Strength Reduction and Expansion of Mortars with Fly Ash

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Abstract

In this investigation, mortar specimens made with two ordinary Portland cements, Type I and V, and Type I cement partially replaced with fly ash were exposed to sulfate solution. Two types of fly ash with different CaO content, namely 8.28% and 17.28% were used. The performance of these cementitious binders, in sulfate environment, was evaluated by determining reduction in compressive strength and measuring expansion.

Test results indicated that the strength reduction in Na_2SO_4 (N<u>S</u>) and expansion in both N<u>S</u> and $MgSO_4$ (M<u>S</u>) of mortar specimens made from Type I cement replaced with 8.28%CaO fly ash was generally excellent compared to Type I cement mortar specimens, but strength reduction in the M<u>S</u> was not satisfactory. For mortar specimens made from Type I cement replaced with 17.28%CaO fly ash in both sulfate environments, the strength reduction had inferior performances; however, the expansion had superior performances when amount of fly ash were increased. The deterioration of cement in sulfate environment is attributed to the initial reaction of sulfate ions (SO_4^{2-}) with calcium hydroxide (CH). The reduction of CH in mortar specimens made from cement replaced with fly ash can reduce the formation of secondary ettringite in N<u>S</u> environment while it provides the M<u>S</u> to react with the primary and secondary calcium silicate hydrate (C-S-H) due to the de-stabilization of these phases by magnesium hydroxide (MH). The use of high CaO fly ash partially replacing in cement though reduces CH due to the consumption of CH by pozzolannic reaction but not as effective as the low CaO fly ash.

Keywords: fly ash, chemical composition, strength, expansion, sulfate solution, sulfate attack

1. Introduction

Deterioration of concrete due to sulfate attack is a commonly observed phenomenon when structures are exposed to sulfate solutions, or are placed in sulfate-bearing soils and/or groundwater. The increased incidence of deterioration of concrete structures exposed to such environments has led some researchers to develop the low C_3A ASTM Type V cement [1]. Fly ash and silica fume have been shown to be effective in mitigating the effects of sulfates [1,2,3]. The use of pozzolan materials as a cement replacement in retarding sulfate deterioration is primarily attributed to the pozzolanic reaction, which consumes the deleterious CH, and to the dilution of the C_3A phase due to reduction in the quantity of cement.

Fly ash production has increased every year in Thailand due to the increment of power requirement. The largest source of energy used for producing electricity in Thailand is from coal. It is estimated that the amount of fly ash produced annually in Thailand is more than 3 million tons. It has been reported that fly ash can be used to replace cement to improve performances of concrete [3]. Sulfate resistance is one of the important performances to be considered if the concrete is to be constructed in sulfate environment. This study finds the effect of chemical composition and content of fly ash on strength reduction and expansion in sulfates solution.

2. Mechanisms of Sulfate Attack on Portland Cements

The mechanisms of deterioration on structural concrete placed in the magnesium

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sulfate ($M\underline{S}$) and sodium sulfate ($N\underline{S}$) environments are not similar as represented by the following equations [2].

2.1 Mechanisms of $M\underline{S}$ Attack

The sulfate deterioration in the $M\underline{S}$ environment is controlled by magnesium-gypsum attack on the calcium silicate hydrate (C-S-H) binder. The first mechanism is based on the conversion of calcium hydroxide (CH) to $C\underline{S}H_2$ (gypsum) according to Eq. (1).

$$CH + M\underline{S} + 2H \rightarrow C\underline{S}H_2 + MH \quad (1)$$

In other mechanic, the $C\underline{S}H_2$ is formed from the decomposition of C-S-H gel as explained in Eq. (2).

$$C_xS_yH_z + xM\underline{S} + (3x+0.5y-z)H \rightarrow xC\underline{S}H_2 + xMH + 0.5yS_2H \quad (2)$$

