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Effectiveness of micronized calcite in reducing expansions due to Alkali Silica Reaction

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Abstract— **This paper investigates the effectiveness of micronized calcite in reducing expansion of concrete due to alkali-silica reaction. Three aggregates; two natural sands and one crushed stone aggregate were used preparing mortar bars in accordance with accelerated mortar bar test method, ASTM C1260. Performance of micronized calcite is determined by examining the expansions due to alkali silica reaction. Micronized calcite added to the mixtures at %10 and %20 replacement levels by weight of cement. Also in this research, effect of different cement usage to expansions was investigated by using the same method. Four different cements were used for this purpose. Usage of micronized calcite at %20 replacement level of cement was effective in mitigating ASR expansions whereas using it at %10 was not enough to suppress them. Different cement usage showed a minor difference between the expansions; however, the final decision about the reactivity of aggregate was indecisive.**

Keywords—**Alkali silica reaction, Micronized calcite, Durability.**

I. Introduction

One of the most severe durability problem of concrete structures is the alkali silica reaction (ASR). This reaction occurs between alkali hydroxide in Portland cement and aggregates that contain reactive silica. This specific reaction typically creates significant concrete expansion and damages which ends up with failure of construction [1]. Durability problems in concrete and reinforced concrete subjected to aggressive environment cause damages in structures before predicted service life. By adding pozzolans to concrete, calcium hydroxide content of cement paste can be reduced and permeability of concrete can be decreased [2].

Filling materials adding up to a certain amount of binder shows a filler effect or particle size effect in cementitious mixtures [3]. This filler effect is defined as the arrangement of small particles that fill the voids and contribute to the increment of compressive strength without any chemical reaction[4,5].Chemical and physical properties of cementitious materials can be enhanced by adding limestone filler to mixture. Researchers claimed that, usage of limestone filler materials between 7 and 10% of cement in mixture improved the mechanical and durability properties of the concrete [6]. Limestone fillers have no pozzolanic effect but react with alumina phase of cement and produce calcium monokarboaluminatehydrates [7]. Calcite initially reacts with C_3A and C_4AF components of cement.

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Calcite particles integrate with cement paste during this reaction [8]. In a study done by researchers, it is stated that; calcite filler accelerates hydration reaction . In the same study, it was observed that in the usage of cement with high C_3A and calcite filler at the same time in the mixture, hydration products become karboalumina hydrates with high binding capacity [9]. Micronized calcite as a filler was added to the investigation for the reason of difference in chemical composition of S4 aggregates. Their calcite contents were different and researchers claimed that expansions are affected by calcite content of that aggregates.

Also in related standard [10] it is stated that, because the specimens are exposed to a NaOH solution, the alkali content of the cement is not a significant factor in affecting expansions. Again, in the same standard, it is stated that the alkali content of the cement had been found to have negligible or minor effects on expansion in this test [11,12]. To investigate this effect, three different cements with different Na_2O^{-} ^{eq} content and five aggregates were used in the study.

II. Materials

A. *Cements and Micronized Calcite*

The binders was normal Portland cement CEM I 42.5R, as specified by European Standard EN 197-1 (EN 197-1, 2000) [13]. Table 1 shows their chemical composition and alkali equivalent (Na_2O equivalent) contents, and Table 2 shows its physical properties. They are labeled as A, B, C, D cement. In this experiment, filler material consist of micronized calcite Chemical composition and physical properties of filler material is shown in Tables 1 and 2, respectively. Micronized calcite used in this study are labeled as (MC).

B. *Aggregates*

Firstly, effectiveness of micronized calcite was investigated. In this purpose mixtures were prepared with three different aggregates (labelled as S1, S2, S3) and one selected cement labeled A. In the second part, effect of different cement usage to ASR expansions was investigated. Mixtures were prepared with five aggregates (labelled as S1, S2, S3, S4, S5) and three cements (B, C, D). Mineralogical compositions of all aggregates were shown in Table 3 and chemical composition of aggregates were shown in Table 4. S4 aggregates were taken two different parts of the same quarry and from now labelled as S4-1 and S4-2.

