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INFLUENCE OF MINERAL ADMIXTURES ON THE ALKALI-AGGREGATE REACTION

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ABSTRACT

Different mineral admixtures were used as cement replacements to study the alkali-aggregate reaction between quartzite and cement paste. The experimental program included expansion measurement of the mortar-bar specimens, observation of the microstructure, and analysis of the gel composition. Two Portland cements with different alkali contents were used to prepare mortar bars containing different amounts of natural pozzolan, fly-ash, and slag. Three natural pozzolans with different alkali contents were also utilized to assess the effect of their alkalies on the mortar expansion. The results indicate that not all gels are equally expansive and that mineral admixtures change the composition of the gel. The double layer theory is used to explain the expansion results of the mortar bars containing different levels and types of mineral admixtures. As this theory predicts, the experimental results show a strong negative correlation between expansion and the charge fraction of bivalent cations in the gel. © *1997 Elsevier Science Ltd*

Introduction

The alkali-aggregate reaction (AAR) is a deleterious reaction that occurs between a reactive aggregate and the cement paste pore solution. The reaction is initiated at the surface of the siliceous aggregate. As a result, a more crystalline, densely structured silicate, such as quartz, is more resistant to attack as compared to an open-structured silicate mineral. Ions present in the pore solution, including hydroxyl, sodium, potassium, and calcium ions, can more freely penetrate a poorly crystalline structure. Studying model solutions, Dent Glasser and Kataoka (1) distinguished four reactions for the silica gel/sodium hydroxide/calcium hydroxide system: 1) dissolution of silica by hydroxyl attack, breaking the Si-O-Si bonds into silanol (Si-OH) bonds; 2) reaction of silanol groups with OH^- in the solution; 3) binding of the sodium ions (Na^+) and calcium ions (Ca^{2+}) at negatively charged sites on the silicate

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surface; and 4) reaction of silicate species in solution with calcium ions in solution to form calcium silicate hydrate (C-S-H). Unreinforced massive structures, such as dams, are particularly sensitive to this deterioration process, which may cause cracks and movement of the concrete blocks and jeopardizes the long-term operation of the affected structures. Charlwood and Solymar (2) reported 104 cases of AAR in dams and spillways around the world; 52 of those hydraulic structures are in North America and 25 in Europe. The expansive reaction can stabilize over time as with Steward Mountain dam, whose reaction stopped after 30 years, or can continue over time as with Fontana Dam, whose reaction continues for over 50 years. This deleterious reaction is not restricted to unreinforced massive structures and it has been reported in reinforced concrete piers and beams (3). While AAR prevention can be achieved by adequate materials selection for the concrete mix proportions, the control of the deleterious reaction, once it starts, is limited at best. A better understanding of the kinetics of the reaction and of the expansion mechanics can provide insight on how to mitigate the damage.

Traditionally, mineral admixtures, such as slag, fly ash, and natural pozzolans, have been used in the concrete mix proportions to mitigate or eliminate the AAR reaction. There is no agreement, however, on the predominant mechanism by which mineral admixtures reduce the AAR expansion. Glasser (3) reviewed the following main theories: 1) the blending agents act as a diluent because they are usually less reactive than Portland cement and liberate alkali at smaller rates; therefore, the blended mixtures are able to maintain a higher effective water-cement ratio than the corresponding mixtures containing only cement, causing a further dilution of the alkali content. Some mineral admixtures, however, can have a higher soluble-alkalis content than cement. So, the beneficial effect may not occur when such admixtures are used; 2) mineral admixtures cause pore-size and grain-size refinement leading to a lower permeability and, consequently, a reduction of the migration of alkalis towards the reactive aggregate; 3) the blending agents lower the $Ca(OH)_2$ content of the cement paste, reducing its pH. Glasser pointed out, however, that the pH is established by the equilibrium between $Ca(OH)_2$, C-S-H, and the pore solution, and that it is independent of the amounts of the individual phases; and 4) the hydration products of blended cement systems have a higher binding power for alkalis than those of Portland cement. The typical Ca/Si ratio of C-S-H in Portland cements is about 1.8, but reduced ratios are observed when mineral admixtures are used. The surface charge on C-S-H depends on its Ca/Si ratio: when the Ca/Si ratio is high, the surface charge of C-S-H is positive and anions are adsorbed on the C-S-H fibers (but not cations as Na^+ and K^+, which remain in the pore solution); when the Ca/Si ratio is lower than about 1.2–1.3, the surface charge of C-S-H becomes negative and alkali cations are incorporated on the C-S-H.

