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Effect of Blended Cements with Natural Zeolite and Industrial By-Products on ASR of Concrete

Cenk Karakurt[1] and İlker Bekir Topçu[2]

[1]Bilecik University, Department of Civil Engineering, 11210, Bilecik, TURKEY. E-mail: <cenk.karakurt@bilecik.edu.tr> [2]Eskisehir Osmangazi University, Department of Civil Engineering, 26480, Eskisehir, TURKEY. E-mail: < ilkerbt@ogu.edu.tr>

ABSTRACT

In this study, influence of blended cements produced with different types of pozzolans on ASR was investigated. For this reason, Manisa Enli Mining crushing by-product natural zeolite (clinoptilolite), Kütahya Tunçbilek Thermal Power Plant fly ash and Ereğli Iron and Steel Factory blast furnace slag are used as industrial by-products in different types of blended cement production. According to mechanical performance of these blended cements, ASR experiments were carried out in accordance with ASTM C 1260 code. The 25x25x285 mm mortar bar specimens were produced with reactive glass and silica sand mixture aggregate. Mortar bar specimens were cured in 1N NaOH solution at 80˚C temperature. The length changes and microstructure investigations of the mortar specimens with different types of blended cements showed that, zeolite, fly ash and blast furnace slag reduces the ASR reaction 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 alkali-silica reaction [Chatterji 2005].

The use of certain aggregates in concrete may result in a chemical process in which particular constituents of the aggregates react with alkali hydroxides present in the concrete pore solution [Haha et.al. 2007]. Damage to concrete structures due to alkali–silica reaction and consequent expansion is being observed in more and more countries. Construction engineers and real state owners are demanding better methods of assessing the alkali–silica reactivity of aggregates before they are used in constructions. In most actual structures, it takes a considerable time, after their constructions, before any sign of distress becomes obvious [Chatterji 2005]. Alkali silica reaction (ASR) causes premature deterioration in concrete. Alkali hydroxides present in concrete pore solution react with amorphous or poorly crystalline silica phases in aggregates, forming a gel which imbibes water and expands [Maas et.al 2007]. The expansive pressure generated by the hydrated alkali silicate has been widely believed to induce the cracking and deterioration of concrete. However it is not necessarily correct. Concrete is a porous material and the hydrated alkali silicate is rheologically a fluid material, so that the hydrated alkali silicate slowly diffuses into the pores and preexisting cracks to loose its expansive pressure. The diffused alkali silicate was proposed to generate an expansive pressure by reacting with Ca^{2+} ions [Ichikawa 2009].

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 and 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 and 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 and Ouki, 2002]. On the other hand, some materials such as fly ash (FA) and ground granulated blast furnace slag (GBFS) can be used as supplementary cementing material, or artificial pozzolan, in concrete industry. The reactivity of FA and GBFS 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 ASR resistance of concrete was investigated. For this reason, Manisa Enli Mining crushing by-product natural zeolite (clinoptilolite) and two different types of industrial by-product of Kütahya Tunçbilek Thermal Power Plant fly ash (FA) and Ereğli Iron and Steel Factory blast furnace slag (GBFS) 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, ASR experiments were carried out in accordance with

ASTM C 1260 code [ASTM C 1260 2007]. 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. Mortar bar specimens were cured in 1N NaOH solution for 14 days. 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 ASR.

EXPERIMENTAL STUDY

The raw materials of blended cement compositions were supplied from different sources. Cement clinker, gypsum and limestone were supplied from Çimsa Eskişehir cement factory. Natural zeolite in clinoptilolite form was provided from Manisa Gördes region. The industrial by-products fly ash (FA) and ground granulated blast furnace slag (GBFS) were supplied from Kütahya Tunçbilek Thermal Power Plant and Ereğli Iron and Steel Factory respectively. 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), FA and GBFS, 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 [Karakurt 2008].