The formation of magnesium hydroxide (MH) in Eq. (1) and (2) causes the reactions to proceed in a repetitive manner with more $C\underline{S}H_2$ accumulating in the pores. A further deleterious action of MH is attributed to its effect on the silicate hydrate (S_2H) formed in Eq. (2). MH, being insoluble, reacts with S_2H and results in the formation of non-cementitious, fibrous magnesium silicate hydrate (M-S-H), according to the following equation

$$4MH + SH_{11} \rightarrow M_4SH_{8.5} + (n\text{-}4.5)H \quad (3)$$

2.2 Mechanisms of $N\underline{S}$ Attack

In case of mechanisms of $N\underline{S}$ attack, the sulfate deterioration in the $N\underline{S}$ environment is primarily dependent on the C_3A content of cement and the quantity of CH produced during the early stages of hydration. CH first reacts with $N\underline{S}$ in a way similar to Eq. (1), as shown in the following equation

$$CH + N\underline{S} + 2H \rightarrow C\underline{S}H_2 + NH \quad (4)$$

This reaction will proceed according to the quantity of CH and the supply of $N\underline{S}$ in the environment. However, the gypsum produced in Eq. (4) would react with the aluminate hydrate (C_4AH_{13}), monosulfate ($C_4A\underline{S}H_{12}$) or the unhydrate C_3A to produce secondary ettringite, in accordance with the following reactions

$$C_4AH_{13} + 3C\underline{S}H_2 + 14H \rightarrow C_6A\underline{S}_3H_{32} + CH \quad (5)$$

$$C_4A\underline{S}H_{12} + 3C\underline{S}H_2 + 16H \rightarrow C_6A\underline{S}_3H_{32} \quad (6)$$

$$C_3A + 3C\underline{S}H_2 + 26H \rightarrow C_6A\underline{S}_3H_{32} \quad (7)$$

3. Materials

The commercially available Type I and Type V cements were used in this investigation. This study utilized lignite fly ashes having two different CaO content, 8.28% and 17.28%CaO, obtained from power plants in Lampang province. Each fly ash was used as 25, 40, 55 and 70 percent replacement by weight of the total binder. The local, natural river sand with a fineness modulus of approximately 3.29, were used. The chemical compositions of the cements and fly ashes used in this investigation are shown in Table 1.

Table 1 Chemical composition of the cements and fly ashes

Chemical Composition	Type I cement (% wt)	Type V cement (% wt)	Fly ash 1, F1 (% wt)	Fly ash 2, F2 (% wt)
SiO_2	20.61	20.97	45.88	38.42
Al_2O_3	5.03	3.49	26.20	19.17
Fe_2O_3	3.03	4.34	10.94	10.93
CaO	64.89	62.86	8.28	17.28
MgO	1.43	3.33	2.83	7.95
Na_20	0.22	0.12	0.90	1.03
K_2O	0.46	0.47	2.78	2.28
SO_3	2.70	2.12	1.04	2.01
LOI	1.23	1.21	0.17	0.05

4. Experimental Investigation

Mortar specimens were tested to determine both the expansion and strength reduction. The mortar specimens were made with sand to binder ratio of 2.0 constantly. Details of mix proportions are given in Table 2. The methods for preparing mortar bar specimens and testing the sulfate expansion were according to ASTM C1012. In case of the determination of strength reduction, mortar cube specimens were performed according to ASTM C109.

Table 2 Mix proportion of mortar specimens tested to determine the strength reduction and expansion

Mix	Symbol	Fly ash (%)	Mix Proportion (g) Cement Type I	V	Type of fly ash F1	F2	Sand	Water
1	C1-0.45	-	1	-	-	-	2	0.45
2	C5-0.45	-	-	1	-	-	2	0.45
3	C1-25F1-0.45	25	0.75	-	0.25	-	2	0.45
4	C1-40F1-0.45	40	0.60	-	0.40	-	2	0.45
5	C1-55F1-0.45	55	0.45	-	0.55	-	2	0.45
6	C1-70F1-0.45	70	0.30	-	0.70	-	2	0.45
7	C1-25F2-0.45	25	0.75	-	-	0.25	2	0.45
8	C1-40F2-0.45	40	0.60	-	-	0.40	2	0.45
9	C1-55F2-0.45	55	0.45	-	-	0.55	2	0.45
10	C1-70F2-0.45	70	0.30	-	-	0.70	2	0.45
11	C1-0.55	-	1	-	-	-	2	0.55
12	C5-0.55	-	-	1	-	-	2	0.55
13	C1-40F1-0.55	40	0.60	-	0.40	-	2	0.55
14	C1-55F1-0.55	55	0.45	-	0.55	-	2	0.55
15	C1-40F2-0.55	40	0.60	-	-	0.40	2	0.55
16	C1-55F2-0.55	55	0.45	-	-	0.55	2	0.55