Recently, Prezzi et al. (4,5) showed that the double layer theory can provide a solid foundation to explain the expansion of AAR gels. According to this model, the gel expands due to electrical double-layer repulsive forces. In general, a solid surface can develop an electrical charge from isomorphic substitutions of ions in the bulk structure of the solid, from chemical reactions at the surface, and from ion adsorption. An ion can be adsorbed on a surface forming an inner-sphere complex when no water molecule is between the surface function group and the ion, or an outer-sphere complex when at least one water molecule exists between the surface and the ion. Ions can also be adsorbed in the diffuse swarm of the double layer in order to neutralize the surface charge. Alkali ions are initially adsorbed at nonbridging oxygen sites of a glass surface largely by electrostatic forces. So the ion exchange is similar to the acid-base behavior of the

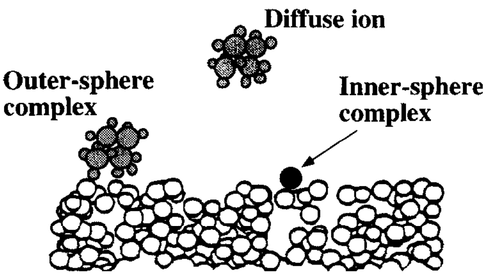


FIG. 1.
Three modes of adsorption of monovalent cations by a glass surface. Modified from Sposito (7); adsorbent based on simulation of silica glass surface by Garofalini (8).

nonbridging site. Molecular dynamics simulations (6) indicate that potassium is adsorbed at nonbridging oxygen sites, but that when these sites become saturated, potassium can be adsorbed at the bridging oxygen associated with strained siloxane bonds; lithium, however, can be initially adsorbed at both nonbridging and strained bridging oxygen sites (Fig. 1).

The objective of this work is to use double layer theory to explain the effects of mineral admixtures on the AAR expansion based on the gel composition. The experimental program included expansion measurement of the mortar-bar specimens, observation of the microstructure, and analysis of the gel composition. Two Portland cements with different alkali contents were used to prepare mortar bars containing different amounts of natural pozzolan, fly-ash, and slag. Three natural pozzolans with different alkali contents were also utilized to assess the effect of their alkalies on the mortar expansion.

Materials and Experimental Methods

Quartzite was used as the reactive aggregate. This metamorphic rock contained quartz grains with an average size of 0.1 mm that showed a frequent wavy extinction of low intensity. The rock had the following oxide composition: 94.98% SiO_2, 1.74% Fe_2O_3, 0.45% Al_2O_3, 0.06% CaO, 0.06% Na_2O, and 0.16% K_2O. Potassium in the aggregate was due to the presence of muscovite, which appeared as suboriented plates scattered or concentrated in subparallel planes.

Two Portland cements were used: Cement 1 with an Na_2O-equivalent alkali content of 1.37% and Cement 2 with an alkali content of 0.68%. The mortar samples were prepared using the following mineral admixtures: fly ash, slag, and three types of natural pozzolans made from calcined clays. Pozzolan C had the highest alkali content with 4.58%, Pozzolan B had the lowest alkali content with 0.10%, and Pozzolan A had an intermediate alkali content of 0.73%. The composition and properties of the mineral admixtures are given in Table 1 and the levels of replacement used in the experimental program are shown in Table 2. Mortar prisms were prepared in accordance with ASTM C 227, cured for 24 h in a fog room at 21 ± 2°C, demoulded, and immersed in water in a closed container maintained at 80°C for 24 h (ASTM C 1260). The length of the specimens was measured before their immersion in a 1-M sodium hydroxide solution in a closed container maintained at 80°C, and