Table 1. Chemical Composition of the Raw Materials

Chemical Composition	Clinker, %	Clinoptilolite, %	FA, %	GBFS, %
SiO_2	20.98	62.78	61.12	35.11
Al_2O_3	5.55	10.66	12.32	17.63
Fe_2O_3	3.85	4.20	6.51	0.35
CaO	65.85	2.37	4.28	37.56
MgO	1.12	1.10	5.88	5.52
K_2O	0.53	0.74	1.73	-
Na_2O	0.14	0.35	2.44	0.32
SO_3	0.97	-	0.1	-
*LOI	2.23	12.40	0.84	0.75

*LOI: Loss on ignition

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 in accordance with ASTM C 1260 in dimension with 25x25x285 mm in order to determine the length change of different types of produced blended cements. The aggregate used in cement mortar preparation was a mix of two kinds of sand in order to obtain a reactive silica environment in the hardened mortar specimens. These aggregates are reactive glass sand and standard Rilem sand and mixed together 50%-wt. The aggregates grain distribution was balanced in accordance with ASTM C 1260 code. Mortar bar specimens were initially cured in curing cabinet for 24 h after the specimens were cured in lime saturated water at 80˚C for 24h. Afterwards, the specimens were immersed in 4% NaOH solution at 80˚C for 14 days. The comparator readings of the mortar bars were carried out at 4, 8 and 14 days.

RESULTS AND DISCUSSION

Compressive strength

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 first group blended cements compressive strength test results are given in Table 2. as seen from Table 2 early age strength development of GBFS blended cements are better than zeolite and FA blended cements. Furthermore, it can be concluded that 20 and 30% replacement ratio of mineral additive is the optimum usage of zeolite, FA and GBFS blended cements.

Table 2. Compressive Strength of Single Composition Blended Cements

Cement Code	Compressive Strength, MPa			
	2 Days	7 Days	28 Days	180 Days
CEM I 42.5	22.0	30.4	45.2	50.7
ZBC-10	12.3	22.5	46.9	57.1
ZBC-20	11.2	20.3	48.2	54.9
ZBC-30	10.9	18.5	45.3	53.0
ZBC-40	7.2	17.2	39.6	50.6
ZBC-45	6.9	15.0	38.1	48.3
FBC-10	11.5	22.0	44.6	52.9
FBC-20	10.6	21.0	45.4	58.0
FBC-30	8.6	19.5	41.0	54.9
FBC-40	8.1	18.7	38.5	50.8
FBC-45	7.8	16.4	37.5	48.7
SBC-10	13.8	35.3	51.6	54.8
SBC-20	12.8	32.2	52.9	56.3
SBC-30	11.3	29.6	48.2	59.4
SBC-40	9.0	24.8	45.5	55.0
SBC-45	8.3	23.1	42.8	53.2

Z: Zeolite, S: Ground Granulated Blast Furnace Slag, F: Fly Ash

The replacement ratio of binary and triple composition blended cements were chosen as 20% and 30% depending on the compressive strength test results of single composition blended cements given in Table 2. Compressive strength test results of the binary and triple composition blended cements are given in Table 3. Test results showed similar behavior as single composition blended cements at early ages. However, the 28 and 180 days compressive strengths of the second group blended cements are better especially for zeolite and GBFS blended cements.

Table 3. Compressive Strength of Different Composition Blended Cements

Cement Code	Compressive Strength, MPa			
	2 Days	7 Days	28 Days	180 Days
ZFBC-20	12.2	25.1	43.7	52.0
ZSBC-10	12.5	27.3	45.5	60.7
ZSBC-20	11.1	24.1	42.5	51.1
FSBC-10	13.3	28.3	43.2	58.2
FSBC-20	12.4	21.8	40.0	55.6
UZBC-10	12.6	28.3	45.4	61.6
UZBC-20	10.2	24.7	40.8	54.8
SFBC-20	13.3	27.9	46.7	56.6
SZBC-20	13.9	25.8	44.2	53.8
ZFSBC	13.6	26.1	48.9	58.1

Z: Zeolite, S: Ground Granulated Blast Furnace Slag, F: Fly Ash

Alkali-silica reaction test results

ASTM C 1260 classifies aggregates with 14-day expansions greater than 0.2% as reactive and those with expansions between 0.1 and 0.2% as potentially reactive. Although ASTM C 1260 was originally designed for quickly identifying reactive aggregates, it has been shown to be effective in determining the ability of supplementary cementing materials to mitigate ASR-related expansion (Maas). The ASR experiments were carried on for 7 different types of blended cements. The chemical composition of the blended cements obtained from XRF tests are given in Table 4. As seen from Table 4 the equivalent alkali content (EAC) of the blended cements are lower than reference cement. EAC plays a significant role on ASR expansion.