C1: Type I cement, C5: Type V cement, F1: fly ash with content 8.28%CaO, F2: fly ash with content 17.28%CaO,
C1-0.45: mortar specimen made of Type I cement with water to binder ratio (w/b) of 0.45,
C1-25F1-0.45: mortar specimen made from Type I cement replaced with 25% F1 with w/b of 0.45

The concentration of SO_4^{2-} in the test solutions was 3.38 percent. Magnesium sulfate and sodium sulfate were used to prepare the test solutions separately. The specimens were immersed in plastic tanks containing these solutions separately. The solutions were changed after 1, 2, 4, 6, 8, and 10 months of exposure.

Mortar specimens were initially water cured for 28 days and then exposed to test solution for 280 days. At predetermined intervals, these specimens were tested to determine the strength reduction and expansion. Companion specimens, cured in potable water, were also tested for comparison of compressive strength. The reduction in compressive strength was calculated as follows

$$\text{Reduction in compressive strength, \%} = \{(A-B)/(A)\} \times 100 \quad (8)$$

where A = average compressive strength of five specimens cured in water, MPa
and B = average compressive strength of five specimens cured in sulfate solution, Mpa

5. Test Results

The test results are presented on two aspects, i.e. the strength reduction and expansion.

5.1 Strength Reduction

Fig. 1(a) shows the strength reduction in mortar specimens made with water to binder ratio (w/b) of 0.45 and placed in M<u>S</u> and N<u>S</u> solution at 112 days of exposure. For mortar specimens replaced in N<u>S</u> solution, the strength reduction in all mortar specimens made from Type I cement replaced with 8.28%CaO fly ash was slightly lower than that in Type V cement mortar specimens. The strength reduction in Type I cement specimens was higher about 1 percent to that of Type V cement mortar specimens. On the other hand, the strength reduction in mortar specimens made from Type I cement replaced with 17.28%CaO fly ash was higher than those in mortar specimens from Type I cement, Type V cement and Type I cement replaced with 8.28%CaO fly ash when the amount of fly ash is increased (up to about 35-45%).

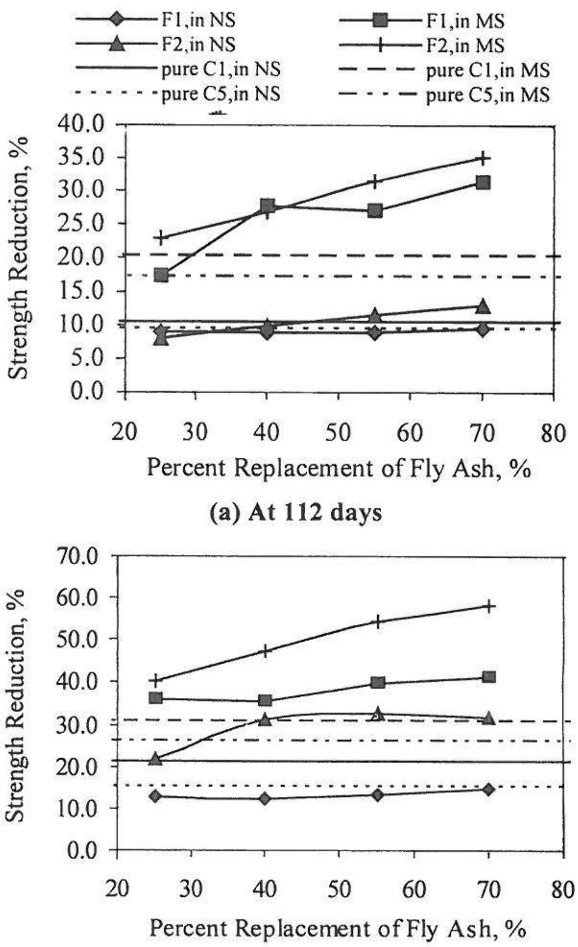
In M<u>S</u> environment, these data indicated that the strength reduction in all mortar specimens made from Type I cement replaced with fly ash was higher than those in specimens made from both Type I and Type V cement. Only specimens with 25% replacement of 8.28%CaO fly ash had strength reduction lower than that of Type I cement mortar specimens. However, the strength reduction in Type V cement mortar specimens was lower than that in Type I cement mortar specimens. Besides, the strength reduction in mortar specimens made from Type I cement replaced with 8.28%CaO fly ash was lower when compared with those of specimens made from Type I cement replaced with 17.28%CaO fly ash. However, the strength reduction in all mortar specimens was observed to be higher in mortar specimens placed in M<u>S</u> than those in N<u>S</u> solution.