TABLE I. CHEMICAL COMPOSITION

Oxide (wt %)	Cement and Micronized Calcite				
	A	*B*	*C*	*D*	*MC*
SiO_2	17.70	19.98	19.76	19.76	0.04
Al_2O_3	3.95	5.32	4.97	4.97	0.03
Fe_2O_3	3.76	3.31	2.66	2.66	0.03
CaO	62.45	63.38	63.25	63.25	-
MgO	1.05	1.06	1.06	1.06	0.45
SO_3	4.12	3.2	3.02	3.02	-
$CaCO_3$	-	-	-	-	99.45
LOI	4.82	0.9	1.78	0.34	-
$(Na_2O)_{eq}$ [a]	1.03	0.87	0.54	0.73	-

a. $(Na_2O)eq = Na_2O + 0.658\ K_2O$

TABLE II. PHYSICAL PROPERTIES

Physical Properties		Cement and Micronized Calcite				
		A	*B*	*C*	*D*	*MC*
Specific Gravity		3.14	3.15	3.12	3.10	2.7
Setting Time	Initial (min)	129	170	210	160	-
	Final (min)	191	210	240	245	-
Soundness (mm)		1.0	1.0	1.0	0.5	-
Specific Surface (cm^2/g)		3950	3590	3680	3770	-
Maksimum Sieve Size (µm)		-	-	-	-	20

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TABLE III. MINEROLOGICAL COMPOSITION

Mineral (Modal %)	Aggregates					
	S1	***S2***	***S3***	***S4-1***	***S4-2***	***S5***
Quartz	78-82	30-95	84-86	90-94	85-90	90-92
Feldspar	5-6	10-15	2-3	3-5	2-4	1-3
Mica	1	15-20	-	1	1	-
Clay+ Carbonate	-	30-35	-	-	-	-
Opaque	-	3-4	-	-	-	-
Turmaline	0.5	-	-	-	-	-
Garnet	1	-	-	-	-	-
Chlorite+ Epidote	1	-	-	-	-	-
Ferric Oxide	1-2	-	<0.5	-	-	-
Calcite	2-3	-	-	3-4	7-8	-
Calcite+ Aragonite	-	-	1-2	-	-	0.5-1
Rock Particles	-	-	10-12	-	-	5-6

TABLE IV. CHEMICAL COMPOSITION

Oxide (wt %)	Aggregates					
	S1	***S2***	***S3***	***S4-1***	***S4-2***	***S5***
SiO_2	56.55	60.64	50.30	61.6	60.9	50.8
Al_2O_3	10.46	4.74	19.27	3.3	3.5	18.9
Fe_2O_3	3.80	2.19	9.52	2.6	2.7	9.4
CaO	12.54	16.97	3.71	16.10	15.80	3.93
MgO	2.31	0.70	4.40	0.78	0.83	4.33
TiO_2	0.50	0.14	1.10	0.19	0.22	1.15
P_2O_5	0.14	0.07	0.19	0.05	0.07	0.17
MnO	0.12	0.12	0.14	0.10	0.13	0.16
Cr_2O_3	0.03	0.01	0.02	0.01	0.04	0.01
$(Na_2O)_{eq}$[a]	3.44	2.23	3.88	2.27	2.25	3.87
LOI	9.16	11.21	5.99	11.3	11.6	6.03

a. $(Na_2O)eq = Na_2O + 0.658\ K_2O$

III. Methods

The efficiency of micronized calcite in controlling ASR expansion were investigated by using the accelerated test method of ASTM C1260 (similar to CSA A23.2-25A-M94 method). They contained %10 and 20% replacement level of micronized calcite by weight of cement. Based on the test method, mortar bars were produced by using 1 part of cement to 2.25 parts of aggregates. Additionally, the water to total cementitious materials (w/c) was kept at 0.47. Two mortar bars (25 × 25 × 225 mm) were cast for each mortar mixture. After 24 hours, mortar bars were removed from the molds and stored in a water bath with tap water at 90°C for a period of 24 hours. After this preconditioning, the length of mortar bars were measured (initial reading). Then they are placed into storage containers filled with 1 normality (1N) of NaOH solution at 80°C for the duration of the test. Subsequent length readings were made on 1th 3th 7th 14th days. Expansions were measured as mortar bars changes in length.