Table 4. Chemical Composition of Blended Cements Used in ASR Tests

Component, %	Cement Code						
	CEM I 2.5	ZBC-30	FBC-30	SBC-30	ZSBC-10	FSBC-10	ZFSBC
SiO_2	20.91	32.80	28.65	25.01	26.27	24.59	29.08
Al_2O_3	5.44	7.41	8.31	7.56	6.94	7.06	7.77
Fe_2O_3	3.71	2.87	4.48	2.63	2.68	3.24	3.28
CaO	63.88	47.24	46.76	55.26	55.54	55.37	49.68
MgO	1.69	2.04	2.94	3.17	2.54	2.70	2.69
P_2O_5	0.12	0.06	0.09	0.07	0.07	0.08	0.07
K_2O	1.12	1.42	1.02	0.79	0.98	0.85	1.10
Na_2O	0.45	0.34	0.36	0.36	0.33	0.35	0.33
SO_3	2.84	2.46	2.79	2.98	2.99	3.11	2.72
Cl^-	0.012	0.011	0.011	0.012	0.012	0.012	0.011
*EAC	1.19	1.17	1.03	0.87	0.97	0.91	1.05

*EAC: Equivalent alkali content

The ASR expansion test results of first group single composition blended cements for 30% replacement ratio are given in Figure 1. It can be clearly said that reference CEM I 42.5 blended cement passes over the 0.2% expansion limit (0.252) at the end of the 16 day specimen age. When compared with the Table 4, the EAC ratio of reference CEM I 42.5 cement (1.19) is the highest value. At the end of the curing regime FBC-30, ZBC-30 and SBC-30 blended cements are blow the *not-reactive* boundary. The best performance was obtained with 30% GBFS blended SBC-30 cement with 0.029% expansion ratio.

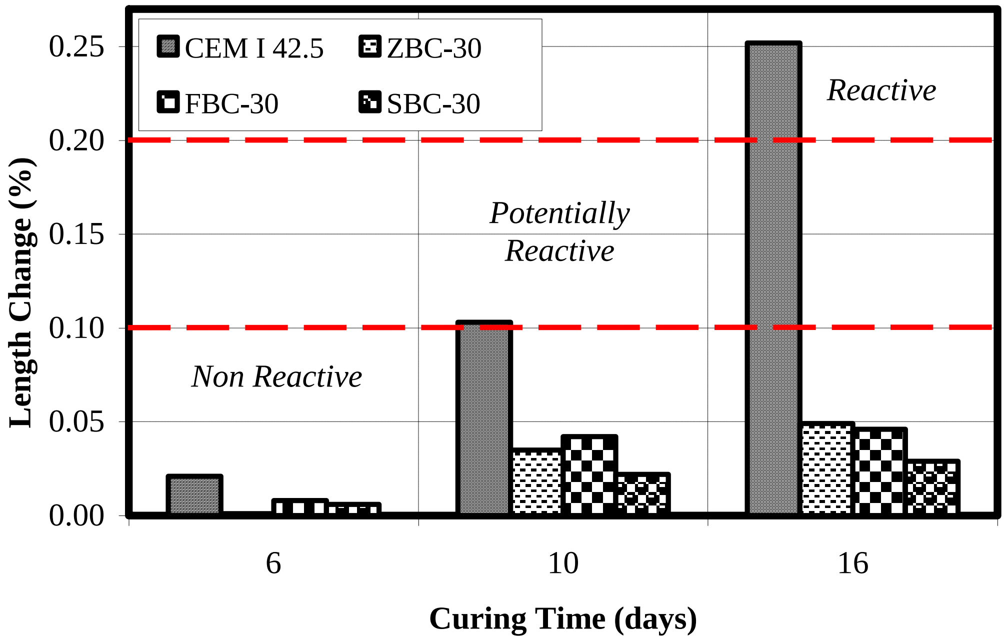

Fig. 1. Length Change of First Group Mortar Bar Specimens

The ASR crack formation on the surface of the CEM I 42.5 reference specimen can be seen clearly with naked eye as given in Figure 2. The cracks radiate from the interior of the aggregate particle and in the ambient cement paste.