At 224 days of exposure (Fig. 1(b)), these data indicated a similar trend to that of the 112 days of exposure. That is, for specimens placed in N<u>S</u> environment, the strength reduction in mortar specimens made from Type I cement replaced with 8.28%CaO fly ash was lower than those in specimens made from both Type I and V cement, while the strength reduction in mortar specimens made from Type I cement replaced with 17.28%CaO fly ash was higher than those in Type I and V cement mortar specimens. For specimens placed in M<u>S</u> environment, it is found that the reduction in strength in all mortar specimens made from Type I cement replaced with fly ash was higher than those in Type I and V cement mortar specimens.

Like water to binder ratio of 0.45, the strength reduction in mortar specimens with water to binder ratio of 0.55 has the same tendency for both 112 and 224 days of exposure as shown in Fig. 2.

Fig. 3 shows the strength reduction in Type I and V cement mortar specimens. These data showed that for specimens placed in M<u>S</u> solution, the strength reduction in both Type I and V cement mortar specimens made with water to binder ratio of 0.45 was higher than those made with water to binder ratio of 0.55 as shown in Fig. 3(a). In the case of specimens placed in N<u>S</u> environment, the contrary results were observed as shown in Fig. 3(b).

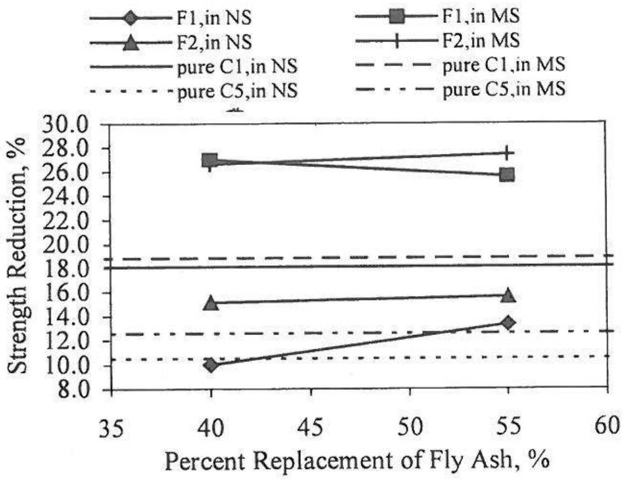
As shown in Fig. 4, the strength reduction in mortar specimens made from Type I cement replaced with fly ash and immersed in sulfate solution at 224 days of exposure was presented. The strength reduction in mortar specimens made from Type I cement replaced with 8.28%CaO fly ash was observed to be lower in mortar specimens made with water to binder ratio of 0.45 than those of 0.55 when placed in N<u>S</u> solution. Whereas in M<u>S</u> solution, the strength reduction was rather close and when fly ash replacement increased, the strength reduction in mortar specimens made with water to binder ratio of 0.55 was slightly lower than those of 0.45 as shown in Fig. 4(a). For another fly ash, 17.28%CaO fly ash, similar results were observed as shown in Fig. 4(b)