TABLE 1
Characteristics and chemical composition of cement and mineral admixture

Property		Cement 1	Cement 2	Natural Pozzolan A	Natural Pozzolan B	Natural Pozzolan C	Fly ash	Slag
Specific Gravity (g/cm^3)		3.14	3.05	2.37	2.77	2.65	2.14	2.90
Fineness (cm^2/g)		3,090	2,980	5,880	7,560	5,580	5,990	4,239
Chemical	CaO	61.08	64.22	0.05	0.37	11.37	1.26	44.66
Analysis	SiO_2	20.81	19.09	74.94	75.09	54.71	56.88	34.07
%	Al_2O_3	4.08	3.85	18.91	17.72	15.36	37.00**	8.09
	Fe_2O_3	3.70	4.83	4.19	5.63	5.36		0.74
	MgO	1.92	1.67	0.42	0.21	3.40	0.92	9.09
	SO_3	2.70	2.15	0.17	0.24	1.05	0.48	0.09
	Na_2O	0.48	0.19	0.54	0.07	2.37	0.27	0.19
	K_2O	1.36	0.75	0.29	0.06	3.37	2.41	0.53
	$CaSO_4$	4.60	3.65	0.29	0.41	1.78	—	0.15
Total alkalies as Na_2Oe*		1.37	0.68	0.73	0.10	4.58	1.85	0.54

*$Na_2O_e = Na_2O + 0.658\ K_2O$

**This value represents the amount of Al_2O_3 and Fe_2O_3

the specimens were removed briefly from the containers and measured before significant cooling occurred.

Polished samples were prepared for SEM observation with BEI, and EDX analysis after a 30-day accelerated expansion test. The accelerating voltage used was 20 KeV with a specimen current of approximately 0.7×10^{-9} Å on brass. The collection time was 150 or 200 s with a dead time of approximately 25%.

Results and Analysis

The purpose of the experimental program was to accelerate the alkali-aggregate reaction to study the relative benefits of using mineral admixtures and how the AAR gel composition was affected by the use of blending materials. This program did not assess how representative

TABLE 2
Specimens made for the expansion test

			CEMENT 1			
replacement	0%	15% Poz. A	20% Poz. A	25% Poz. A	20% Poz. B	20% Poz. C
w/c	0.56	0.57	0.57	0.58	0.57	0.57
replacement	15% FA*	25% FA	30% FA	50% Slag	60% Slag	70% Slag
w/c	0.58	0.58	0.58	0.57	0.57	0.59
			CEMENT 2			
replacement	0%	15% Slag	25% Slag	35% Slag	45% Slag	55% Slag
w/c	0.60	0.62	0.60	0.62	0.67	0.65
replacement	65% Slag	70% Slag	75% Slag	80% Slag		
w/c	0.68	0.68	0.70	0.71		

*Fly ash.

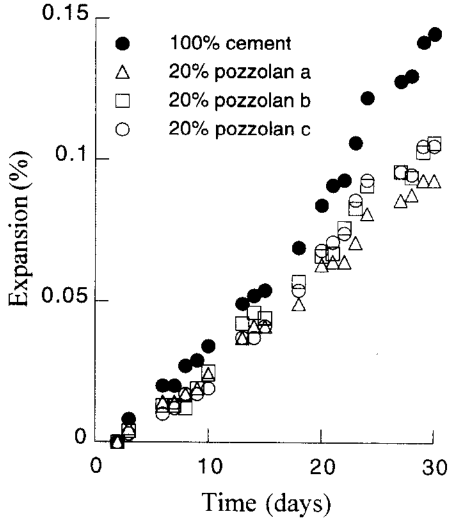


FIG. 2.
Expansion of mortar bars prepared with Cement 1 and different types of pozzolan.

these test methods are of real concrete structures. Figure 2 compares the effectiveness of the three types of natural pozzolans in reducing the expansive behavior of samples prepared with the Cement 1. Pozzolan A showed superior performance in reducing the expansion. It is noted, however, that, even though the pozzolans had different amounts of alkali, their effect on the expansion was not much different at this replacement level. One possible explanation is that the alkalies in the natural pozzolans were only partially released. The influence of the level of pozzolan replacement on the mortar bar expansion is shown in Figure 3. At 30 days,