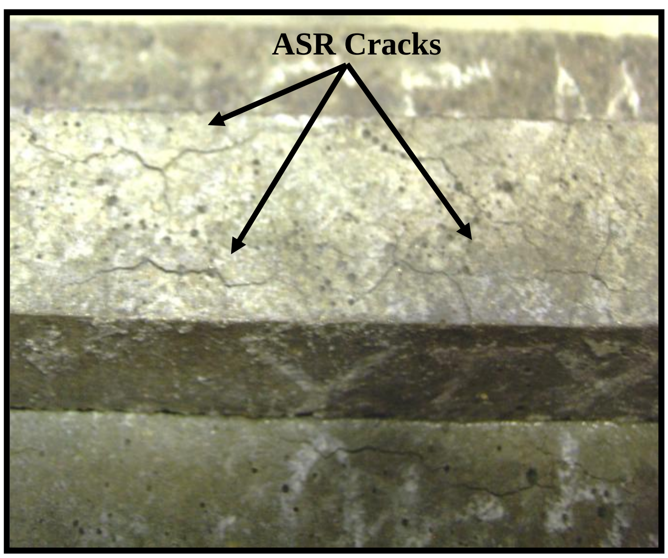

Fig. 2. ASR Cracks on the Surface of the Reference Specimen

The second group blended cements ASR expansion results are given in Figure 3. As seen from Figure 3 all types of blended cements expansion ratios are below the expansion limit as defined in ASTM C 1260. The highest expansion was determined for ZSBC-10 (10% zeolite and 10% GBFS) blended cement with 0.085 expansion ratio. The increased amount of C-S-H gels in the composite due to the reaction between $Ca(OH)_2$ and pozzolanic mineral additives in blended cement compositions decreases the ASR gel formation of cement based composite materials. The pozzolanic reaction and decreased EAC of blended cement increases the durability of concrete against ASR.

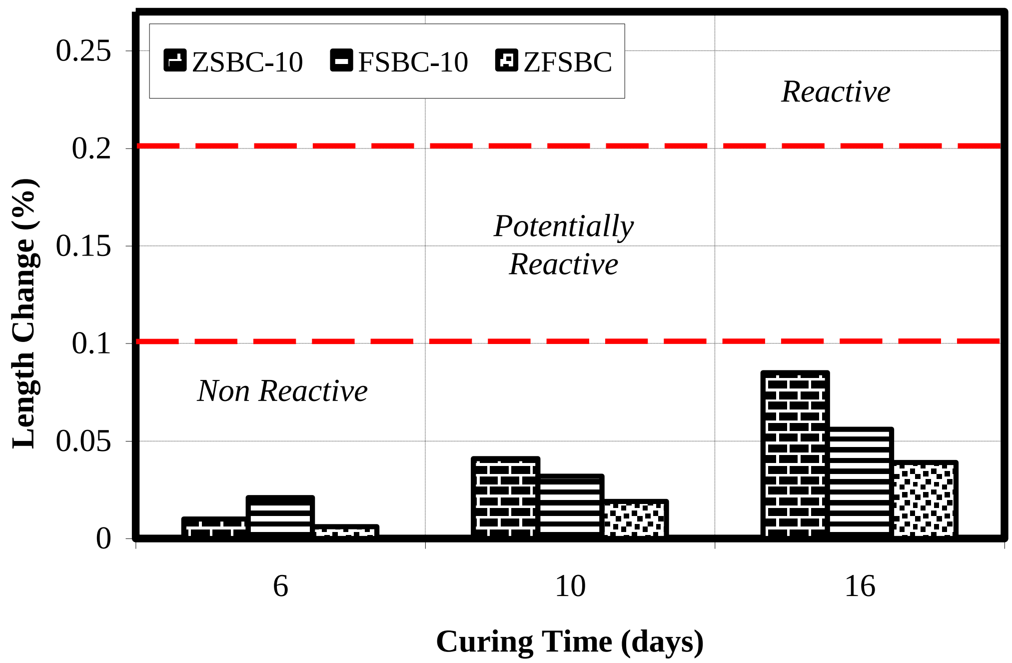

Fig.3. Length Change of Second Group Mortar Bar Specimens

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 ASR of concrete is related with the EAC, reactive silica content of the aggregate and presence of water. The higher amount of mineral additives in blended cement production reduces the early age strength of concrete. However, the ASR formation and deterioration in composite specimens reduces depending on the increasing replacement ratios in blended cements. The optimum replacement ratio can be defined as 30% when strength and durability properties considered together. The best ASR resistance was obtained with GBFS blended cements. Utilization of economic blended cements in ASR risk environments has beneficial effects on concrete durability.

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