In the second part, effect of different cement usage to ASR expansions in ASTM C1260 method was investigated. Based on the test method, mortar bars containing S1, S2, S3, S4-1, S4-2 and S5 aggregate, and B, C, D cements were used while preparing the mortar bars.

IV. Results

Expansions of mortar bars prepared with MC and their control bars are shown in Table V. Figure 1, 2, and 3 represents the expansion results up to 14 days for the mortar bars cast with %10 and %20 replacement of MC and S1, S2, and S3 aggregates. Effect of different cement usage was investigated by using mortar bars were prepared with S1, S2, S3, S4, and S5 aggregates and Cement B, C, and D. Expansions of mortar bars are given in Table VI and shown in Figure 4.

TABLE V. EXPANSIONS OF MICRONIZED CALCITE MORTAR BARS

Aggregate	**Time (Days)**	**Expansion Results of Mortar Bars (%)**		
		Control Bar	***%10 MC***	***%20 MC***
S1	1th	0.73	0.08	0.03
	3th	0.95	0.20	0.21
	7th	1.22	0.40	0.37
	14th	**1.27**	**0.55**	**0.40**
S2	1th	0.03	0.04	0.00
	3th	0.09	0.08	0.01
	7th	0.23	0.26	0.12
	14th	**0.32**	**0.30**	**0.17**
S3	1th	0.00	0.01	0.02
	3th	0.01	0.03	0.03
	7th	0.16	0.14	0.10
	14th	**0.24**	**0.19**	**0.13**

TABLE VI. EXPANSIONS OF DIFFERENT CEMENT MORTAR BARS

Aggregate	**Time (Days)**	**Expansion Results of Mortar Bars (%)**		
		B Cement	***C Cement***	***D Cement***
S1	1th	0.02	0.01	0.03
	3th	0.53	0.37	0.32
	7th	0.66	0.49	0.44
	14th	**0.82**	**0.63**	**0.54**
S2	1th	0.01	0.03	0.02
	3th	0.14	0.12	0.14
	7th	0.24	0.24	0.37
	14th	**0.47**	**0.51**	**0.46**
S3	1th	0.00	0.00	0.00
	3th	0.01	0.02	0.03
	7th	0.08	0.09	0.10
	14th	**0.16**	**0.18**	**0.20**
S4-1	1th	0.09	0.08	0.07
	3th	0.12	0.10	0.11
	7th	0.34	0.29	0.31
	14th	**0.42**	**0.36**	**0.40**
S4-2	1th	0.09	0.08	0.04
	3th	0.15	0.12	0.12
	7th	0.22	0.17	0.21
	14th	**0.29**	**0.22**	**0.27**
S5	1th	0.00	0.00	0.00
	3th	0.02	0.02	0.02
	7th	0.08	0.06	0.07
	14th	**0.16**	**0.15**	**0.16**

Figure 1. Expansions of mortar bars cast with S1 aggregate.

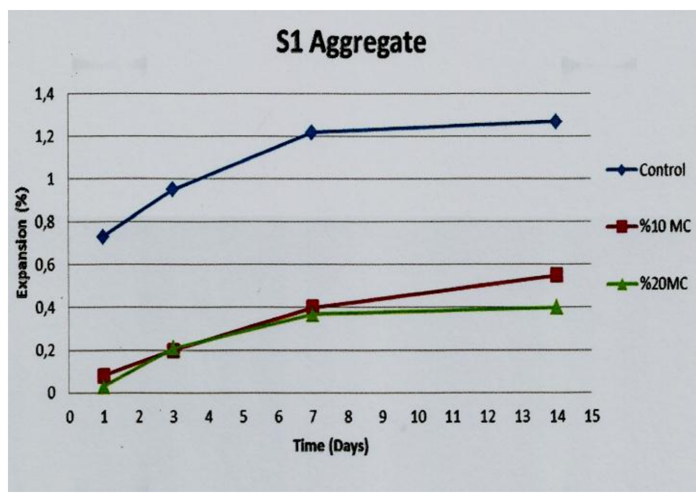

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Figure 2. Expansions of mortar bars cast with S2 aggregate.