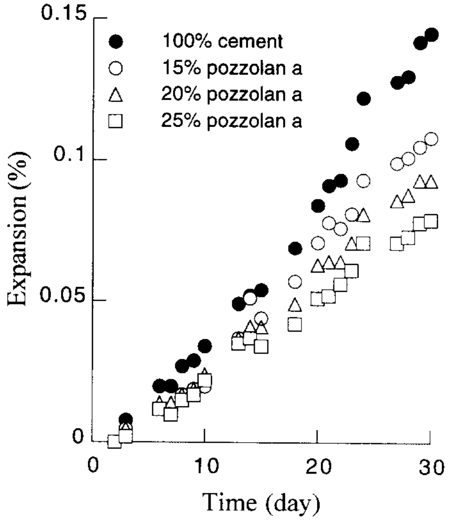


FIG. 3.
Expansion of mortar bars prepared with Cement 1 and different amounts of Pozzolan A.

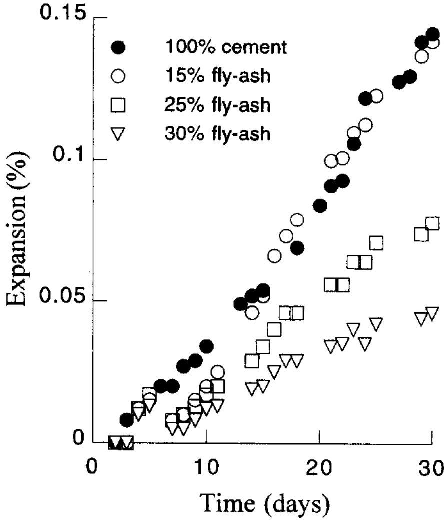


FIG. 4.
Expansion of mortar bars prepared with Cement 1 and different amounts of fly-ash.

the mortar bars without any admixture expanded 0.15%, whereas those with 25% Pozzolan A expanded 0.08%. Figure 4 shows the influence of the fly-ash replacements on the mortar-bar expansion. A 15% replacement did not have any effect in the expansion. However, significant improvements in reducing the expansion were obtained for higher replacement levels. Porter (9) also observed that small amounts of mineral admixtures may cause greater expansion in mortar, and it has been suggested (10) that at a low replacement level the alkalies contributed by fly ash is greater than those contributed by the Portland cement.

Figure 5 compares the efficiency of different levels of slag in reducing the expansion in specimens made with Cement 1. Only limited improvement was observed when 50% slag replacement was used, but greater reductions in expansion were noted for higher replacement levels. Figure 6 compares the effect of slag replacement level in reducing the expansion for mortar prepared with Cement 2. Slag replacements up to 45% did not effectively reduce the mortar-bar expansion. However, remarkable reductions in expansion were observed for higher slag replacement. For the specimens with slag replacement greater than 65%, ASR expansion is as low as 0.01%. Although the total alkalies in the slag was lower than that in Portland Cement 2, the large decrease in ASR expansion between the specimen with 45% slag replacement and the specimen with 55% slag replacement cannot be explained by reduction in available alkali content alone. As discussed below, the double layer theory will be used to explain this behavior.

The microstructure of some selected mortar specimens with different types or contents of mineral admixtures was observed by scanning electron microscope (SEM) with backscattered electron image (BEI). The alkali-silica gel was easily identifiable and it was predominantly localized around the large aggregates, in the pores, and sometimes just outside of the pores (Fig. 7). Gels were found in all specimens, independent of the presence of a mineral admixture, except for the specimen with 80% slag replacement. The amount of gel was usually higher for specimens that did not contain a mineral admixture. The aggregates

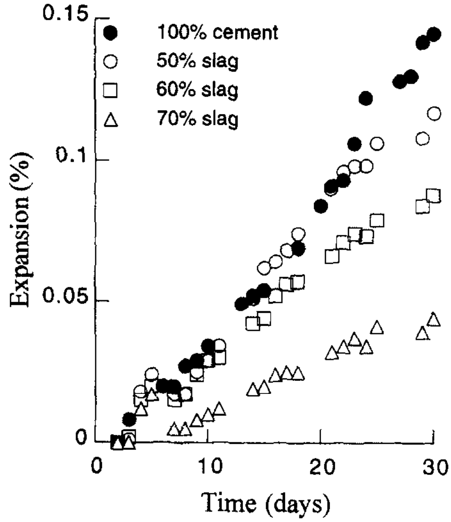


FIG. 5.
Expansion of mortar bars prepared with Cement 1 and different amounts of slag.

cracked significantly as a result of the expansive reaction, and most of the cracks in the cement paste radiated from the aggregates.

