC-30	8.12	15.6	36.59	43.74
NTC-40	5.67	14.00	32.28	40.68
NTC-45	4.32	12.5	28.81	39.23
ZBETC-20	11.51	21.78	36.25	43.67
ZBVTC-20	10.45	20.37	35.75	44.43
ETVTÇ-10	10.56	20.13	34.56	41.43
ETVTÇ-20	8.24	18.25	33.16	40.20
ETZKÇ-10	12.87	26.12	43.81	54.65
ETZKÇ-20	10.12	23.21	43.46	52.32
VTETÇ-20	9.07	18.09	32.52	41.6
VTZKÇ-10	12.56	23.50	42.96	53.72
VTZKÇ-20	11.43	22.90	40.00	45.75

Table 2: Compressive strength test results of produced blended cements.

As seen from Fig.1 reference mortar specimen produced with CEM I 42.5 reaches as 0.518% above the 0.10% expansion limit after 26 weeks sulfate exposure period. Also, mortar bar expansion of ETC-30 type cement produced with 30% Eskisehir tuff replacement ratio was determined as 0.109% a little bit higher than the reference line on Fig.1.

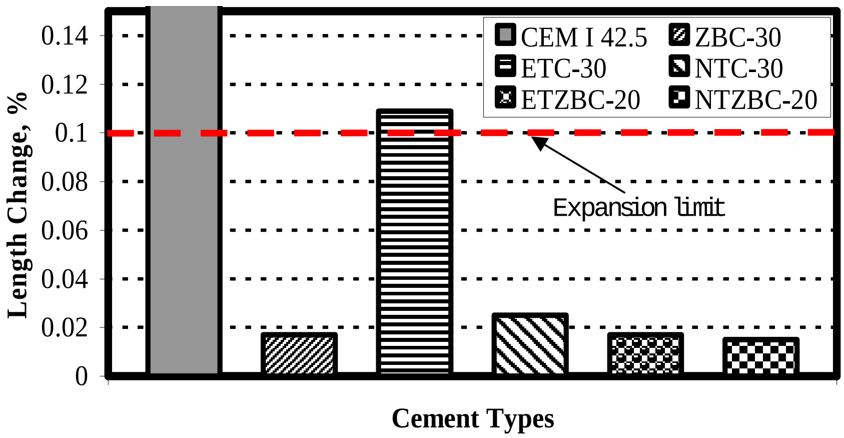

Figure 1: The length changes of mortar bar specimens.

On the other hand, blended cements produced with clinoptilolite and Nevşehir tuff were varied around 0.02%. These results are lower than reference CEM I 42.5 ordinary Portland cement. It can be concluded that performance of ZBC-30, NTC-30, ETZBC-20 and NTZCB-20 can be defined as high sulfate resistance cements. The physical deterioration of mortar specimens are given in Fig.2. At the end of 6 months curing regime ordinary Portland cement mortar lost its volume stability and stiffness. However, clinoptilolite and Nevsehir tuff blended cements did not change their shape.

Figure 2: Physical deterioration of mortar bars at 6 months sulfate exposure.

According to these results natural zeolite blended cements is more durable than ordinary Portland cement, under aggressive sulfate environments. It also seems that as the proportion of the replacement of clinker by pozzolanic material increased, the sulfate resistance of the mixture also increased. This conclusion, which is in accordance with other research results indicates that the decrease of C_3A content of the mixture in combination with the reduction of large pores caused by the pozzolanic reaction, are more critical than the total porosity alone (which increases as the w/c ratio also increases) when sulfate resistance is of primary interest (Sideris et al., 2006).

Mechanical behavior of different cement mortars during the sulfate test were investigated with compressive strength test results. As seen from Table 3 compressive strength of CEM I 42.5 cement was increased up to 59 MPa more rapidly than other cements at early ages. This increase should be attributed with the supplementary ettringite formation in the C-S-H structure of the composite. However, at the end of 8 weeks this trend changed and strength reduction occurred with the expansion of ettringite salt in the composite structure. The same behavior was seen on ETC-30 specimens. On the other hand ZBC-30 and NTZBC-10 cement mortars were increased their compressive strength 61.00 MPa and 64.32 MPa respectively, at the end of the experimental study. Compressive strength test results show a good agreement with volume expansion of cement mortars.

Curing Time, weeks	Compressive strength, MPa					
	CEM I 42.5	**ZBC-30**	**ETC-30**	**NTC-30**	**ETZBC-20**	**NTZBC-10**
1	20.43	21.03	20.40	21.50	20.50	20.74
2	34.13	28.30	26.44	29.35	27.84	32.65
3	40.23	34.30	35.86	36.57	37.50	40.14
4	48.54	44.54	42.93	43.56	41.25	47.05
8	59.28	52.31	47.29	45.91	51.82	58.17
13	55.06	54.19	50.95	47.58	52.13	61.95
15	54.30	58.45	52.87	48.01	53.05	63.23
20	52.55	60.14	51.37	49.26	55.50	64.11
26	38.32	61.00	50.55	49.27	59.05	64.32

Table 3: Compressive strength variation of blended cements under sulfate exposure for 26 weeks.

Ultrasonic methods are generally used for analyzing the porous structure, mechanical strength of concrete and to detect internal defects (voids, cracks, delaminations, etc.) (Lafhaj et al., 2006). Mortar specimens were subjected to UPV test to determine the crack formation of the composite material. As seen from Table 4, the UPV values of mortars were increased with the curing time. However, the ultrasound pulse velocity (UPV) value of CEM I 42.5 specimen was reduced after 8 weeks exposure time. This significant reduction showed that the increasing volume expansion of the composite structure was the cause of the initial crack formation. Higher C_3A content of ordinary Portland cement causes rapid ettringite formation in the composite structure compared with other types of cements. The same UPV reduction occurred for Eskisehir trass used ETC-30 blended cement specimen. On the other hand, ZBC-30, ETZBC-20 and NTZBC-20 blended cements were increased the UPV values purposefully with the pozzolanic reaction between mineral additives and $Ca(OH)_2$.

Curing Time, weeks	Ultrasound Pulse Velocity, km/sec.					
	CEM I 42.5	**ZBC-30**	**ETC-30**	**NTC-30**	**ETZBC-20**	**NTZBC-10**
1	3.554	3.433	3.421	3.496	3.473	3.562
2	4.074	3.751	3.612	3.720	3.671	4.000
3	4.244	4.055	4.123	4.138	3.878	4.265
4	4.374	4.288	4.156	4.213	4.033	2.310
8	4.594	4.134	4.166	4.301	4.155	4.419
13	4.327	4.144	4.266	4.347	4.177	4.481
15	4.247	4.165	4.371	4.350	4.180	4.520
20	4.201	4.232	4.312	4.432	4.188	4.597
26	3.770	4.255	4.213	4.432	4.210	4.637

Table 4: Ultrasound pulse velocity variation of blended cements under sulfate exposure for 26 weeks.

Conclusions

Improving the durability of concrete structure members is an important point to achieve a sustainable development in structure industry. Prolonging the service life of concrete in aggressive environments is possible with increasing the durability of these members. The sulfate resistance of concrete is related with the ettringite, gypsum and thaumasite formation in the composite. The main cause of ettringite is C_3A content of cement used in concrete. Ordinary sulfate resistance cements are low C_3A (less than 5%) cements. According to test results zeolite blended cements showed high sulfate resistance performance against reference Portland cement. Utilization of economic blended cements in sulfate environments has beneficial effects on concrete durability.

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