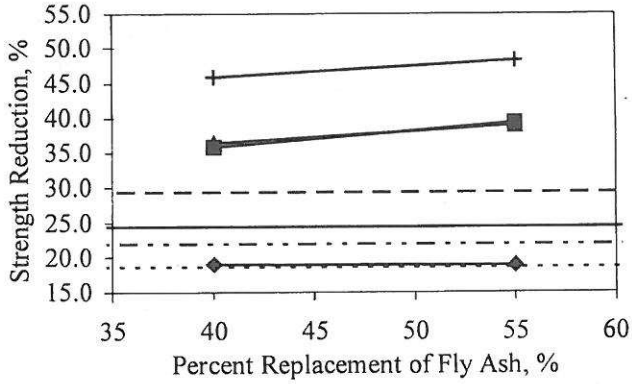
(a) At 112 days

(b) At 224 days

Fig. 1 Relationship between strength reduction and percent replacement of fly ash in mortar specimens with w/b of 0.45 and immersed in sulfate solution

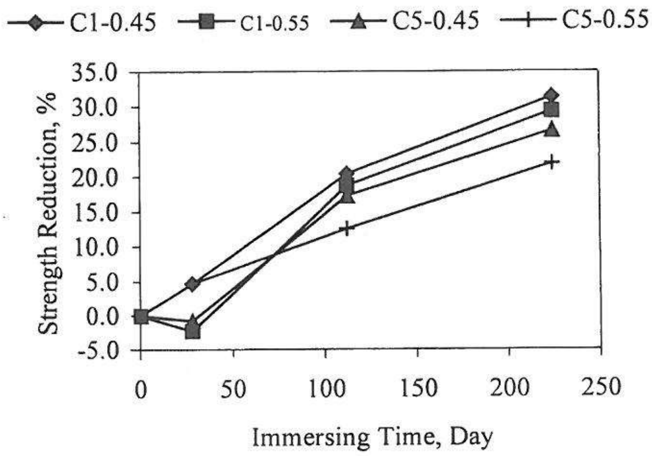


(a) At 112 days



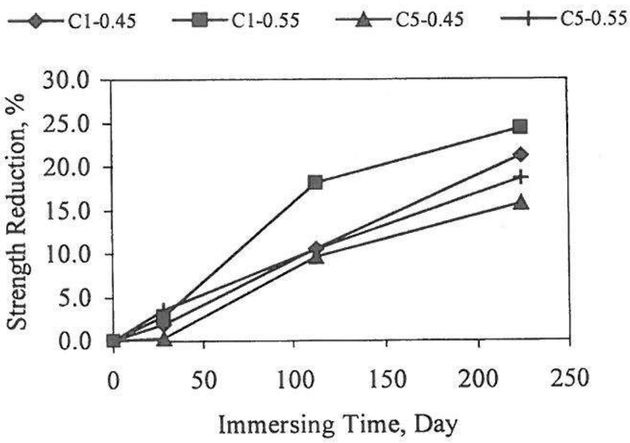
(b) At 224 days

Fig. 2 Relationship between strength reduction and percent replacement of fly ash in mortar specimens with w/b of 0.55 and immersed in sulfate solution



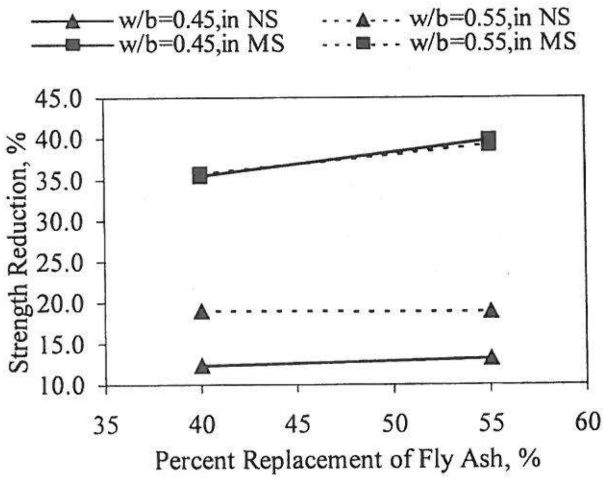
(a) Magnesium sulfate

Fig.3 Relationship between strength reduction and period of immersion in mortar specimens immersed in sulfate solution