After locating the reaction sites (gel regions) in the specimens examined in the electron microscope, an energy dispersive x-ray was used to perform semiquantitative chemical analysis of the gel. Table 3 gives the average chemical composition of AAR gel for the samples investigated. According to the double layer theory, greater expansions are generated when more monovalent than divalent ions are present in the diffuse layer. This model

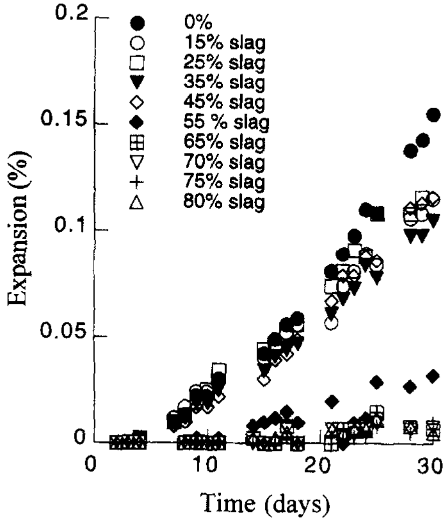
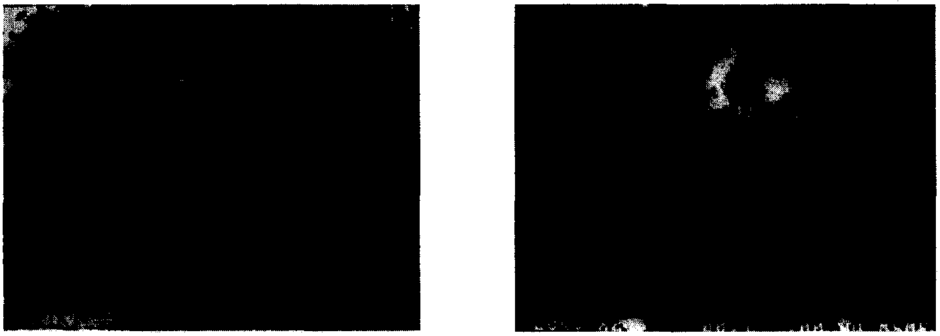


FIG. 6.
Expansion of mortar bars prepared with Cement 2 and different amounts of slag.

(a) cement 1 **(b) cement 2**



(c) cement 1 and 20 % pozzolan type c **(d) cement 1 and 25 % fly ash**

(e) Gel in Specimen made with cement 2 and 45% slag **(f) Gel in Specimen made with cement 2 and 55% slag**

FIG. 7.
Gel in specimens with different mineral admixtures.

explains why the mortar samples with 45% slag expanded much more than the ones with 55% of slag: the latter specimens had gels with a lower content of Na_2O_e and the highest CaO/Na_2O_e ratio. The gels formed in the reference specimens (without mineral admixtures) produced the largest expansions and had the highest Na_2O_e content (and the lowest CaO/Na_2O_e ratio). Samples with 25% pozzolan and fly-ash replacements had limited expansion and intermediate values of Na_2O_e and CaO/Na_2O_e ratio. Based on the elec-

TABLE 3
Average chemical composition for AAR gel formed in samples prepared with different mineral admixtures

Samples	ref. Cement 1	Cement 1 + 25% Pozzolan A	Cement 1 + 25% fly ash	ref. Cement 2	Cement 2 + 45% slag	Cement 2 + 55% slag
expansion (%) at 30 days	0.145	0.079	0.078	0.155	0.116	0.032
Chemical Composition of the Gels as Assessed by EDS						
SiO_2	53.40	60.18	58.05	51.51	67.18	51.07
CaO	30.32	24.27	28.84	20.52	29.83	37.92
Na_2O	10.69	8.16	6.73	7.74	6.21	3.31
K_2O	0.58	1.53	1.96	3.26	0.85	0.60
Al_2O_3	2.57	3.14	2.56	13.23	3.08	3.94
FeO	0.70	0.92	0.67	1.87	0.71	0.74
MgO	0.78	0.87	0.00	1.01	0.65	1.09
SO_3	0.96	1.10	1.17	0.85	0.89	1.36
Na_2Oe	11.06	9.17	8.03	9.89	6.76	3.70
$CaO/(Na_2O)e$	3.10	3.49	3.59	2.16	4.80	12.15
$SiO_2/(Na_2O)e$	5.06	7.73	7.25	5.43	9.15	13.23