Figure 3. Expansions of mortar bars cast with S3 aggregate.

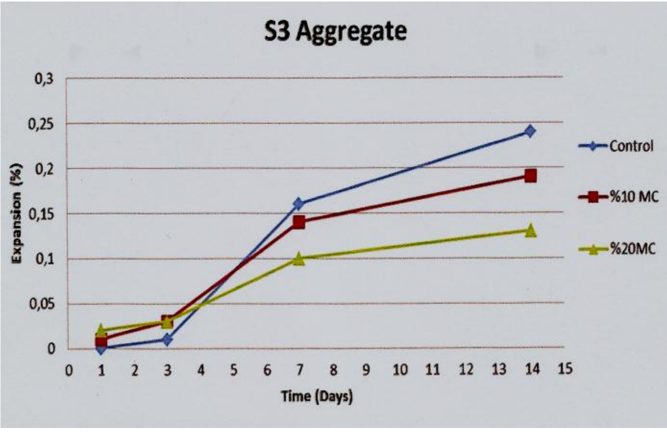
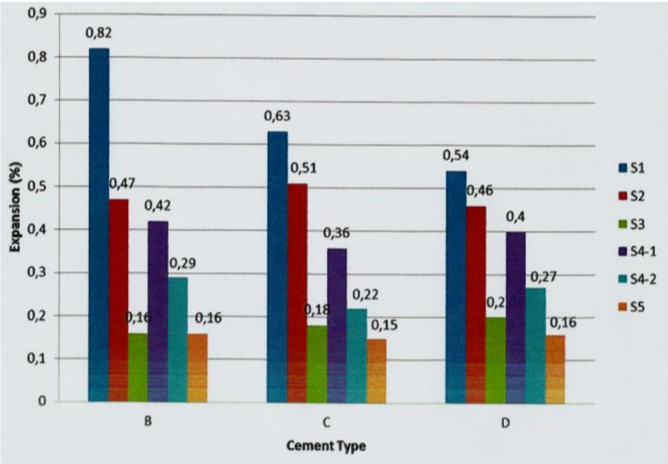


Figure 4. Effect of different cement usage to expansions.



Aggregate which has higher expansion than 0.2% at the end of 14 days are defined as highly reactive aggregate by researchers [14]. Considering the average of 14 days expansions, S1, S2, and S4-1, S4-2 aggregates are highly reactive aggregates. Aggregates showing expansion between 0.10 and 0.20% at the end of 14 days was defined as potentially reactive aggregate by researchers [14]. Considering the average of 14 days expansions S3 and S5 aggregates can be included in this potentially reactive aggregate class.

V. Conclusion

1. Mortar bars prepared with S1 aggregate showed very high final expansion, %1.27, at the end of 14 days and was found highly reactive due to ASR. %10 and %20 level of replacement was not enough to control deleterious expansion and couldn't lower the expansions under acceptable limits.

2. Samples prepared with S2 aggregate showed medium final expansion, %0.32, at the end of 14 days and was found reactive due to ASR. %10 level of replacement was not enough to control deleterious expansion but %20 level of replacement lowered the expansions under acceptable limits.

3. Mortar bars cast with S3 aggregate showed low expansions, %0.24, at the end of 14 days and was found reactive due to ASR. %10 and %20 level of replacement successfully lowered the expansions under acceptable limits.

4. Degree of the expansions decreased as the level of filler addition increased in all mortar bars.

5. It was also observed from the results, that micronized calcite is effective on suppression of ASR.
6. Mortar bars cast with same aggregate but different cements have different expansions but they did not show distinct results from each other.

7. The final decision about the reactivity of aggregates was unchanged except from S3 aggregate. Decision about the reactivity of S3 aggregate depends on the cement because expansion results was very close to the limits so we should always write Na_2O^{-eq} content and type of cement in technical reports.

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