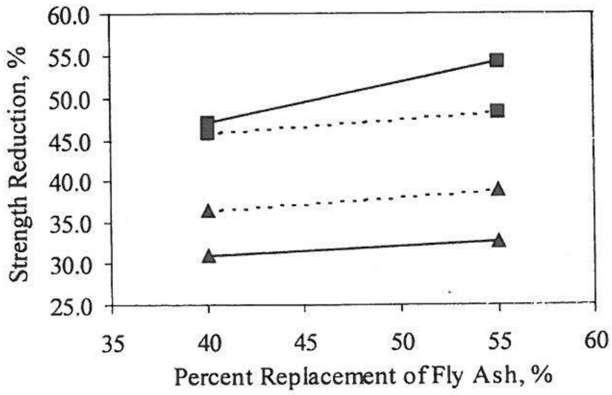


(b) Sodium sulfate

Fig.3 Relationship between strength reduction and period of immersion in mortar specimens immersed in sulfate solution



(a) 8.28%CaO fly ash



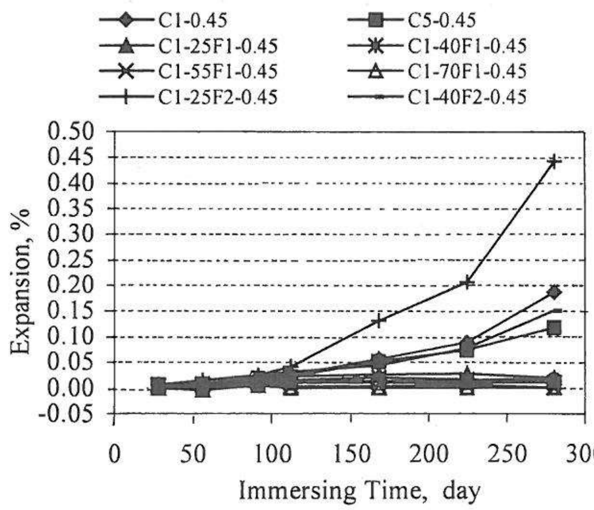
(b) 17.28%CaO fly ash

Fig.4 Relationship between strength reduction and percent replacement of fly ash in mortar specimens immersed in sulfate solution at 224 days

5.2 Expansion

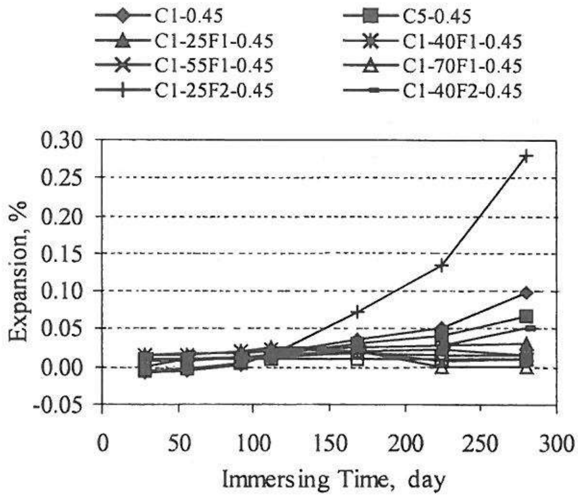
Fig. 5 shows the relationship between expansion and period of immersion in mortar specimens with water to binder of 0.45 and immersed in sulfate solution. These data indicated that for specimens placed in NS environment (Fig. 5(a)), the expansion in Type I cement mortar bar specimens was higher than that in Type V cement specimens. For the specimens made from Type I cement replaced with fly ash, the expansion of all fly ash replaced specimens, except for the specimens with Type I cement replaced with 25 percentages of 17.28%CaO fly ash, was quite small when compared with those in Type I and V cement specimens. It should be noted that the expansion of Type I cement replaced with 40 percentages of 17.28%CaO fly ash specimens was slightly smaller than that in Type I cement specimens and much larger than many other fly ash replaced specimens. The same tendency was observed for the specimens placed in MS solution, but degree of expansion was smaller than those in NS solution.

Like water to binder ratio of 0.45, the expansion in mortar bar specimens with water to binder ratio of 0.55 has the same tendency in both NS and MS environment as shown in Fig. 6.