trical double layer concept that swelling requires monovalent cations and under the assumption that most of the cations in the gels are exchangeable, a negative correlation should exist between the charge fraction of bivalent cations (Ca and Mg) in the gels and the percent expansion. This latter charge fraction, E_{BIV}, is calculated with the following formula (5,7):

$$E_{BIV} = \frac{(mol\mathrm{CaO} + mol\mathrm{MgO})}{(mol\mathrm{CaO} + mol\mathrm{MgO} + mol\mathrm{Na_2O} + mol\mathrm{K_2O})}$$

where *mol* refers to the number of moles of an oxide component. The ratio E_{BIV} is the fraction of total moles of cation charge (bound to O^{2-}) attributed to Ca and Mg. A graph of % expansion vs. E_{BIV} is shown in Figure 8, where an excellent negative correlation is observed. Figure 9 indicates the correlation between % expansion, E_{BIV}, and % of slag. The work of Keren and Stainberg (11) on bentonite clay indicates that the relationship between E_{BIV} and water retention is not linear over the whole range of E_{BIV} (0 to 1). However, their results agree with the present study, which shows a linear relationship for values of E_{BIV} ranging from 0.7 to 0.9.

Conclusions

Low fly-ash replacements did not reduce the AAR expansion. However, higher replacement levels produced significant reduction in expansion. The alkali content in the natural pozzolans used in this research did not have a major effect on the overall performance of the pozzolan. With higher slag replacements, AAR expansion was practically nonexistent.

Not all alkali-silica gels are equally expansive. Alkali and calcium contents in

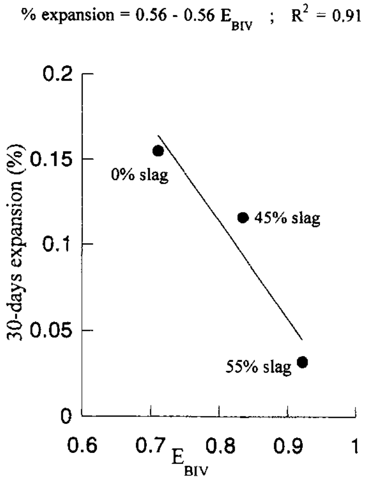


FIG. 8.
Expansion of mortar bars as a function of mole fraction ratio E_{BIV}.

alkali-silica gels play important roles in the expansion capability of mortar or concrete. The higher the $CaO/(Na_2O)_e$ ratio in alkali-silica gel, the lower the gel's capacity for expansion. As predicted by the double layer theory, experimental results show a strong negative correlation between expansion and charge fraction of bivalent cations in the gel.

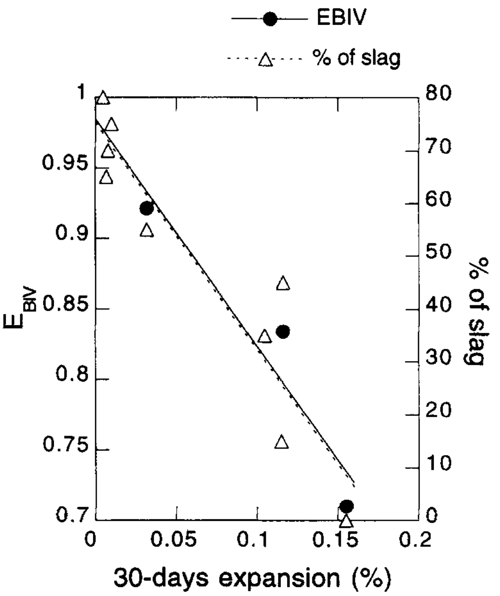


FIG. 9.
Relashionship between 30-days expansion and E_{BIV} and percentage of slag.

Acknowledgments

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