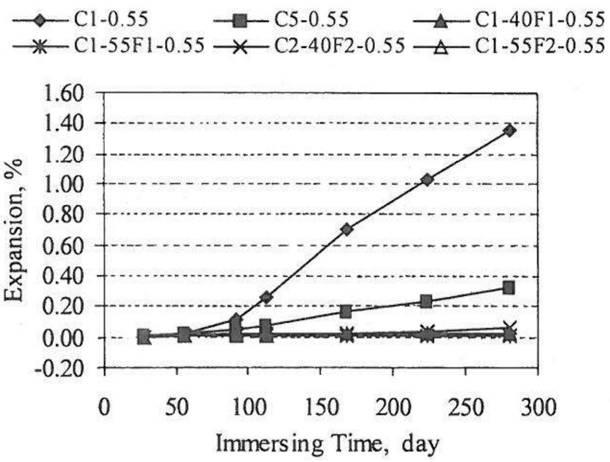
(a) Sodium sulfate solution

Fig.5 Relationship between expansion and period of immersion in mortar specimens with water to binder of 0.45 and immersed in sulfate solution

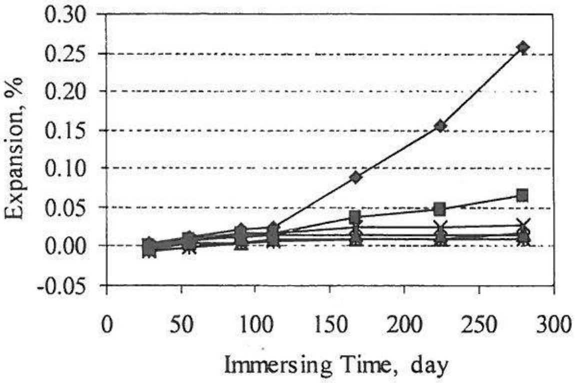


(b) Magnesium sulfate solution

Fig.5 Relationship between expansion and period of immersion in mortar specimens with water to binder of 0.45 and immersed in sulfate solution



(a) Sodium sulfate solution



(b) Magnesium sulfate solution

Fig.6 Relationship between expansion and period of immersion in mortar specimens with water to binder of 0.55 and immersed in sulfate solution

6. Discussions

The data on strength reduction and expansion in mortar specimens after 224 days of exposure in the NS and MS environments are summarized in Table 3. The strength reduction and expansion in Type V cement mortar specimens was lower than that in Type I cement mortar specimens placed in both NS and MS environment. This is because smaller quantity of C_3A in Type V cement (1.91%) than that in Type I cement (8.21%) leads to less amount of ettringite known as harmful. In case of mortar specimens made from Type I cement replaced with 8.28%CaO fly ash, the strength reduction was lower than that in Type I cement mortar specimens when they were placed in NS solution. Moreover, the expansion in specimens was smaller than that in Type I cement mortar specimens when they were placed in both NS and MS solution. This is because Type I cement replaced with 8.28%CaO fly ash not only has smaller quantity of C_3A than Type I cement due to partial fly ash replacement but also the quantity of gypsum formed in Eq. (4) will be smaller than Type I cement due to pozzolanic reaction consuming a part of the CH produced by the hydration of cement. However, the strength reduction was higher than that in Type I cement mortar specimens when placed in MS solution since pozzolanic reaction in fly ash cement increased amount of C-S-H after that the formation of non-cementitious, fibrous magnesium silicate hydrate (M-S-H), increased according to Eq. (2)-(3).

For mortar specimens made from Type I cement replaced with 17.28%CaO fly ash, the strength reduction in specimens was higher than that in Type I cement mortar specimens when they were placed in both NS and MS solution possibly due to high gypsum content in the fly ash. Due to the same reason, the expansion in 25% fly ash specimen was significantly larger than that in Type I cement mortar specimens when placed in both NS and MS solution. For 55% and 70% fly ash specimens, the expansion was quite smaller than that in Type I cement mortar specimens placed in sulfate solution possibly because the specimens replaced with large amount of fly ash have high pozzolanic reaction, thereby CH decreased, and the benefit from this CH reduction may counteract the effect of high gypsum content in the fly ash.

When compared the results obtained from specimens using 8.28% and 17.28%CaO fly ash, it is noted that the strength reduction and expansion in mortar specimens made from Type I cement replaced with 8.28%CaO fly ash were smaller than those in mortar specimens made from Type I cement replaced with 17.28%CaO fly ash in both NS and MS solution. This is due to the fact that higher amount of CaO in fly ash increases the CH and ettringite possibly from higher gypsum content in high CaO fly ash.

It is noted that although the mortar specimens made from Type I cement replaced with fly ash had superior expansion when compared to Type I cement mortar specimens, the strength reduction was inferior. It is recommended here that not only expansion but also the strength reduction should be paid attention in sulfate resisting concrete.

For the effect of water to binder ratio in strength reduction and expansion of mortar specimens exposed to sulfate solution, the mortar specimens in all cement made with a low water to binder ratio indicated superior performance in NS solution in term of strength reduction and in both NS and MS solution in term of expansion than all cement mortar specimens made with a high water to binder ratio. Since mortar specimens made with a low water to binder ratio are denser and has smaller porosity than mortar specimens made with a high water to binder ratio, thereby significantly reducing the permeability and diffusion of SO_4^{2-} ions into the specimen. However, the strength reduction in MS solution of all mortar specimens made with low water to binder ratio was larger than that made with high water to binder ratio may be because the lower w/b specimens have denser structure, thereby providing limited space for the expansive products to occupy [2].

Table 3 Strength reduction and expansion in specimens made from Type I, Type V and Type I cement replaced with fly ash exposed to NS and MS environments

Mix	Symbol	Strength reduction at 224 days, %		Expansion for 280 days, %	
		NS	MS	NS	MS
1	C1-0.45	21.2	31.4	0.185	0.097
2	C5-0.45	15.8	26.6	0.117	0.067
3	C1-25F1-0.45	12.9	35.8	0.018	0.030
4	C1-40F1-0.45	12.3	35.5	0.010	0.014
5	C1-55F1-0.45	13.2	39.9	0.004	0.009
6	C1-70F1-0.45	14.5	41.3	0.004	0.009
7	C1-25F2-0.45	21.7	40.0	0.441	0.279
8	C1-40F2-0.45	31.0	47.1	0.149	0.052
9	C1-55F2-0.45	32.7	54.4	0.017	0.016
10	C1-70F2-0.45	31.8	58.2	0.010	0.009
11	C1-0.55	24.4	29.4	1.351	0.256
12	C5-0.55	18.6	21.9	0.322	0.064
13	C1-40F1-0.55	19.0	35.8	0.021	0.015
14	C1-55F1-0.55	18.9	39.3	0.014	0.008
15	C1-40F2-0.55	36.4	45.9	0.055	0.028
16	C1-55F2-0.55	39.0	48.2	0.018	0.017

7. Conclusions

1. Higher reduction in strength was observed in mortar specimens made from Type I cement replaced with high CaO Fly ash (17.28%CaO) when compared to Type I cement mortar specimens placed in both NS and MS environment. The strength reduction was, however, observed to be relatively lower in mortar specimens made from Type I cement replaced with low CaO Fly ash (8.28%CaO) exposed to the NS environment when compared to that in Type I cement mortar specimens. However, strength reduction was observed to be smaller in all cement mortar specimens placed in NS solution when compared to those in MS solution.

2. Expansion was observed to be larger in both Type I and V cement mortar specimens when compared to mortar specimens made from Type I cement replaced with fly ash, except for the mortar specimens made from Type I cement replaced with 25% of high CaO fly ash (17.28%CaO). However, the expansion of all mortar specimens placed in NS environment was larger than that in MS environment.

3. The lower expansion observed in mortar specimens made from Type I cement replaced with fly ash, compared to Type I cement mortar specimens, placed in NS, may be attributed to the reduction in the quantity of CH due to pozzolanic action. Further, the formation of secondary C-S-H gel due to pozzolanic reaction significantly reduces the diffusion of SO_4^{2-} ions.

4. The inferior performance of mortar specimens made from Type I cement replaced with high CaO Fly ash (17.28%CaO), in sulfate environment, compared to mortar specimens made from Type I cement replaced with low CaO Fly ash (8.28%CaO) is possibly attributed to the higher free lime and $CaSO_4$ which results in larger CH and ettringite

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